Computational Mechanical Modeling
of the Behavior of Carbon Nanotubes

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Abstract: This paper presents a computational method for the mechanical simulation of carbon nanotubes, whose complexity is linear on the number of atoms. The regularity of a graphene lattice at its energy ground permits the definition of a tiling scheme that is applied to the surface of nanometric carbon pipes. The scheme employs elementary Y-shaped cells and proposes a coherent combination of a discrete approach with a continuous elastic beam reference for the numerical simulation of complex structures. In the molecular region, the employed potential is obtained from the local harmonic approximation and leads to an explicit formulation of the acting forces, therefore permitting the dynamical prediction of large deformations as bending and torsion. The study includes a numerical consistency check based on the conservation of the global energy of the molecular system. As a conclusion, future developments and possible applications of the proposed scheme are presented.

Key–Words: Carbon Nanotubes, Molecular Dynamics, Numerical Simulation, Mathematical Modeling, Computational Method

1 Introduction

Carbon nanotubes (CNTs) attract increasing attention since the initial report on their existence [1], followed by subsequent reports on the possibility of feasible conditions for their synthesis in sizeable quantities [2] and simulations of their growth process [3]. Their physical properties make them extraordinary research objects: they exhibit fascinating mechanical, electronic and thermal peculiarities. From the mechanical point of view, their large tensile strength is combined with extreme flexibility; these exceptional properties contribute to the outstanding potential of CNTs. Interestingly, they can be filled with fluids or with fullerenes [4, 5, 6, 7, 8, 9, 10]. Their behavior under deformation is the subject of intense investigations; nonetheless, mechanical experiments at this scale are themselves still under development: at the nanometric length scale, correct determination of the sample, selective placement of the research object, precise load imposition and appropriate measurement are challenging tasks to experimentalists [11, 12]. Therefore, the computational investigation of the mechanical properties is fully justified in order to

○ explain the observed results [13],

○ obtain information that is currently inaccessible in experiments [14],

○ guide the exploration of new research frontiers [15].

Current research on CNTs and related carbon nanostructures is still at an early stage of development, but these objects are already beginning to exhibit their exceptional properties, many of which may lead to practical applications [16]. In particular, the biocompatibility of the tubules, combined with their outstanding strength, attracts a great interest for biomedical applications. In a growing number of laboratories around the world, CNTs and nanohorns [17] are considered as efficient storage systems, with promising applications for hydrogen storage in fuel cells [18, 19]. Moreover, CNTs are known to resist degradation in the types of chemical environment present in the human body and are considered also for drug delivery: they could be implanted without trauma at the sites where a drug must be slowly released. Their considerable potential in cellular experiments is motivated by their future use as nanopipettes for the distribution of extremely small volumes of liquid or gas onto surfaces or into living cells. Also, their property of high capillarity increments the interest of their application in nanofluidics [20, 21].

CNTs are extremely flexible and, at the same time, thin, long but also rigid and strong. Even extreme deformations are reversible: when strongly bent, they buckle instead of breaking and their initial

shape is rapidly restored. This peculiarity can be also exploited for a new generation of scanning probe tips for Atomic Force Microscopy [22], obtained by attaching a CNT to a standard microscope tip. Another example of their mechanical usefulness as tools for control in nanofluidics is given by nanotweezers [23], where two tubules are mounted on independent electrodes over a micropipette and can pick up submicron particles. The tweezing action is caused by the electrostatic attraction between the two nanotubes when a bias is applied between them.

This paper is organized as follows. First, this section presents the tubules and their possible applications. The introduction justifies the necessity of mathematical modeling and of an efficient method for the numerical simulation of these structures. In the following section, the formal modeling framework is presented, comprising the geometrical aspects and the choice of the specific molecular potential. Then, the numerical method is proposed; it can simulate the mechanical deformation of the tubules and, consequently, permits a form of precise mechanical control of the axial bending. Finally, conclusions and outlook for future works follow.

