COMPUTATIONAL MODELING OF CARBON
NANOTUBE TURFS

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Computational modeling of carbon nanotube turfs

Abstract

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Carbon nanotubes grown on a substrate form a turf – a complex structure of intertwined, mostly nominally vertical tubes, cross-linked by adhesive contact and few bracing tubes. The turfs are compliant and good thermal and electrical conductors. The objective of this work is to understand the deformation of turfs using computational models. We consider two approaches

a) A phenomenological constitutive model of the turf developed from the micromechanical analysis of the turf deformation. We benchmark the developed model using a finite element implementation and compare using the results from nanoindentation tests on CNT turfs. The model includes: nonlinear elastic deformation, small Kelvin-Voigt type relaxation, caused by the thermally activated sliding of contacts, and adhesive contact between the turf and the indenter. The pre-existing (locked-in) strain energy of bent nanotubes produces a high initial tangent modulus, followed by an order of magnitude decrease in the tangent modulus with increasing deformation. The strong adhesion between the turf and indenter tip is due to the van der Waals interactions. The finite element simulations capture the results
from the nanoindentation experiments, including the loading, visco-elastic relaxation, unloading and adhesive pull-off.

b) A detailed discrete model of the turf developed by discretizing the CNTs using inextensible elastica elements with their equivalent material properties obtained from molecular dynamic simulations. The model includes a Lennard Jones type force law and a frictional component to model the interaction between segments of neighboring tubes. The equations of motion are integrated using an explicit integration technique and the response of the turf to external loading is studied. Periodic boundary conditions are used to model infinitely large turfs. Under flat punch indentation, the tendency of the carbon nanotubes to coalesce together and undergo coordinated buckling similar to experimental observations is captured. We also study the influence of the average initial curvature on the buckling wavelengths. There is a strong qualitative agreement in the nominal stress-strain response between the numerical results and experiments.
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CHAPTER 1
INTRODUCTION

Carbon Nanotubes (CNTs) have attracted attention during the past decade as a result of their superior properties; See for example Bernholtz et al. (2002) for investigations on the mechanical properties, Kim et al. (2001) and McClain et al. (2007) for electrical properties and Osman and Srivastava (2001) on the thermal properties. Of interest in this work is the collective mechanical behavior of CNTs as in carbon nanotube turfs. Nanotube turfs as seen in Figure 1.1 are a complex arrangement of intertwined, nominally straight multi-walled CNTs. In a stress-free state, the CNTs are bent and pre-buckled and this configuration serves to brace the structure. The suitability of using their excellent mechanical, electrical in nanoscale sensors and thermal switches has been investigated by Christensen et al. (2003) and Cola et al. (2007).

The collective mechanical behavior of CNTs has been analyzed by a number of researchers. Initial efforts by Qi et al. (2003) and Waters et al. (2004) focused on the behavior of short widely spaced tubes commonly referred to as Vertically Aligned Carbon Nanotube forests (VACNT). These VACNT structures are distinct from CNT turfs in that the tubes heights are of the order of tens of nanometers and are vertically straight without making contacts with neighboring tubes. Turfs have longer tubes with their height ranging from tens of micrometers to few hundred micrometers. During the growth process of turfs, the thermal vibrations enable the tubes to bend and make van der Waals type contact with neighboring tubes resulting in bent and prebuckled segments.
Nanoindentation experiments by McCarter (2006) and Qiu et al (2008) have demonstrated that the turfs are compliable and exhibit time-dependent reversible deformation under moderate strains. Under compression, the turfs exhibit initial high tangent modulus followed by an order of magnitude relaxation in the elastic modulus. The subsequent analysis of the micromechanics of deformation of the turf reported by Mesarovic et al. (2007) show that the behavior can be explained by the bending of the free CNT segment supported by adhesive contacts at the ends. The assumption of the stability of the adhesive contacts during external loading has been further confirmed by Qiu et al (2010).

