# **Carbon Nanotubes: Supramolecular Mechanics**

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# INTRODUCTION

Supramolecular interactions are usually short-range (near contact) forces between the molecules, too weak to cause the intermolecular changes or bond formation between the particles. At the same time, their strength and range are sufficient to cause self-assembly of the molecular units or certain elastic deformations of these building blocks. Because of the weakness of supramolecular interactions, the resulting organization is sensitive to external conditions and ensures certain ease of transformations in response to external fields. Well known is a fascinating class of liquid crystals, whose "liquid" aspect is exactly a result of relatively small energy of intermolecular forces. Nanoparticles and especially nanotubes offer a kind of building blocks that can be efficiently glued by weak supramolecular forces in a self-assembly process. In case of nanotubes, because of their hollow structure and large aspect ratio, same forces or interaction between them can cause deformations of bending, torsion, flattening polygonization, etc. In turn, the degree of such deformation can enhance (like in case of partial polygonization of nanotubes in the array bundles) supramolecular attraction or decrease it under other circumstances. Supramolecular behavior of nanotubes is therefore intrinsically coupled with their own mechanical properties which we will discuss in some detail.

Unique mechanical properties of carbon nanotubes indirectly lead to unusual role of the forces *between* them. These *supramolecular* interactions are normally weak and, for most molecular species, are easily overcome by thermal agitation. However, they turn out to be significant in case of nanotubes, building up very strong attractive potentials over the extensive aligned contacts ( $\sim 0.5 \text{ eV}/$ nm). The general aspects and issues of supramolecular mechanics are discussed, including an overview of the mechanical properties of nanotubes, especially linear elastic parameters and their relation with persistence length, nonlinear elastic instabilities, and buckling. Furthermore, inelastic relaxation, yield strength, and fracture mechanisms, including their kinetic theory, are also discussed. A discussion of theoretical and computational studies is supplemented by brief summaries of experimental results for the entire range of the deformation amplitudes. Atomistic scenarios of "strong" supramolecular interactions, when polymerization and coalescence welding occur, are also discussed because of their significance in potential applications.

#### **OVERVIEW**

Nanomechanics is generally distinguished from the wellestablished dynamics of molecules in that it relies on the heuristics and methods of mechanical engineering and structural mechanics. It deals with objects of distinct shape and function: rods, beams, shells, plates, membranes, etc. At the same time, because of the small length scale, nanomechanics also relies on physics of interatomic and molecular forces, quantum chemistry, solid state theory, and statistical thermodynamics. With these come a variety of numerical and computational methods (molecular dynamics, Monte Carlo simulations, classical empirical interatomic potentials, tight-binding approximation, density functional theory, etc.). This cross-disciplinary aspect makes this area both complex and exciting for research and education.

Among the numerous subjects of nanomechanics research (tips, contact junctions, pores, whiskers, etc.), carbon nanotubes  $(CNTs)^{[1]}$  have earned a spotlight (see Ref. [2] for a popular review). Their atomically precise structure, elongated and hollow, an effective absence of a surface (which is no different than the bulk, at least for the single-walled cylinders, SWNTs), and superlative covalent bond strength are among the traits that put CNTs in the focus of nanomechanics. Discussion of numerous other objects as well as details of the multiscale methods involved in nanomechanics (for example, see recent monograph<sup>[3]</sup>) is far beyond the scope of this article.

It is noteworthy that the term *resilient* has been first applied not to nanotubes, but to smaller fullerene cages, in the study of high-energy collisions of  $C_{60}$ ,  $C_{70}$ , and  $C_{84}$  bouncing from a solid wall of H-terminated diamond. The



absence of any fragmentation or other irreversible atomic rearrangement in the rebounding cages was somewhat surprising and indicated the ability of fullerenes to sustain great elastic distortion. The very same property of resilience becomes more significant in case of carbon nanotubes because their elongated shape, with the aspect ratio close to a thousand, makes the mechanical properties especially interesting and important because of potential structural applications. An accurate simulation (with realistic interatomic and van der Waals forces) in Fig.  $1^{[4]}$ vividly illustrates the appeal of CNTs as a nanomechanical object: well-defined cylindrical shape, compliance to external forces, and an expected type of response qualitatively analogous to a common macroscopic behavior places these objects between molecular chemical physics, elasticity theory, and mechanical engineering.

The utility of nanotubes as elements in nanoscale devices or composite materials remains a powerful motivation for the research in this area. While the feasibility of the practical realization of these applications is currently unknown, another incentive comes from the fundamental materials physics. There is an interesting duality in the nanotubes. Carbon nanotubes possess simultaneously molecular size and morphology as well as sufficient translational symmetry to perform as very small (nano-) crystals with well-defined primitive cell, surface, possibility of



**Fig. 1** Simulations of the axial and radial deformation of nanotubes. (a) Axial deformation resulting from the crossing of two (10,10) nanotubes. (b) Perspective close-up of the same crossing showing that both tubes are deformed near the contact region. (c) Computed radial deformations of single-wall nanotubes adsorbed on graphite. (From Ref. [4].)

transport, etc. Moreover, in many respects, they can be studied as well defined as engineering structures and many properties can be discussed in traditional terms of moduli, stiffness or compliance, or geometric size and shape. The mesoscopic dimensions (a nanometer diameter) combined with the regular, almost translation-invariant morphology along the micrometer lengths (unlike other polymers, usually coiled) make nanotubes a unique and attractive object of study.

In the following, "Linear Elastic Properties" discusses theoretical linear elasticity and results for the elastic moduli, compared wherever possible with the experimental data. In "Van der Waals Interactions," the weak supramolecular interactions are quantified in the form of van der Waals force potential, and the large-scale mechanical deformations of nanotubes caused by their attraction to each other are outlined. The nonlinear elastic behavior, buckling instabilities, and shell model are presented in "Supramolecular Morphology Changes Within Elastic Shell Model," with mentioning of experimental evidence parallel to theoretical results. Yield and failure mechanisms in tensile load are presented in "Failure and Relaxation Mechanisms," with the emphasis on the combined dislocation theory and computational approach. More recent results of kinetic theory of fracture and strength evaluation in application to CNTs are briefly presented in "Kinetic Approach to Strength-Failure Evaluation"; fast molecular tension tests are recalled in the context of kinetic theory. "Coalescence of Nanotubes as a Reversed Failure" presents some of the more recent result on CNT *coalescence welding*, a process essentially reverse to fracture. In "Tensegrity at Supramolecular Scale," we also briefly discuss the concept of *tensegrity* and how it might be implemented in nanoscale by combining mechanically stiff and flexible supramolecular units. Throughout the discussions, we do not attempt to provide a comprehensive review of broad activities in the field. Broader or a more comprehensive discussion can be found in other relatively recent reviews by the author.<sup>[2,5]</sup>