1.1   From Graphene to Carbon Nanotubes

Graphite and diamond are allotropes of carbon that are known from ancient times; other allotropes, like fullerenes and CNTs, have been discovered only ten to twenty years ago [1]. Graphite is made of layers of graphene, but the latter is not an allotrope of carbon because of its finite thickness. More precisely, a sheet of graphene at rest consist of a hexagonal lattice of carbon atoms, where the atoms occupy the vertices of the hexagons; perfect sheets consists purely of hexagonal cells, while defects are constituted by spurious pentagonal and heptagonal cells. Graphene is the two-dimensional counterpart of graphite and, from many points of view, is the best theoretically studied structure of carbon and the starting point in several calculations regarding graphite, CNTs [24] and fullerenes.

The results of various experiments with transmission electron microscopy [25], Raman scattering [26], resistivity [27], scanning tunneling microscopy [28] and susceptibility are consistent with the identification of CNTs with cylindrical graphene sheets of sp^2-bonded carbon atoms. Hence, they can be easily described as rolled graphene sheets, whose mechanical properties follow from the nature of the bonds between the carbon atoms. These in-plane bonds are the strong covalent bonds that bind the atoms in a graphene sheet.

In graphite, two-dimensional graphene sheets are stacked to form the three-dimensional structure. In each layer of graphene, successive layers are stacked in an interleaving sequence. The interlayer distance is $d_p = 0.335$ nm and the nearest-neighbor distance is $a_{CC} = 0.142$ nm [29]. At room temperature, the latter distance a_{CC} is the smallest of all the solid elements at room temperature and this implies, combined with the large distance between the layers, that the surfaces are electrically, chemically, and mechanically nearly unconditioned. That's the reason why most of the physical and chemical properties of graphite and of CNTs can be understood from graphene.

1.2   Chirality

CNTs are usually classified into Single-Walled (SWCNTs) and Multi-Walled (MWCNTs) Carbon Nanotubes; the former class consisting of single graphene sheets and the latter comprising several nested SWCNTs. For the sake of simplicity, the present work concerns cylindrical portions of SWCNTs but it is not limited to those structures; it successfully applies also to carbon nanohorns [30] and nanotori [31].

SWCNTs can be mathematically classified according to their helicity and radius. The classification is based on an ordered pair of integers $(n, m) \in \mathbb{N}^2$. A mathematical description of a perfect graphene sheet at rest is presented here, in order to simplify further formalizations.

Let a graphene sheet at its ground energy configuration be on the plane that is described by $\mathbb{R}^2$. Then, let $\mathbf{Q}_1 \in \mathbb{R}^2$ be the position of the atom Q_1, considered as a single point on that plane. Let $\mathbf{Q}_2$ be the position of another atom, namely Q_2, in the lattice, such that the latter shares a covalent bond with the former in $\mathbf{Q}_1$. Let a vector be $\mathbf{Q}_x = \overrightarrow{\mathbf{Q}_1\mathbf{Q}_2}$ and let be $\mathbf{Q}_y$ another vector such that

$$\mathbf{Q}_x \perp \mathbf{Q}_y \tag{1}$$

and that

$$\|\mathbf{Q}_x\|_2 = \|\mathbf{Q}_y\|_2. \tag{2}$$

Because of the hexagonal nature of the lattice, two additional vectors are specified in order to simplify the classification of SWCNTs according to their chirality. These are defined as follows:

$$\begin{aligned}
\mathbf{a}_1 &= \frac{3}{2}\mathbf{Q}_x + \frac{\sqrt{3}}{2}\mathbf{Q}_y, \\
\mathbf{a}_2 &= \frac{3}{2}\mathbf{Q}_x - \frac{\sqrt{3}}{2}\mathbf{Q}_y.
\end{aligned} \tag{3}$$

The ordered pair of integers $(n, m) \in \mathbb{N}^2$ has the additional constraint

$$m \leq n, \tag{4}$$

which is introduced in order to eliminate the multiple definitions caused by the sixfold geometry of the hexagonal lattice and its point group symmetry. This pair of integers defines a chiral vector [32]

$$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2, \tag{5}$$

that connects two crystallographically equivalent sites on the graphene lattice [33] and permits the definition of the chiral angle of the tubule θ and of its diameter D_t. The former is given by

$$\theta_t = \arctan\left(\frac{\sqrt{3}m}{(m+2n)}\right) \tag{6}$$

and the latter by

$$D_t = \frac{\sqrt{3}}{\pi} a_{CC} \sqrt{m^2 + mn + n^2}. \tag{7}$$

According to their chirality, CNTs are named "zigzag" when identified by the couple $(n,0)$, "armchair" by the couple (n,n), and "general chiral" otherwise [32]. Chirality must be considered in precise computations of the mechanical behavior, since it influences the mechanical properties of the tubules [34].