Uniaxial compression experiments on CNT turfs by Hutchens (2010) indicate foam like material behavior of turfs. Further, experiments by Cao et al. (2005), Zbib et al, (2008) and Maschmann et al. (2011) under uniform compression uncovered a curious type of nonlocal behavior – collective reorientation and buckling of the bottom layer, followed by the sequence of buckling of adjacent layers. The curious aspect of this
behavior is that the nonlocality occurs under uniform loading, but not under non-uniform loading such as indentation experiments by McCarter et al. (2006) and Qiu et al. (2010). It has been suggested by Hutchens et al. (2010) that such behavior is the result of either non-homogenous properties of a material, or a structure-like behavior, not describable by continuum mechanics. In a recent work Qiu et al. (2011) reported new experimental results design specifically to answer the above questions. It was shown that the turf is indeed a material, indicating that collective reorientation and buckling of the bottom layer is the result of boundary conditions. A detailed analysis of the coordinated buckling in CNT turfs by Maschmann et al. (2011) showed that the location of the coordinated buckling depends on height of the turf. The coordinated buckling in turfs with heights < 200\(\mu\text{m}\) occurred at the top near the indenter surface. With further increasing height (650\(\mu\text{m}\)) the coordinated buckling occurred both at the surface and at the substrate. Buckling transitioned to the center and bottom of the turf for longer turf structures (1.2mm).

The goal of the current work is to gain further understanding of the mechanical behavior turfs through computational models. Computational models of CNTs have traditionally focused on the properties of individual nanotubes using molecular dynamic (MD) simulations. Yakobson et al. (1996) have analyzed the mechanical properties of single and multi-walled CNTs under axial compression, bending and tension using MD simulations. The results showed that the strain energy of the CNTs increased quadratically under external loading till the buckling point. The result is significant as it demonstrated that a CNT could be modeled using continuum shell model or beam model with an equivalent bending modulus further enabling the use of computationally efficient
techniques like the finite element analysis to model CNTs. Pantano et al. (2004) used a
detailed finite element shell model to represent the walls of the CNT and demonstrated
the capability of accurately capturing the deformation of both single and multi-walled
CNTs. Further they showed that the nonbonded interaction between the adjacent walls in
a multi-walled CNT and the interaction between two CNTs can be accurately captured
using a Lennard-Jones type interaction law as calculated by Zhao and Spain (1989).

The finite element shell model while computationally efficient when compared to
molecular dynamic simulations is still expensive to model the collective behavior of
CNTs. Given that most applications of CNTs require knowledge of their collective
behavior (Christensen et al. (2003) and Cola et al. (2007)), recent efforts have focused on
the development of computationally efficient models. This has lead to two broad classes
of models; a continuum representation of the collective behavior of CNTs and a discrete
representation which involves modeling of individual CNTs. The continuum
representation of the CNTs is based on a number of experiments characterizing the
material like behavior of CNT turfs. Yurdumakan (2005) have also demonstrated the
capability of inverting the turf structure whereby the turf retains its structural integrity
confirming the material behavior.

Fraternali et al. (2011) have developed a one-dimensional model of CNT turfs
using a series of bi-stable (nonlinear) springs. Appropriate spring potentials are chosen
study the softening and strain localization behavior leading to a hardening-softening-
hardening property of the springs. They adopt a two scale approach by using two-scale
approach to describe the deformation of the tubes: a microscopic time scale to describe
the dynamic buckling of the tubes and a macroscopic time scale to describe the bending
and interaction between the tubes. The later also leads to energy dissipation and subsequent hysteretic behavior seen in CNT turfs. By fitting with experimental observations, their model is capable of describing the stress-strain response over several cycles in the turfs.

Recent work by Hutchens et al. (2011) extended this model to a 2d axisymmetric case using a compressible elastic-viscoplastic constitutive model and is used to predict the coordinated buckling in CNT turfs. Their continuum model showed the experimentally observed buckling of the turfs at the substrate with the buckles propagating towards the surface with increasing deformation for a turf with homogenous properties. Attempts to study the influence of the micromechanical parameters like density of the turf and length of the tubes on wavelength of the buckles are done by varying the parameters in the viscoplastic model. Small gradients in the material properties enable the buckling sequence to be reversed by occurring from top surface towards the substrate. These continuum models are useful in capturing qualitatively the deformation behavior of CNT turfs seen in turfs. However the influence of micromechanical parameters like density, height of the turfs and average initial curvature of the tubes on the experimental observations like coordinated buckling remain open and reinforce the need of detailed computational models.