# LINEAR ELASTIC PROPERTIES

Numerous theoretical calculations are dedicated to linear elastic properties when displacements (strain) are proportional to forces (stress). We recently revisited<sup>[6]</sup> this issue to compare within the same method the elasticity of three different materials: pure carbon (C), boron nitride (BN), and fluorinated carbon ( $C_2F$ ). Because of obvious uncertainty in definition of a nanotube "cross section," the results should be represented by the values of in-plane



stiffness, C (J/m<sup>2</sup>). The values computed with Gaussianbased density functional theory are C=345, 271, and 328 N/m for C, BN, and C<sub>2</sub>F, respectively. These values in ab initio calculations are almost independent of nanotube diameter and chirality [consistent with the isotropic elasticity of a hexagonal two-dimensional (2-D) lattice], somewhat in contrast to previous reports based on tight binding or classical empirical approximations. Notably, substantial fluorination causes almost no change in the inplane stiffness because the bonding involves mainly  $\pi$ system while the stiffness is largely a result of in-plane  $\sigma$ system. For "material" property assessments, the values of bulk moduli (based on a graphite-type 0.34-nm spacing of layers) yield 1029, 810, and 979 GPa-all very high. Knowing the elastic shell parameter C immediately leads to accurate calculation of a nanotube beam-bending stiffness K (proportional to the cube of diameter,  $\sim d^3$ ) as discussed later in "Van der Waals Interactions" and "Coalescence of Nanotubes as a Reversed Failure." It also allowed us to compute vibration frequencies of the tubules, e.g., symmetric breathing mode frequency,  $f \sim 1/d$ ,<sup>[6]</sup> detectable in Raman spectroscopy.

An unexpected feature discovered in the course of that study<sup>[6]</sup> is the localized strain induced by the attachment of fluorine. This shifts the energy minimum of the C<sub>2</sub>F shell lattice from an "unstrained" sheet toward the highly curved polygonal cylinders (for C<sub>2</sub>F composition of a near square shape, Fig. 2). Equilibrium free angle is  $\sim 72^{\circ}$ .

Theoretical values agree reasonably well with experimental values of the Young's modulus. It was first estimated<sup>[7]</sup> by measuring freestanding room-temperature vibrations in a transmission electron microscope (TEM). The motion of a vibrating cantilever is governed by the known fourth-order wave equation,  $y_{tttt} = -(YI/\rho A)y_{xxxx}$ , where A is the cross-sectional area and  $\rho$  is the density of the rod material. For a clamped rod, the boundary con-



**Fig. 2** Geometries of the polygonal fluorinated carbon tubes: (a) square  $F_{4^-}(10,10)$  and (b) pentagonal  $F_{5^-}(10,10)$ . (From Ref. [6].)

ditions are such that the function and its first derivative are zero at the origin and the second and third derivative are zero at the end of the rod. Thermal nanotube vibrations are essentially elastic, relaxed phonons in equilibrium with the environment; therefore the amplitude of vibration changes stochastically with time. The amplitude of those oscillations was defined by means of careful TEM observations of a number of CNTs and yields the values of moduli within a range near 1 TPa.

Another way to probe the mechanical properties of nanotubes is to use the tip of an atomic force microscope (AFM) to bend an anchored CNT while simultaneously recording the force exerted by the tube as a function of the displacement from its equilibrium position.<sup>[8]</sup> Obtained values also vary from sample to sample but generally are close to Y=1 TPa. Similar values have been obtained in Ref. [9] with yet another accurate technique based on a resonant electrostatic deflection of a multiwall carbon nanotube under an external a.c. field. The detected decrease in stiffness must be related to the emergence of a different bending mode for the nanotube. In fact, this corresponds to a wavelike distortion buckling of the inner side of the CNT. Nonlinear behavior is discussed in more detail in the next section. Although experimental data on elastic modulus are not very uniform, it corresponds to the values of in-plane rigidity C=340-440 N/m to the values Y=1.0-1.3 GPa for multiwall tubules and to Y=4C/d = (1.36 - 1.76) TPa nm/d for SWNTs of diameter d.

### VAN DER WAALS INTERACTIONS

Supramolecular interactions between the SWNTs are mainly because of van der Waals forces (VdW), except special situations when local charge or covalently bonded functional group introduce additional electrostatic fields. Van der Waals forces play also an important role in the interaction of the nanotubes with the substrata. The different shells of a MWNT (multiwall nanotube) interact primarily by van der Waals forces; single-wall tubes form ropes for the same reason.

An interesting manifestation of van der Waals interactions involves the self-interaction between two segments of the same single-wall CNT to produce a closed ring (loop).<sup>[10]</sup> Single-walled nanotube rings were first observed in trace amounts in the products of laser ablation of graphite and assigned a toroidal structure. More recently, rings of SWNTs were synthesized with large yields (~50%) from straight nanotube segments. These rings were shown to be loops and not tori.<sup>[10]</sup> The synthesis involves the irradiation of raw SWNTs in a sulfuric acid– hydrogen peroxide solution by ultrasound. This treatment

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both etches the CNTs, shortening their length to about 3-4  $\mu$ m, and induces ring formation.

Fundamentally, van der Waals attraction between the CNT is a result of dispersion forces, i.e., electrostatic dipole-to-dipole interaction (which gives  $V \sim 1/r^3$  dependence of potential energy), and because the dipoles are mutually induced excited states, this actually yields nonzero effect only in the second-order perturbation theory, an always negative shift in potential energy  $U^{(2)} \sim -V^2 \sim -1/r^6$ .

For nanotubes and other carbon-cage structures, the van der Waals energy can be obtained from a universal graphitic potential<sup>[11]</sup> and for (10,10) tubes is

$$U(s) = -0.9516 \text{ eV/nm } (5/3)[(1 + 0.291s)^{-4} - (2/5)(1 + 0.291s)^{-10}]$$
(1)

Equilibrium point s=0 corresponds to intercenter distance 1.67 nm that is wall-to-wall distance 0.315 nm, with the potential well depth about 0.95 eV/nm. This value is equivalent to energy of 0.04 eV per each pair of C-atoms facing across the van der Waals spacing, or near 0.9 kcal/mol (e.g., of inserted spacer group that would push the nanotubes off the energy-minimum position). Although significant, this attraction energy decays fast with the nanotube separation: to the half of the value at only 1 Å from equilibrium and almost vanishes at 3–5 Å, as Fig. 3 shows.