2 Numerical Modeling

CNTs are at the boundary between structures and molecules. Reflecting their condition, modeling approaches can be generally classified into two categories: atomistic and continuum modeling [24, 13]. For the former approach, the major computational technique is molecular dynamics, which is very comprehensive but also computationally expensive; interactions are obtained by multi-body potentials with simple analytical forms and their complexity grows polynomially with the number of atoms but seldom linearly. As a result, operable applications are limited to small and short-lived systems. As to the second approach, it simplifies the model by treating CNTs as continuum elastic shells or as membranes with bending stiffness, extending classical continuum mechanics. However, these latter models risk to be too reductionist; without a combined approach, they are almost unable to account for forces acting on individual atoms and for the lattice vacancies that constitute realistic defects [35].

2.1 Lattice Modeling

Lattice modeling is a field of active research which is common in several disciplines; here, the discrete mechanical model consists of atoms and interatomic

bonds. Reflecting the repetitive display of the lattice on a graphene sheet, a numbering scheme is presented in order to define the discrete counterpart of the reference configuration in continuum mechanics. The identification of the atoms with the vertices of the hexagons holds even when a mechanical deformation modifies the regular pattern, producing hexagons that are not planar nor isometric. Thus, the numbering can be performed with reference to the unstressed configuration of the sheet, obtaining a structure that describes the entire sheet as the tiling repetition of an elementary Y-shaped cell. First, this modeling technique is applied to graphene [36] and, finally, to CNTs.

Formally, a sheet of graphene $\mathcal{G}(\mathcal{A},\mathcal{B},\mathcal{C})$ is composed by a set of carbon atoms $\mathcal{A}$, a set of binary bonds $\mathcal{B}$ and a set $\mathcal{C}$ of couples of bonds that share a common atom. Every atom $a \in \mathcal{A}$ is considered as a material point with mass m_a. It has a unique label and its time-dependent position, which are respectively represented as follows:

$$\begin{aligned} \text{lab}_a &\in \mathbb{Z}^2 \times \{1,2\}, \\ \text{pos}_a(t) &\in \mathbb{R}^3, \ \ \forall t \in [t_0,+\infty). \end{aligned} \tag{8}$$

Every bond $b \in \mathcal{B}$ is an ordered pair of atoms and, similarly, every $c \in \mathcal{C}$ is an ordered pair or bonds

$$\begin{aligned} b &= (b_1,b_2), \\ c &= (c_1,c_2). \end{aligned} \tag{9}$$

Now, let the set of vectors $\{\mathbf{i}_x,\mathbf{i}_y,\mathbf{i}_z\}$ be an orthonormal basis for $\mathbb{R}^3$ and let the graphene sheet $\mathcal{G}$ be at rest on the plane given by $\text{span}\{\mathbf{i}_x,\mathbf{i}_y\}$ at time $\widehat{t} \in [t_0,+\infty)$, that is

$$\forall a \in \mathcal{A} \ \ \text{pos}_a(\widehat{t}) \in \text{span}\{\mathbf{i}_x,\mathbf{i}_y\}. \tag{10}$$

Let the origin of $\mathbb{R}^3$ coincide with the position of the atom $a_O \in \mathcal{A}$. Because of the hexagonal structure of the lattice, another useful coordinate system that is not orthonormal can be specified for the physical space. Two new linearly independent vectors $\mathbf{J}_1, \mathbf{J}_2$ are introduced, such that

$$\begin{aligned} \mathbf{J}_1 &= \sqrt{3}\mathbf{i}_x, \\ \mathbf{J}_2 &= \sqrt{3}\left(\frac{1}{2}\mathbf{i}_x + \frac{\sqrt{3}}{2}\mathbf{i}_y\right). \end{aligned} \tag{11}$$