The earlier molecular dynamic simulations like those by Yakobson et al. 1998 and Bernholc et al. 1998 are detailed to understand the mechanism of deformation of CNTs but are expensive permitting the modeling of a few tubes over small time scales (order of nanoseconds). Recent efforts to address these limitations by Buehler (2006), Volkov and Zhigilei (2009) and Anderson et al. (2010) have lead to mesoscopic scale models using
coarsened particle methods. These models are computationally efficient permitting the modeling of multiple CNTs and over longer time scales. They have shown that the continuum parameters like the elastic modulus, bending modulus and the torsional modulus calculated from MD simulations are sufficient to accurately represent the deformation of CNTs. In the mesoscopic models, the CNTs which can be thought of coaxial graphene sheets rolled to form seamless cylinders (see Venema et al. (2000) for the atomic structure of single walled CNTs) are represented as a series of particles instead of modeling each carbon atom as in the molecular dynamic simulations. The interaction between the CNTs is modeled using phenomenological potentials derived from observations from MD simulations. This has lead to a computationally efficient modeling capable of modeling large number of CNTs over longer time scales compared to MD simulations. Here we seek to utilize the methodology adopted by Buehler (2006), Volkov and Zhigilei (2009) and Anderson et al. (2010) but use a finite element model to develop a detailed discrete model of the CNT turf.

This thesis is organized as follows: In Chapter 2 we discuss the development of the continuum model based on the experimental observation of a foam-like behavior of the CNT turf. In Chapter 3, we describe the development of the equations of motion and the elastica finite element. The details of the discrete model are described in Chapter 4. The results from the computational analyses are presented in Chapter 5 followed by conclusions in Chapter 6.
2.1 Structure and Micromechanics of a CNT turf

As shown in Figure 1.1, for most CNTs, their end-to-end line is close to vertical, but the segments are curved, and some have inclined or even horizontal end-to-end lines. The contacts between adjacent tubes are van der Waals bonded (Ajayan & Banhart, 2004). CNTs have high surface energy in air and low interface energy between in mutual contact, so the system tends to lower its energy through contact. Thus, the total energy of the assembly, \( E \), is given as

\[
E = U - \Gamma ,
\]

where \( U \) is the total elastic bending energy of CNTs, while \( \Gamma \) is the contact (adhesive) energy, defined as the difference between the total interface and surface energy of the assembly and the surface energy of an imaginary contact-free assembly. As the configurational space is very large, many energy minima are expected. However, the experimentally observed mechanical reversibility (McCarter et al, 2006) indicates broad convex regions around the minima, so that – after moderate strains – the structure returns to its initial state. Nominally, the absolute energy minimum is achieved when the structure collapses laterally, i.e., with all tubes straight and in full contact (Liu et al, 2005). During initial stages of growth, the collapse is prevented by the substrate constraint. As the turf grows, the inclined and horizontal segments prevent the lateral collapse.
The standard nanoindentation experiments (McCarter et al, 2006) using a Hysitron Triboscope with a blunt Berkovich tip was carried on CNT turfs, with the following conclusions (cf. Figure 6):

(a) For moderately large strains the deformation is fully reversible.

(b) The turf exhibits time dependent relaxation. The relevant mechanism is the thermally activated sliding and rearrangements of CNT contacts.

(c) The load – indentation depth curve for the initial spherical portion of the indentation is almost linear, similar to the behavior of an elastic – ideally plastic solid (Mesarovic & Fleck, 1999).

(d) The net tensile load required to pull-off the indenter from the turf during the retraction phase demonstrates adhesion of the turf with the indenter.

Mesarovic et al (2007) have shown that the mechanism of deformation in the turf is easily understood by means of a simple micromechanical model of a free CNT segment with an initial curvature and contact patches at both the ends. Extended to the behavior of an assembly of such segments, the model implies a high initial tangent modulus followed by a rapid decrease in tangent modulus with increasing strain (hence the almost linear indentation loading curve). This prediction has been tested in the continuous stiffness indentation tests (Oliver & Pharr, 1992). The results, reported by McCarter et al (2006), are consistent with the micromechanical model.