The formation of coils by CNTs is particularly intriguing. While coils of biomolecules and polymers are well-known structures, they are stabilized by a number of interactions that include hydrogen bonds and ionic interactions. On the other hand, the formation of nanotube coils is surprising given the high flexural rigidity (K=Young's modulus times areal moment of inertia) of CNTs and the fact that CNT coils can only be stabilized



**Fig. 3** Van der Waals energy per unit length is shown as function of displacement from equilibrium. From top down, three lines correspond to the tube deflecting from a contact with one, a pair, or a triplet of others; shallow plot corresponds to deflection in tangential direction (From Ref. [12].)

by van der Waals forces. However, estimates based on continuum mechanics show that, in fact, it is easy to compensate for the strain energy induced by the coiling process through the strong adhesion between tube segments in the coil. Details of this analysis can be found in the original reports<sup>[10]</sup> or in our recent review.<sup>[5]</sup> Here we will outline briefly a different and more common situation where the competition of elastic energy and the intertubular linkage is important. Following our recent work,<sup>[12]</sup> we will discuss the connection between the nanomechanics of CNTs and their *random* curling in a suspension or a raw synthesized material of bucky paper.

Single-walled nanotubes are often compared with polymer chains as having very high rigidity and therefore large persistence length. To quantify this argument, we note that a defectless CNT has almost no static flexing, although 5/7 defects, for example, introduce small kink angle  $5-15^{\circ}$  and could cause some static curvature, but their energies are high and concentration is usually negligible. Only dynamic elastic flexibility should be considered. If  $\mathbf{u}(s)$  is a unit direction vector tangent to the CNT at contour length point *s*, and the bending stiffness is *K*, then statistical probability of certain shape  $\mathbf{u}(s)$  is

$$P[\mathbf{u}(s)] = \exp[-1/2(K/k_{\rm b}T)\int (\partial \mathbf{u}/\partial s)^2 \mathrm{d}s]$$
$$= \exp[-(1/2)L\int (\partial \mathbf{u}/\partial s)^2 \mathrm{d}s] \tag{2}$$

Here persistence length is  $L=(K/k_bT)$ . For a (10,10) SWNT of radius R=0.7 nm and the effective wall thickness h=0.09 nm (see "Linear Elastic Properties" and "Van Der Waals Interactions"), the bending stiffness is very close to  $K=\pi CR^3$  (C=345 N/m is the in-plane stiffness, based on ab initio calculations). Persistence length at room temperature therefore is  $L_1[(10,10), 293 \text{ K}] \sim 0.1$ mm, in the macroscopic range much greater than for most polymer molecules. The result can be generalized for a single SWNT of radius R,

$$L_1 = (30K/T)(R/0.7 \text{ nm})^3 \text{ mm}$$
(3)

or *N* times more for a bundle of *N* tubes (assuming additive stiffness for the case of weak lateral cohesion of the constituent SWNTs). For example, for a smallest close packed bundle of seven (one surrounded by six neighbors), this yields  $L_7=1$  mm. Such incoherent bundle and a solid-coherent bundle with perfect lateral adhesion provide the lower and upper limits for the persistence length,  $NL_1 < L_N < N^2 L_1$ . Remarkably, these calculations show that the true thermodynamic persistence length of small CNT bundles or even an individual SWNT is in the macroscopic range from a fraction of a millimeter and greater. This means that highly curved structures often observed in





**Fig. 4** Raw-produced SWNTs often form ropes–bundles entangled bent into a rubbery structure called "bucky paper." The length scale of bends is much smaller than the persistence length for the constituent filaments. Shown here is such material produced by HiPco (high pressure CO) synthesis method (From O'Connell et al., Chem. Phys. Lett., 342, 265, 2001.)

bucky-paper mats (Fig. 4) are attributed not to thermodynamic fluctuations, but rather to residual mechanical forces preventing these coils from unfolding. Elastic energy of a typical micron size  $(r \sim 1 \ \mu\text{m})$  curl-arc is much greater than thermal,  $U_{\text{curl}} \sim k_b T (L/r)^2 \gg k_b T$ .<sup>[12]</sup> At the same time, a force required to maintain this shape  $F_{\text{curl}} \sim K/r^2 = N$  pN, several piconewtons, where N is the number of SWNTs in each bundle. This is much less than a force per single chemical bond (~1 nN), and therefore any occasional lateral bonding between the tubules can be sufficient to prevent them from disentanglement.

## SUPRAMOLECULAR MORPHOLOGY CHANGES WITHIN ELASTIC SHELL MODEL

Almost any molecular structure can sustain very large deformations, compared with the range common in macroscopic mechanics. A less obvious property of CNTs is that the specific features of large nonlinear strain can be understood and predicted in terms of continuum theories. One of the outstanding features of nanotubes is their hollow structure, built of atoms densely packed along a closed surface that defines the overall shape. This also manifests itself in dynamic properties of molecules, resembling so much the macroscopic objects of continuum elasticity known as *shells*. Macroscopic shells and rods have long been of interest: the first study dates back to Euler, who discovered the elastic instability. A rod subject to longitudinal compression remains straight but shortens by some fraction  $\varepsilon$ , proportional to the force, until a crit-

ical value (the Euler force) is reached. It then becomes unstable and buckles sideways at  $\varepsilon > \varepsilon_{cr}$ , while the force almost does not vary. For hollow tubules, there is also a possibility of local buckling in addition to buckling as a whole. Therefore more than one bifurcation can be observed, thus causing an overall nonlinear response to the large deforming forces (note that local mechanics of the constituent shells may well still remain within the elastic domain).

REPRINTS

ORDER

In nanomechanics, the theory of shells was first applied in our early analysis of buckling and since then serves a useful guide.<sup>[13–16]</sup> Its relevance for a covalent-bonded system of only a few atoms in diameter was far from being



**Fig. 5** Simulation of a (7,7) nanotube exposed to axial compression, L=6 nm. The strain energy (a) displays four singularities corresponding to shape changes. At  $\varepsilon_c=0.05$ , the cylinder buckles into the pattern (b), displaying two identical flattenings—"fins" perpendicular to each other. Further increase of  $\varepsilon$  enhances this pattern gradually until at  $\varepsilon_2=0.076$ , the tube switches to a three-fin pattern (c), which still possesses a straight axis. In a buckling sideways at  $\varepsilon_3=0.09$ , the flattenings serve as hinges, and only a plane of symmetry is preserved (d). At  $\varepsilon_4=0.13$ , an entirely squashed asymmetric configuration forms (e). (From Ref. [13].)





obvious. Molecular dynamics simulations seem better suited for objects that are small.