As the length of the carbon–carbon bond a_{CC} is subnanometric [36], it's convenient to introduce the scaled versions of the previous vectors: $\mathbf{j} = a_{CC}\mathbf{J}$. Without loss of generality, it can be assumed that the vector

$$\mathbf{s} = a_{CC}\left(\frac{\sqrt{3}}{2}\mathbf{i}_x + \frac{1}{2}\mathbf{i}_y\right) \tag{12}$$

connects two bonded atoms of $\mathcal{G}$. Two rhomboidal grids $\mathcal{A}_1, \mathcal{A}_2$ are defined on the plane $\text{span}\{\mathbf{j}_1, \mathbf{j}_2\}$; these are two lattices of atoms that partition $\mathcal{A}$. The former is defined by

$$
\begin{aligned}
\mathcal{A}_1 = \{a \in \mathcal{A} | \, \text{pos}_a(\widehat{t}) = \alpha_1 \mathbf{j}_1 + \alpha_2 \mathbf{j}_2, \\
(\alpha_1, \alpha_2) \in \mathbb{Z}^2\}
\end{aligned}
\tag{13}
$$

and the latter is the shifted version $\mathcal{A}_2 = \mathcal{A} \backslash \mathcal{A}_1$ by the shifting vector $\mathbf{s}$. As a consequence of this partition, it's possible to associate a unique label to every atom $a \in \mathcal{A}_k \subset \mathcal{A}$ following the rule

$$
\text{lab}_a = (\alpha_1, \alpha_2, k) \Leftrightarrow \text{pos}_a(\widehat{t}) = \alpha_1 \mathbf{j}_1 + \alpha_2 \mathbf{j}_2 + \delta_{k1} \mathbf{s},
\tag{14}
$$

where δ_{k1} is the Kronecker's delta.

2.2 Elementary Cells

The Y-shaped cell is the elementary tile that covers the entire graphene sheet. There is a different cell for every atom $a \in \mathcal{A}_1$ and every cell is uniquely identified by the ordered pair of integers $(\alpha_1, \alpha_2) \in \mathbb{Z}^2$ that appears in $\text{lab}_a = (\alpha_1, \alpha_2, 1)$. Three bonds and two atoms constitute a cell and, hence, every cell $Y(\alpha_1, \alpha_2)$ is given by the quintuple

$$
\begin{aligned}
Y(\alpha_1, \alpha_2) = (a_1(\alpha_1, \alpha_2), a_2(\alpha_1, \alpha_2), \\
b_1(\alpha_1, \alpha_2), b_2(\alpha_1, \alpha_2), b_3(\alpha_1, \alpha_2)),
\end{aligned}
\tag{15}
$$

where, for $i = 1, 2$,

$$
a_i(\alpha_1, \alpha_2) = (\alpha_1, \alpha_2, i) \in \mathcal{A}_i.
\tag{16}
$$

As every bond is specified by an ordered pair of neighboring atoms, for every cell $Y(\alpha_1, \alpha_2)$ the pattern is

$$
b_k(\alpha_1, \alpha_2) = ((\alpha_1 - \delta_{k1}, \alpha_2 - \delta_{k2}, 2), (\alpha_1, \alpha_2, 1)).
\tag{17}
$$

A vector is associated with every bond $b = (a_1, a_2)$, $b \in \mathcal{B}$ at time t; it is represented as

$$
\mathbf{B}(t) = \text{pos}_{a_1}(t) - \text{pos}_{a_2}(t)
\tag{18}
$$

and its length $l(t)$ is given by $l(t) = \|\mathbf{B}(t)\|_2$. In addition to atoms and interatomic bonds, the numbering scheme must be extended in order to include also couples of bonds that share a common atom. Six couples of bonds are associated to every Y-shaped elementary cell. Let a generic cell be $Y(\alpha_1, \alpha_2)$; then the couples are named $c_i(\alpha_1, \alpha_2)$ for $i = 1, 2, \ldots, 6$ and are described by the following ordered pairs of bonds:

$$
\begin{aligned}
c_1(\alpha_1, \alpha_2) &= (b_2(\alpha_1, \alpha_2), b_3(\alpha_1, \alpha_2)), \\
c_2(\alpha_1, \alpha_2) &= (b_3(\alpha_1, \alpha_2), b_1(\alpha_1, \alpha_2)), \\
c_3(\alpha_1, \alpha_2) &= (b_1(\alpha_1, \alpha_2), b_2(\alpha_1, \alpha_2)), \\
c_4(\alpha_1, \alpha_2) &= (b_2(\alpha_1, \alpha_2), b_3(\alpha_1, \alpha_2 - 1)), \\
c_5(\alpha_1, \alpha_2) &= (b_3(\alpha_1, \alpha_2), b_1(\alpha_1 - 1, \alpha_2)), \\
c_6(\alpha_1, \alpha_2) &= (b_1(\alpha_1, \alpha_2), b_2(\alpha_1 + 1, \alpha_2 + 1)).
\end{aligned}
\tag{19}
$$