Fig. 5 shows a simulated nanotube exposed to axial compression. The atomic interaction was modeled by the Tersoff-Brenner potential, which reproduces the lattice constants and binding energies of graphite and diamond. The end atoms were shifted along the axis by small steps and the whole tube was relaxed by conjugate-gradient method while keeping the ends constrained. At small strains, the total energy (Fig. 5a) grows as  $E(\varepsilon) = (1/2)E''\varepsilon^2$ . The presence of four singularities at higher strains was quite a striking feature and the patterns (b)–(e) illustrate the corresponding morphological changes. The shading indicates strain energy per atom, equally spaced from below 0.5 eV (brightest) to above 1.5 eV (darkest). The sequence of singularities in  $E(\varepsilon)$  corresponds to a loss of molecular symmetry from  $D_{\infty h}$  to  $S_4$ ,  $D_{2h}$ ,  $C_{2h}$ , and  $C_1$ . This evolution of the molecular structure can be put in the framework of continuum elasticity.

The intrinsic symmetry of a graphite sheet is hexagonal, and the elastic properties of 2-D hexagonal structure are isotropic. A curved sheet can also be approximated by a uniform shell with only two elastic parameters: flexural rigidity D and its in-plane stiffness C. The energy of a shell is given by a surface integral of the quadratic form of local deformation,

$$E = \frac{1}{2} \int \int \{D[(\kappa_x + \kappa_y)^2 - 2(1 - v) \\ (\kappa_x \kappa_y - \kappa_{xy}^2)] + \frac{C}{(1 - v^2)} [(\varepsilon_x + \varepsilon_y)^2 \\ - 2(1 - v)(\varepsilon_x \varepsilon_y - \varepsilon_{xy}^2)]\} dS$$
(4)

where  $\kappa$  is the curvature variation,  $\varepsilon$  is the in-plane strain, and x and y are local coordinates. To adapt this formalism to a graphitic tubule, the values of D and C can be identified by comparison with the detailed ab initio and semiempirical studies of nanotube energetics at small strains. Indeed, the second derivative of total energy with respect to axial strain corresponds to the in-plane rigidity C (cf. "Linear Elastic Properties"). Similarly, the strain energy as a function of tube diameter d corresponds to  $2D/d^2$  in Eq. 4. Using recent ab initio calculations,<sup>[6]</sup> one obtains  $C=56 \text{ eV/atom}=340 \text{ J/m}^2$  and D=1.46 eV. The Poisson ratio v=0.15 was extracted from a reduction of the diameter of a tube stretched in simulations. A similar value is obtained from experimental elastic constants of single crystal graphite. One can make a further step toward a more tangible picture of a tube as having wall thickness h and Young modulus  $Y_s$ . Using the standard relations  $D=Yh^3/12(1-v^2)$  and  $C=Y_sh$ , one finds  $Y_s=3.9$ TPa and h=0.089 nm. With these parameters, linear



**Fig. 6** The critical strain levels for a continuous, 1-nm-wide shell tube as a function of its scaled length L/N. A buckling pattern (M,N) is defined by the number of halfwaves 2M and N in y and x directions, respectively, e.g., a (4,4)-pattern is shown in the inset. The effective moduli and thickness are fit to graphene. (From Ref. [13].)

stability analysis allows one to assess the nanotube behavior under strain.

To illustrate the efficiency of the shell model, consider briefly the case of imposed axial compression. A trial perturbation of a cylinder has a form of Fourier harmonics, with *M* azimuthal lobes and *N* halfwaves along the tube (Fig. 6 inset), i.e., sines and cosines of arguments 2My/d and  $N\pi x/L$ . At a critical level of the imposed strain,  $\varepsilon_c(M,N)$ , the energy variation (4.1) vanishes for this shape disturbance. The cylinder becomes unstable and lowers its energy by assuming an (M,N) pattern. For tubes of d=1nm with the shell parameters identified above, the critical strain is shown in Fig. 6. According to these plots, for a tube with L>10 nm, the bifurcation is first attained for M=1, N=1. The tube preserves its circular cross section and buckles sideways as a whole; the critical strain is close to that for a simple rod,

$$\varepsilon_{\rm c} = 1/2(\pi d/L)^2 \tag{5}$$

or four times less for a tube with hinged (unclamped) ends. For a shorter tube, the situation is different. The lowest critical strain occurs for M=2 (and  $N \ge 1$ , see Fig. 6), with a few separated flattenings in directions perpendicular to each other, while the axis remains straight. For such a local buckling, in contrast to (4.2), the critical strain depends little on length and estimates to  $\varepsilon_c = 4\sqrt{D/C}d^{-1} = (2/\sqrt{3})(1 - v^2)^{-1/2}hd^{-1}$  in the so-called *Lorenz* limit. For a nanotube, one finds

$$\varepsilon_{\rm c} = 0.1 \, {\rm nm}/d$$

(6)

Specifically, for the 1-nm-wide tube of length L=6 nm, the lowest critical strains occur for M=2 and N=2 or 3 (Fig. 6). This is in accord with the two- and three-fin patterns seen in Fig. 5b and c. Higher singularities cannot be quantified by the linear analysis, but they look like a sideways beam buckling, which at this stage becomes a nonuniform object.

Axially compressed tubes of greater length and/or tubes simulated with hinged ends (equivalent to a doubled length) first buckle sideways as a whole at a strain consistent with (5). After that, the compression at the ends results in bending and a local buckling inward. This illustrates the importance of the "beam-bending" mode, the softest for a long molecule and most likely to attain significant amplitudes because of either thermal vibrations or environmental forces. In simulations of bending, a torque rather than force is applied at the ends and the bending angle  $\theta$  increases stepwise. While a notch in the energy plot can be mistaken for numerical noise, its derivative  $dE/d\theta$  drops significantly. This unambiguously shows an increase in tube compliance-a signature of a buckling event. In bending, only one side of a tube is compressed and thus can buckle. Assuming that it buckles when its local strain,  $\varepsilon = \kappa d/2$ , where  $\kappa$  is the local curvature, is close to that in axial compression, Eq. 6, we estimate the critical curvature as

$$\kappa_{\rm c} = 0.2 \,\,\mathrm{nm}/d^2 \tag{7}$$

In simulation of *torsion*, the increase of azimuthal angle  $\phi$  between the tube ends results in abrupt changes of energy and morphology.<sup>[13,14,17]</sup> In continuum model, the analysis based on Eq. 4 is similar to that outlined above, except that it involves skew harmonics of arguments such as  $N\pi x/L\pm 2My/d$ . For overall beam buckling (*M*=1),

$$\phi_{\rm c} = 2(1+\nu)\pi \tag{8}$$

and for the cylinder-helix flattening (M=2),

$$\phi_{\rm c} = 0.06 \ {\rm nm}^{3/2} L/d^{5/2} \tag{9}$$

The latter should occur first for  $L < 140d^{5/2}$  nm, which is true for all tubes we simulated. However, in simulations, it occurs later than predicted by Eq. 9. The ends, kept circular in simulation, which is physically justifiable, by a presence of rigid caps on normally closed ends of a molecule, deter the thorough flattening necessary for the helix to form (unlike the local flattening in the case of an axial load).

Experimental evidence provides sufficient support to the notion of high resilience of SWNT. An early observation of noticeable flattening of the walls in a close contact of two MWNT has been attributed to van der Waals forces pressing the cylinders to each other.<sup>[18]</sup> Collapsed forms of the nanotube ("nanoribbons"), also caused by van der Waals attraction, have been observed in experiment, and their stability can be explained by the competition between the van der Waals and elastic energies.<sup>[19]</sup> Any additional torsional strain imposed on a tube in experimental environment also favors flattening<sup>[13,14]</sup> and facilitates the collapse. Graphically more striking evidence of resilience is provided by bent structures,<sup>[20]</sup> as well as the more detailed observations that actually stimulated our research in nanomechanics.<sup>[21]</sup> An accurate measurement with the atomic force microscope (AFM) tip detects the "failure" of a multiwall tubule in bending,<sup>[8]</sup> which essentially represents nonlinear buckling on the compressive side of the bent tube. The estimated measured local stress is 15-28 GPa, very close to the calculated value.<sup>[22,23]</sup> Buckling and ripple of the outmost layers in a dynamic resonant bending has been directly observed and is responsible for the apparent softening of MWNT of larger diameters.<sup>[5,24]</sup>

#### FAILURE AND RELAXATION MECHANISMS

The important issue of ultimate tensile strength of CNTs is inherently related with the atomic relaxation in the lattice under high strain. This thermally activated process was first predicted to consist of a sequence of individual bond rotations in the approach based on dislocation theory.<sup>[22,25,26]</sup> Careful computer simulations demonstrate feasibility of this mechanism and allowed us to quantify important energy aspects.<sup>[27,28]</sup> It has been shown that in a crystal lattice such as the wall of a CNT, a yield to deformation must begin with a homogeneous nucleation of a slip by the shear stress present. The nonbasal edge dislocations emerging in such slip have a well-defined core, a pentagon-heptagon pair, 5/7. Therefore the prime dipole is equivalent to the Stone-Wales (SW) defect. The nucleation of this prime dislocation dipole "unlocks" the nanotube for further relaxation: either brittle cleavage or a plastic flow. Remarkably, the latter corresponds to a motion of dislocations along the helical paths (glide "planes") within the nanotube wall. This causes a stepwise (quantized) necking, when the domains of different chiral symmetry and therefore different electronic structure are formed, thus coupling the mechanical and electrical properties.<sup>[22,25,26]</sup> It has further been shown<sup>[22,23,25,28-30]</sup> that the energy of such nucleation explicitly depends on CNT helicity (chirality).

Below, we deduce starting with dislocation theory the atomistics of mechanical relaxation under extreme tension. Locally, the wall of a nanotube differs little from a

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single graphene sheet, a 2-D crystal of carbon. When a uniaxial tension  $\sigma$  (N/m—for the 2-D wall, it is convenient to use force per unit length of its circumference) is applied, it can be represented as a sum of expansion (locally isotropic within the wall) and a shear of a magnitude  $\sigma/2$ (directed at  $\pm 45^{\circ}$  with respect to tension). Generally, in a macroscopic crystal, the shear stress relaxes by a movement of *dislocations*, the edges of the atomic extraplanes. Burgers vector **b** quantifies the mismatch in the lattice as a result of a dislocation. Its glide requires only local atomic rearrangements and presents the easiest way for strain release, provided sufficient thermal agitation. In an initially *perfect* lattice such as the wall of a nanotube, a yield to a great axial tension begins with a homogeneous nucleation of a slip, when a dipole of dislocations [a tiny loop in three-dimensional (3-D) case] first has to form. The formation and further glide are driven by the reduction of the applied-stress energy, as characterized by the elastic Peach-Koehler force on a dislocation. The force component along **b** is proportional to the shear in this direction and thus depends on the angle between the Burgers vector and the circumference of the tube,

$$f_{\rm b} = -(1/2)\sigma|b|\sin 2\theta \tag{10}$$

The max  $|f_b|$  is attained on two  $\pm 45^\circ$  lines, which mark the directions of a slip in an isotropic material under tension.

The graphene wall of the nanotube is not isotropic; its hexagonal symmetry governs the three glide planes—the three lines of closest zigzag atomic packing, oriented at  $120^{\circ}$  to each other (corresponding to the  $\{10\overline{1} \ l\}$  set of planes in 3-D graphite). At nonzero shear, these directions are prone to slip. The corresponding *c*-axis edge dislocations involved in such slip are indeed known in graphite. The six possible Burgers vectors  $1/3a\langle 2\overline{110}\rangle$  have a magnitude b=a=0.246 nm (lattice constant), and the dislocation core is identified as a 5/7 pentagon-heptagon pair in the honeycomb lattice of hexagons. Therefore the primary nucleated dipole must have a 5/7/7/5 configuration (a 5/7 attached to an inverted 7/5 core). This configuration is obtained in the perfect lattice (or a nanotube wall) by a 90° rotation of a single C—C bond, well known in fullerene science as a Stone-Wales diatomic interchange. One is led to conclude that the SW transformation is equivalent to the smallest slip in a hexagonal lattice and must play a key role in the nanotube relaxation under external force.