Let $c = (b_1, b_2) \in \mathcal{C}$ be a couple of bonds that share a common atom, then the angle $p_c(t)$ between the bonds is given by

$$
p_c(t) = \frac{\mathbf{B}_1^T(t) \mathbf{B}_2(t)}{l_1(t) \, l_2(t)},
\tag{20}
$$

where $\mathbf{B}_i$ and l_i are, respectively, the vector and the length associated to the bond b_i for $i = 1, 2$.

The presented numbering scheme successfully applies also to SWCNTs, where it's adopted according to the constraints on the integer indices of the generic Y-shaped element $Y(\alpha_1, \alpha_2)$ that derive from the surface being cylindrical instead of planar. As a result, every single SWCNT can be denoted by $\mathcal{S} = (\mathcal{A}, \mathcal{B}, \mathcal{C})$ and will show a different but regular tiling pattern of the structure. Depending from the curvature of the surface and the chirality of the tubule (and also from its temperature), the length of the parameter a_{CC} may not be the same of a graphene sheet at rest, which is assumed to be $a_{CC} = 1.4$ Å [36] in the computational environment; the simulations can consider also SWCNTs that aren't already at the mechanical equilibrium.

3 Numerical Simulation

The behavior and the energetics of molecules are fundamentally quantum mechanical. However, it's possible to successfully employ the use of classical mechanics with a force-field approximation: the system's energy is expressed only as a function of the nuclear positions, according with the Born-Oppenheimer approximation. Being an atomistic method, every atom that constitutes the system is modeled as a single material particle. An appropriate potential is introduced in order to predict the energy associated with the given conformation of the molecule.

3.1 Empiric Potential

Let $\Psi(t)$ be a time-dependent vector with $3|\mathcal{A}|$ elements that contains the positions of every atom in the

SWCNT $\mathcal{S} = (\mathcal{A}, \mathcal{B}, \mathcal{C})$. More formally, this molecular conformation vector can be specified as follows:

$$\Psi(t) = [\text{pos}_{a_1}^T(t), \text{pos}_{a_2}^T(t), \ldots, \text{pos}_{a_n}^T(t)]^T \quad (21)$$

and $\mathcal{A} = \{a_i\}_{i=1}^n$. Given a molecular conformation $\Psi(t)$, the potential function $V : \mathbb{R}^{3n} \to \mathcal{R}$ can be written as

$$V(\Psi(t)) = V_c(\Psi(t)) + V_n(\Psi(t)), \quad (22)$$

where $V_c(\Psi(t))$ is the partial accounting for covalent bonds and $V_n(\Psi(t))$ for noncovalent interactions. Developing further the description of the potential energy from (22), the covalent portion can be expanded as follows

$$V_c(\Psi(t)) = V_b(\Psi(t)) + V_a(\Psi(t)) + V_d(\Psi(t)). \quad (23)$$

This representation considers the bond stretching, angle bending and dihedral interactions. The noncovalent portion accounts for the non-bonded electrostatic and van der Waals interactions. A rich literature in molecular mechanics is devoted to finding the most useful and realistic forms of these potential energy terms. Consequently, specific functional forms can be used for the energy terms, according to the different materials and the most disparate loading conditions that are considered in the simulation. For SWCNTs, only the term V_c is widely considered of interest when small strains are applied to the molecule, while the other term is usually negligible [37]. In such cases, only the terms accounting for bond stretching and angle variation are significant for the system potential. Therefore, the resulting potential energy is reasonably approximated by