The preferred glide is the closest to the maximum shear  $\pm 45^{\circ}$  lines and depends on how the graphene strip is rolled up into a cylinder. This depends on nanotube helicity specified by the chiral indices  $(c_1, c_2)$  or a chiral angle  $\theta$ indicating how far the circumference departs from the leading zigzag motif  $\mathbf{a}_1$ . The max  $|f_b|$  is attained for the dislocations with  $\mathbf{b}=\pm(0,1)$  and their glide reduces the strain energy

$$E_{\rm g} = -|f_{\rm b}a| = -Ca^2/2\sin(2\theta + 60)\varepsilon$$
(11)

per one displacement, a. Here  $\varepsilon$  is the applied strain and C=Yh=342 N/m can be derived from the Young's modulus of Y=1020 GPa and the interlayer spacing h=0.335nm in graphite; one then obtains  $Ca^2/2=64.5$  eV. Eq. 11 allows one to compare different CNTs (assuming similar amount of preexisting dislocations): the more energetically favorable is the glide in a tube, the earlier it must yield to applied strain.

In a pristine nanotube molecule, the 5/7 dislocations have to first emerge as a dipole by a prime SW transformation. Topologically, the SW defect is equivalent to either one of the two dipoles, each formed by an  $\sim a/2$ slip. Applying Eq. 11 to each of the slips, one finds

$$E_{\rm SW} = E_{\rm O} - A\varepsilon - B\sin(2\theta + 30)\varepsilon \tag{12}$$

The first two terms, the zero-strain formation energy and possible isotropic dilation, do not depend on chiral symmetry. The symmetry-dependent third term, which can also be derived as a leading term in the Fourier series, describes the fact that SW rotation gains more energy in



Fig. 7 SW transformations of an equatorially oriented bond into a vertical position create a nucleus of relaxation (top left corner). It evolves further as either a crack-brittle fracture route, left column-or as a couple of dislocations gliding away along the spiral slip "plane" (plastic yield, top row). In both cases, only SW rotations are required as elementary steps. The stepwise change of the nanotube diameter reflects the change of chirality, bottom right image, causing the corresponding variations of electrical properties (From Ref. [25].)

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an armchair ( $\theta$ =30°) CNT, making it thermodynamically the weakest and most inclined to SW nucleation of the dislocations, in contrast to the zigzag ( $\theta$ =0) where the nucleation is least favorable.

Consider for example a (c,c) armchair CNT as a typical representative (we will also see below that this armchair type can undergo a more general scenario of relaxation). The initial stress-induced SW rotation creates a geometry that can be viewed as either a dislocation dipole or a tiny crack along the equator. Once "unlocked," the SW defect can ease further relaxation. At this stage, both brittle (dislocation pileup and crack extension) and plastic (separation of dislocations and their glide away from each other) routes are possible, the former usually at larger stress and the latter at higher temperatures.

Formally, both routes correspond to a further sequence of SW switches. The 90° rotation of the bonds at the "crack tip" (Fig. 7, left column) will result in a 7/8/7 flaw and then 7/8/8/7, etc. This further strains the bonds partitions between the larger polygons, leading eventually to their breakage, with the formation of greater openings such as 7/14/7, etc. If the crack, represented by this sequence, surpasses the critical Griffith size, it cleaves the tubule.

In a more interesting distinct alternative, the SW rotation of another bond (Fig. 7, top row) divides the 5/7 and 7/ 5, as they become two dislocation cores separated by a single row of hexagons. A next similar SW switch results in a double-row separated pair of the 5/7's and so on. This corresponds, at very high temperatures, to a plastic flow *inside* the nanotube molecule, when the 5/7 and 7/5 twins glide away from each other driven by the elastic forces, thus reducing the total strain energy (cf. Eq. 11). One remarkable feature of such glide is a result of mere cylindrical geometry: the glide "planes" in case of nanotubes are actually spirals, and the slow thermally activated Brownian walk of the dislocations proceeds along these well-defined trajectories. Similarly, their extraplanes are just the rows of atoms also curved into the helices.

A nanotube with a 5/7 defect in its wall loses axial symmetry and has a bent equilibrium shape; the calculations show<sup>[31]</sup> the junction angles  $<15^{\circ}$ . Interestingly then, an exposure of an even achiral nanotube to the axially symmetric tension generates two 5/7 dislocations, and when the tension is removed, the tube "freezes" in an asymmetric configuration, S-shaped or C-shaped, depending on the distance of glide, i.e., time of exposure. This seemingly "symmetry-violating" mechanical test is a truly nanoscale phenomenon. Of course, the symmetry is conserved statistically because many different shapes form under identical conditions.

When the dislocations sweep a noticeable distance, they leave behind a tube segment changed strictly following the topological rules of dislocation theory. By considering a planar development of the tube segment containing a 5/7, for the new chirality vector  $\mathbf{c}'$ , one finds

$$(c'_1, c'_2) = (c_1, c_2) - (b_1, b_2)$$
 (13)

with the corresponding reduction of diameter, d. While the dislocations of the first dipole glide away, a generation of another dipole results, in further narrowing and proportional elongation under stress, thus forming a neck as shown above. The orientation of a generated dislocation dipole is determined every time by the Burgers vector closest to the lines of maximum shear  $(\pm 45^{\circ} \text{ cross at the})$ endpoint of the current circumference vector c). The evolution of a (c,c) tube will be:  $(c,c) \rightarrow (c,c-1) \rightarrow$  $(c,c-2) \rightarrow \dots (c,0) \rightarrow [(c-1,1) \text{ or } (c,-1)] \rightarrow (c-1,0) \rightarrow$  $[(c-2,1) \text{ or } (c-1,-1)] \rightarrow (c-2,0) \rightarrow [(c-3,1) \text{ or }$ (c-2,-1)]  $\rightarrow$  (c-3,0), etc. It abandons the armchair (c,c)type entirely, but then oscillates in the vicinity of zigzag (c,0) kind, which appears a peculiar attractor. Correspondingly, the diameter for a (10,10) tube changes stepwise, d=1.36, 1.29, 1.22, 1.16 nm, etc., the local stress grows in proportion, and this quantized necking can be terminated by a cleave at late stages. Interestingly, such plastic flow is accompanied by the change of electronic structure of the emerging domains, governed by the vector  $(c_1,c_2)$ . The armchair tubes are metallic, and others are semiconducting with the different band gap values. The 5/7 pair separating two domains of different chirality has been discussed as a pure-carbon heterojunction, is argued to cause the current rectification detected in a nanotube nanodevice,<sup>[32]</sup> and can be used to modify, in a controlled way, the electronic structure of the tube. Here we see how this electronic heterogeneity can arise from a mechanical relaxation at high temperature: if the initial tube was armchair-metallic, the plastic dilation transforms it into a semiconducting type irreversibly.<sup>[25,26,33]</sup>

While the above analysis is based on atomic picture (structure and interactions), recent developments<sup>[34]</sup> offer an approach where the fracture nucleation can be described rather elegantly within nonlinear continuum me-



а





**Fig. 9** T=3000 K, strain 3%, plastic flow behavior (about 2.5 nsec). The shaded area indicates the migration path of the 5/7 edge dislocation. (From Ref. [28].)

chanics (based on classical interatomic forces for carbon). Whether this approach can describe change in chirality, temperature dependence, or temporal aspects of relaxation should yet be explored.

The dislocation theory allows one to expand the approach to other materials, and we have recently applied it to boron nitride (BN) nanotubes.<sup>[35,36]</sup> While the binding energy in BN is lower than in CNT, the formation of 5/7/7/5 defect can be more costly because of Coulomb repulsion between emerging BB and NN pairs (Fig. 8a) (bonding in BN is partially ionic with strong preference to chemical neighbor alternation in the lattice). Another

dislocation pair 4/8/8/4 that preserves the alternation must be considered (Fig. 8b). It turns out that the quantitative results are sensitive to the level of theory accuracy. Tight binding approximation<sup>[37]</sup> underestimates the repulsion by almost 3 eV.<sup>[35,36]</sup> Ab initio DFT calculations show that 5/7/7/5 is metastable lowest energy defect in BN, and its formation energy 5.5 eV is higher than 3.0 eV in carbon,<sup>[35,36]</sup> thus suggesting higher thermodynamic stability of BN under tensile load. Relaxation under compression is different as it involves skin-type buckling also investigated recently.<sup>[38]</sup>

# KINETIC APPROACH TO STRENGTH-FAILURE EVALUATION

Computer simulations have provided a compelling evidence of the mechanisms discussed above. By carefully tuning a *quasi-static* tension in the tubule and gradually elevating its temperature, with extensive periods of MD annealing, the first stages of the mechanical yield of CNT have been observed (Fig. 9).<sup>[27,28]</sup> In simulation of tensile load, the novel patterns in plasticity and breakage, just as described above, clearly emerge. At very *high strain* rate, the details of primary defects cannot be seen and they only begin to emerge at higher strain level, giving impression of exceedingly high breaking strain.<sup>[17]</sup>

Fracture, of course, is a *kinetic* process where time is an important parameter. Even a small tension, as any non-hydrostatic stress, makes material thermodynamically metastable and a generation of defects energetically favorable. Thus the important issue of strength remains beyond the defect formation energy and its reduction with the applied tension. Recently, we developed kinetic theory



**Fig. 10** Activation barrier values (here computed within classical multibody potential, a) serve as input to the rate equation (14) and the calculation of the yield strain as a function of time (here from 1 msec to 1 year, b), temperature (here 300 K), and chiral symmetry ( $\chi$ ). (From Ref. [30].)

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in application to CNT.<sup>[30,39]</sup> In this approach, we evaluate conditions (strain  $\varepsilon$ , temperature *T*) when the probability *P* of defect formation becomes significant within laboratory test time  $\Delta t$ ,

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$$P = v\Delta t N_{\rm B}/3 \sum_{m} \exp[-E_m(\varepsilon,\chi)/k_{\rm b}T] \sim 1$$
(14)

Here  $v = k_{\rm b}T/h$  is the usual attempt frequency and  $N_{\rm B}$  is the number of bonds in the sample. Activation barrier  $E_{\rm m}(\varepsilon,\chi)$ must be computed as a function of strain and chirality  $\chi$  of the tubule, and then the solution of this equation with respect to  $\varepsilon$  gives the breaking strain values. This approach involved substantial computational work in finding the saddle points and energies (Fig. 10a) for a variety of conditions and for several transition state modes (index *m* in the summation above). Obtained yield strain near 17% (Fig. 10b,<sup>[30,39]</sup>) is in reasonable agreement with the series of experimental reports. We currently are implementing similar approach with ab initio level of saddle point barrier calculations.<sup>[40]</sup> Preliminary data show higher 8–9 eV barriers, but their reduction with tension is also faster.

Previously performed high strain rate simulations have shown temperature dependence of breaking strain,<sup>[14,17]</sup> consistent with the kinetic theory.<sup>[30]</sup> In a constant strain rate arrangement (when the ends of the sample are pulled



**Fig. 11** 2-D geodesic projection (left) and the actual 3-D structures (right) show the transformations from a pair of separate (5,5) tubes (a) to a single defect-free nanotube. Primary "polymerization" links form as two other bonds break (b, dashed lines). The  $\pi/2$  rotations of the links (the bonds subject to such SW flip are dotted) and the SW flips of the four other bonds in (c) produce a (5,0) neck (d). It widens by means of another 10 SW rotations, forming a perfect single (5,5) tubule (not shown). (From Ref. [42].)



**Fig. 12** 2-D projections (left) and the computed 3-D intermediate structures (right) in the coalescence of the two (10,10) nanotubes: separate caps (a) in a sequence similar to Fig. 8 develop a (5,5) junction (b), which then shortens (c) and widens into a (10,5) neck (d). Glide of the shaded 5/7 dislocations completes the annealing into a perfect (10,10) CNT (not shown). Due to the fifth-fold symmetry, only two cells are displayed. (From Ref. [42].)

from the equilibrium with certain rate), the rate equation is slightly modified to its integral form. However, the main contribution comes from the vicinity of the upper limit,

$$P = vN_{\rm B}/3 \int \sum_{m} \exp\{-E_m[\varepsilon(t),\chi]/k_{\rm b}T\} dt \sim 1 \qquad (15)$$

Simple analysis reveals certain invariant  $T \times \log(v\Delta t)$  of the time of failure and temperature (provided the constant strain). Detailed simulations could shed additional light on this aspect (Cho et al., private communication, 2002). More significant finding reported recently<sup>[41]</sup> is that kinetic probability of SW bond rotation at room temperatures can be rather small and the actual mechanism of failure is a brittle cleave, through a sequence of "latticetrapped" states corresponding to individual broken bonds, from one to two, three, etc.<sup>[41]</sup>

# COALESCENCE OF NANOTUBES AS A REVERSED FAILURE

Understanding the details of failure mechanism has led us recently  $^{[42-44]}$  to investigate an opposite process, a





coalescence of nanoscale clusters analogous to macroscopic sintering or welding. Fusion of smaller components into a larger whole is a ubiquitous process in condensed matter. In molecular scale, it corresponds to chemical synthesis, where exact rearrangement of atoms can be recognized. Coalescence or sintering of macroscopic parts is usually driven by the well-defined thermodynamic forces (frequently, surface energy reduction), but the atomic evolution path is redundant and its exact identification is irrelevant. Exploring a possibility of the two particles merging with atomic precision becomes compelling in nanometer scale, where one aspires to "arrange the atoms one by one." Are the initial and final states connected by a feasible path of atomic movements, or separated by insurmountable barriers? Direct molecular dynamics (MD) investigation is usually hampered by energy landscape traps and beyond very few atomic steps needs to be augmented with additional analysis.