$$V(\Psi(t)) \simeq V_b(\Psi(t)) + V_a(\Psi(t)). \quad (24)$$

In classical molecular mechanics, many functions have been introduced for the formulation of the appropriate potential energies. In this paper, under the assumption of small local deformations, it's adequate and convenient to employ the simple harmonic approximation for angles and bonds. This constraint is only local and doesn't forbid the simulation of large global deformations. Moreover, several calculations in computational chemistry have shown that a reasonable approximation to the potential energy of a molecular system can be provided by harmonic functions when the atoms are near to their equilibrium positions [38]. Binary bonds are modeled as springs and their stretch is subject to Hooke's Law. The spring parameters are obtained from experimental data; they are the equilibrium distance a_{CC} of the bond at rest and the spring constant k_l of linear elasticity [36]. The

same applies for torsion springs; their equilibrium angle is $2\pi/3$ and their spring constant is k_p. When a SWCNT is subjected to external forces, the displacements of individual atoms are constrained by bond stretching and angle bending; the global deformation is the result of these interactions.

The stretch potential of a single bond b can be expressed as

$$V_b(\mathbf{B}(t)) = \frac{k_l}{2} \left(l(t) - a_{CC} \right)^2. \quad (25)$$

Similarly, adjacent bonds tend to maintain their equilibrium angles and, again, the bending potential for the couple $c = (b_1, b_2)$ is given by

$$V_c([\mathbf{B}_1^T(t), \mathbf{B}_2^T(t)]^T) = \frac{k_p}{2} \left(\arccos p_c(t) - \frac{2\pi}{3} \right)^2. \quad (26)$$

The potential of the molecule with the conformation $\Psi(t)$ can be expressed as the summation of the term in (25) and (26) for every bond and every couple of adjacent bonds. The result is the global potential at time t:

$$V(\Psi(t)) = \sum_{b \in \mathcal{B}} V_b(\Psi(t)) + \sum_{c \in \mathcal{C}} V_c(\Psi(t)). \quad (27)$$

Since the function $\arccos$ is not differentiable when its argument belongs to the set $\{+1, -1\}$, it's convenient to replace the entire formula $(\arccos(x) - 2\pi/3)$ with another function $h : [-1, 1] \to \mathbb{R}$, such that

$$\forall x \in [-1, 1] \ \ h(x) \simeq \left(\arccos(x) - \frac{2\pi}{3} \right). \quad (28)$$

That is, h approximates its behavior but it's differentiable for $x \in \{+1, -1\}$.

A recognizable benefit of the above formulation is that the potential energy of the system is separated into individual energy terms according to their physical meaning and to the single atomic constituents. In this context, the harmonic approximation fits the fluctuation of the system around an equilibrium state and it's similar to the linearized theory of elasticity in continuum mechanics.

3.2 Gradient of the Scalar Potential

Let Ω be a test molecular conformation; then, at every time t, the derivative of $V(\Psi(t))$ with respect to Ω is

given by

$$
\begin{aligned}
V'(\Psi(t))(\Omega) = & \underbrace{\sum_{b \in \mathcal{B}_t} V_b'(\Psi(t))(\Omega)}_{V_{bond}'(\Psi(t))(\Omega)} \\
& + \underbrace{\sum_{c \in \mathcal{C}_t} V_c'(\Psi(t))(\Omega)}_{V_{angle}'(\Psi(t))(\Omega)}.
\end{aligned}
\tag{29}
$$

whose terms can be expanded as follows

$$
\begin{aligned}
V_{bond}'(\Psi(t), \Omega) = & \sum_{b \in \mathcal{B}_t} k_l (l_{[\Psi(t)]} - a_{CC}) \cdot \\
& \cdot \frac{\mathbf{B}_{b[\Psi(t)]}^T \mathbf{B}_{b[\Omega]}}{l_{[\Psi(t)]}}, \\
V_{angle}'(\Psi(t), \Omega) = & k_p \overline{h}(p_{c[\Psi(t)]}) Z(\Psi(t), \Omega) \cdot \\
& \cdot (w_2(\Psi(t), \Omega) - w_1(\Psi(t), \Omega))
\end{aligned}
\tag{30}
$$

and

$$
Z(\Psi(t), \Omega) = \left(\frac{\mathbf{B}_{1[\Psi(t)]} \wedge \mathbf{B}_{2[\Psi(t)]}}{l_{1[\Psi(t)]} l_{2[\Psi(t)]}} \right)^T.
\tag{31}
$$

Recalling (28), the function $\overline{h} : [-1, 1] \to \mathbb{R}$ is defined as

$$
\overline{h}(x) = h(x) \frac{dh(x)}{dt} \simeq - \left(\frac{\mathrm{acos}(x) - \frac{2\pi}{3}}{\sqrt{1 - x^2}} \right).
\tag{32}
$$