An example of very small particles is offered by fullerene cages and CNTs. Fusion of fullerenes has been previously reported and the lateral merging (diameterdoubling) of CNT has been observed and simulated.<sup>[45,46]</sup> In contrast, head-to-head coalescence of CNT segments remained unexplored and of particular theoretical and practical interest: Is it permitted by rigorous topology rules to eliminate all the pentagons always present in the CNT ends and thus dissolve the caps completely? Can this occur through a series of well-defined elementary steps and what is overall energy change if the system evolves through the intermediate disordered states to the final purely hexagonal lattice of continuous tubule? If feasible, such "welding" can lead to increase of connectivity in CNT arrays in bundles/ropes and crystals and thus significantly improve the mechanical, thermal, and electrical properties of material. In addition, determining the atomistic steps of small-diameter tube coalescence (with the end caps identical to half-buckyball) can shed light on the underlying mechanism of condensed phase conversion or CNT synthesis from C<sub>60</sub> components.

In Ref. [42] we have reported for the first time atomically precise routes for complete coalescence of generic fullerene cages: cap-to-cap CNT and C<sub>60</sub> merging together to form defectless final structure. The entire process is reduced to sequence of Stone–Wales bond switches and therefore is likely the lowest energy path of transformation. Several other examples of merging follow immediately as special cases: coalescence of buckyballs in peapod, joining of the two (5,5) tubes as in Fig. 11, "welding" the (10,10) to (10,10) following Fig. 12, etc. The approach remains valid for arbitrary tubes with the important constraint of unavoidable grain boundary for the tubes of different chirality. The junction of (n,m) and (n',m') must contain 5/7 dislocations or their equivalent of



**Fig. 13** Molecular mechanics (relaxed with realistic interatomic force-field and weak van der Walls interaction) simulation of the simplest tensegrity structure c3t9 of carbon nanotube beams connected by covalently attached to the cap pentagons polyethylene chains (From Ref. [49].)

(n-n',m-m') total Burgers vector.<sup>[25]</sup> The proposed mechanism<sup>[42–44]</sup> has important implications for nanotube material (crystals, ropes) processing and property enhancement, engineering of nanoscale junctions of various types, possible growth mechanisms with the C60 and other nanoparticles as feedstock. In the context of nanomechanics, an interesting feature of the late stages of coalescence is the annealing and annihilation of 5/7 pairs in a process exactly reverse to the formation and glide of these dislocation cores in the course of yield and failure under tension. On the other hand, although covalent bond flip represents intramolecular process, it is remarkable how it can lead to possibility of global supramolecular shape changes and reactions, from merging coalescence to interpenetration and encapsulation.

# TENSEGRITY AT SUPRAMOLECULAR SCALE

Usual supramolecular interactions possess the same generic properties as any other interatomic forces: weak but always present attraction at large distances (from tens of nanometers) results in a relatively shallow potential minimum at intermolecular vicinity of 0.2–0.5 nm spacing. Closer, it turns into a steep repulsive potential which, upon sufficient compression, can yield to a covalent bonding. Therefore supramolecular forces by themselves are unlikely to be able to support low-density assembly of molecules and nanotubes in particular: they would form aligned bundles or at least relatively dense random mats. In this context, it became of interest recently to explore transferability of certain ideas of macroengineering and to



connect rigid nanotubes by chemically attached polymer segments to keep them apart. This seems at a first glance counterintuitive-how adding *flexible* links can prevent rigid beams from lumping together? However, at the macroscopic scale, the idea goes back to Fuller,<sup>[47]</sup> who has proposed and patented tensile-integrity structures, hence the terms *tensegrity* in the literature. Tensegrity is a design principle that describes how network structures achieve shape stability. The main point is that a disconnected set of rigid beams can be tethered by sparse series of tensile threads (each perfectly bendable and unsupportive to any compression) in such a way that global structure can become rigid, sustain compressive global load, and possess all-finite vibration eigenfrequencies. Such engineered structures can be found in architecture, furniture, entertainment, and aerospace applications (because of lightweight and "foldability"). In cell biology, cytoskeleton is also suggested to possess tensegrity properties.<sup>[48]</sup> Fig. 13 shows simplest simulated tensegrity unit (3 beams compression members connected by 9 chains tension members, c3t9 per Skelton's nomenclature) composed of rigid carbon nanotubes tethered by polymer chains.<sup>[49]</sup> We have analyzed stability changes in such and several similar structures upon removal of one chain or adding a few extras.

### CONCLUSION

Mechanics of nanotubes has attracted keen interest since their discovery and over the past decade. Above, we have described several established facts and properties together with other, yet speculative aspects and possibilities. It may be useful to reiterate in conclusion some observations and notions of the field as discussed in this article.

Because of qualitative differences, nanotube mechanics can be subdivided into intramolecular, involving bond rearrangements and atomic removal or insertion within the carbon lattice of the tube wall, and supramolecular mechanics of interactions *between* the tube molecules. As illustrated above, the latter can be a result of weak distant interactions via dispersion van der Waals forces, stronger direct electrostatic potentials, or by means of much stronger covalent linkage-tethering of nanotubes through intermediate functional groups or elongated chains (as in the example of tensegrity designs). While supramolecular interactions play central role in colloid chemistry, in numerous biochemical processes, and have been broadly studied, in case of nanotubes, certain special aspects stand out. Great strength of carbon lattice makes it qualitatively different from most other molecules often involved in supramolecular processes: lowest activation barrier for intratube bond rearrangements is 7–9 eV high, which makes even covalent bonding with some other species or between the tubes relatively small supramolecular pertubation.

In contrast, the very same stiffness and "surface" smoothness of the tubes results in dramatic amplification or the traditionally weak dispersion forces. Van der Waals interactions add up along the tube–tube contact and yield typically  $\sim 1$  eV per each nanometer of length, i.e., many electron volts for a typical lateral contact. In turn, this makes solubility or even mechanical separation of nanotube bundles a very challenging task. These distinct features of supramolecular mechanics of nanotubes play critical role in their assembly in arrays-bundles of ropes, nematic crystals, or in their distribution in and coupling with solvents or matrix substances in composite materials.

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