It's defined for all $b \in \mathcal{B}$

$$
w_b(\Psi(t), \Omega) = \frac{\mathbf{B}_{b[\Psi(t)]}(t)}{\left(l_{[\Psi(t)]}(t) \right)^2} \wedge \left(\mathbf{B}_{b[\Omega]} \right),
\tag{33}
$$

where $\mathbf{B}_{b[\Psi]}$ is the vector related to the bond in $\Psi(t)$ and similarly for $\mathbf{B}_{b[\Omega]}$.

From this significant result, it's possible to directly calculate the gradient of the scalar potential. More precisely, the i-th component of the gradient of V is given by

$$
[\nabla V(\Psi(t))]_i = V'(\Psi(t))(\Omega_i),
\tag{34}
$$

where Ω_i is the i-th vector of the cardinal basis of $\mathbb{R}^{3n}$. As a result, its elements are zeros everywhere except in its i-th position, that has unitary value.

3.3 Dynamics and Conservation

The molecular system has $6n$ degrees of freedom: the simulation computes the trajectory in a $6n$-dimensional phase space. These degrees are represented by two $3n$-dimensional vectors: the conformation vector $\Psi(t)$ and the vector of the momenta

$\Gamma(t) n m_a$. The result is the following dynamical system

$$
\begin{cases}
\dfrac{d\Psi(t)}{dt} = \Gamma(t) \\
\dfrac{d\Gamma(t)}{dt} = -\dfrac{\nabla V(\Psi(t))}{n m_a}.
\end{cases}
\tag{35}
$$

When the loads are constant over time, the conservation of the total energy E is implied by the formulation. In this case it can be written as

$$
\begin{aligned}
E(\Psi(t)) = & \nabla V(\Psi(t)) - \nabla L(\Psi(t)) + \\
& + \frac{m_a}{2} \sum_{a \in \mathcal{A}} \left(\frac{d\mathrm{pos}_a^T(t)}{dt} \frac{d\mathrm{pos}_a(t)}{dt} \right).
\end{aligned}
\tag{36}
$$

and permits the consistency check for the simulation.

Being a dynamical system with a direct evaluation of the gradient, the time integration scheme is the core of the computation. Here, the velocity-Verlet integration scheme is used to overcome the difficulty of the coherent evaluation of the velocities in the standard Verlet scheme [39, 40, 41, 42]. Hence, the resulting scheme with a step h and that accounts for the velocity is given by

$$
\begin{cases}
\Psi(t + h) \simeq \Psi(t) + h\Gamma(t) - \dfrac{h^2 \nabla I(\Psi(t))}{2 n m_a}, \\
\Gamma(t + h) \simeq -h \dfrac{\nabla I(\Psi(t)) + \nabla I(\Psi(t + h))}{2}.
\end{cases}
\tag{37}
$$

with a $O(h^4)$ local approximation both in velocity and position and a global $O(h^2)$ error [40].

4 Conclusions

Most of the focus in this paper has been to address the promising mechanical attributes that are related to the dynamical behavior of the SWCNTs. As stated in the introduction, effort still remains to be done on the experimental measurement of the mechanical properties of the tubules and on the applicability of the manipulation techniques. Here, progress made on the theoretical and computational fronts has also been briefly summarized.

The bending of CNTs is the main part of the numerical experimentation of this work. Individual tubules and also bundles of regularly displaced nanopipes were successfully controlled by bending the tubules until the molecular surface eliminated the internal volume. The consistency of the numerical method was tested with the computation of the Young's modulus (of the order of 1 TPa, depending on the diameter) and of the Poisson's ratio (of about 0.19, slightly depending on the chirality) for the tubules,

considered as elastic beams. The computed results have been tested against theoretical, experimental and computational data obtained so far [43] and provide good agreement. The continuous part can be modeled with the Exponential Cauchy-Born Rule [13] and numerically solved using computational mechanics approaches.

There are also a lot of unresolved issues in theoretical analysis of combined approaches that can consider also the effect of realistic defects. In fact, innovative numerical simulation schemes are being developed. The applicability of the results largely depends on a more complete improvement of the computational methods.

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