2.2 Constitutive Model

The experimental measurements of the the tangent modulus of CNT turfs (Figure 2(a), McCarter et al, 2006) are consistent with the super-compressible foam behavior (Cao et
al, 2005, Hutchens et al, 2010). The initially high tangent modulus drops by an order of magnitude with increasing strain. Using these observations, we represent the turf as isotropic compressible elastomeric hyperfoam material with a Kelvin-Voigt relaxation component. In the hyperfoam model by Storakers (1986), the strain energy density $U$ is expressed as a sum of the terms of non-integer powers of principal stretches, $\lambda_i$ ($i=1,2,3$). For the sake of simplicity, we use only one term in the series:

$$
U = \frac{2\mu}{\alpha^2} \left[ \lambda_1^\alpha + \lambda_2^\alpha + \lambda_3^\alpha - 3 + \frac{(\lambda_1 \lambda_2 \lambda_3)^{\alpha\beta} - 1}{\beta} \right].
$$

(2.2)

Here, $\alpha$ and $\beta$ are material parameters. The parameter $\beta$ determines the degree of compressibility of the material and is related to the Poisson’s ratio by

$$
\nu = \frac{\beta}{1 + 2\beta}.
$$

(2.3)

From (2.2) the nominal stresses, conjugate to the principal stretches can be expressed as

$$
\sigma_j = \frac{1}{\lambda_j \alpha} \frac{2\mu}{\lambda_j} \left( \lambda_j^\alpha - J^\alpha \beta \right),
$$

(2.4)

where $j = 1$ to 3, and no summation over $j$ is implied. A ground-state (zero-stress state) is assumed to exist with an initial shear $\mu_0$ and bulk modulus $K_0$:

$$
\mu_0 = \mu ; \quad K_0 = 2\mu \left( \beta + \frac{1}{3} \right).
$$

(2.5)

Difficulties in measuring lateral deformation at nanoscale, leave us without accurate value for the Poisson’s ratio. However, our computations indicate that the results are insensitive to this value. The results presented here are obtained with Poisson’s ratio equal to zero. Based on the above assumptions, the relation for the nominal stresses for the turf reduces to
\[ \sigma_j = \frac{1}{\lambda_j} \frac{2\mu}{\alpha} \left( \lambda_j^\alpha - 1 \right). \]  

(2.6)

The time dependent relaxation seen in the nanoindentation experiments is due to thermal sliding of contacts between the tubes. The time dependent relaxation is incorporated by assuming that the instantaneous shear modulus of the material \( \mu(t) \), varies as

\[ \mu(t) = \mu_\infty + (\mu_0 - \mu_\infty) e^{-t/\tau}, \]  

(2.7)

where \( \mu_0 \) is the initial shear modulus, \( \tau \) is the characteristic relaxation time, and \( \mu_\infty \) is the relaxed shear modulus. Using the results from the controlled-depth indentation experiments, shown in Figure 2.1(b), at constant indentation depth, the resultant load relaxes as

\[ P(t) = P_{\text{inf}} + (P_0 - P_{\text{inf}}) e^{-t/\tau} \]  

(2.8)

where \( P_0 \) is the initial load and \( P_{\text{inf}} \) is the load when \( t \to \infty \). To obtain the relaxation time \( \tau \) from experiments, we use the fit to the experimental force-time curve (Figure 2.1(b)). The values of \( P_{\text{inf}} \), \( (P_0 - P_{\text{inf}}) \) and \( \tau \) are obtained using the Newton-Raphson technique by minimizing the value of error between (8) and experimental results.
The characteristic relaxation times during loading and unloading are the same: approximately 2.3 seconds. With the exception of the initial portion of the relaxation time (<0.25 seconds), a good agreement with the experimental relaxation curve can be obtained with a single term in the Kelvin-Voigt model (Figure 2.1(b)). To complete the specification of the Kelvin-Voigt model, we specify the relative loss of shear modulus upon relaxation:

\[ \bar{\mu} = \frac{\mu_0 - \mu_\infty}{\mu_0}. \]  

(2.9)

Comparing the magnitude of relaxation in the FE results with the nanoindentation experiments during the constant load / depth portion over a range of values of \( \bar{\mu} \), we estimate that the appropriate value \( \bar{\mu} \) to be 0.35.

**Figure 2.1** (a) Tangent modulus of the turf as function of indentation depth using the continuous nanoindentation experiments measured at different locations on the CNT turf reported by McCarter et al (2006) (b) Determination of the characteristic relaxation time of the turf using a curve fit between (8) and the indenter force at the constant depth portion of the depth controlled nanoindentation experiment.
2.3 Finite Element Model

We use the commercial finite element software ABAQU S (2006) and its user defined subroutine capabilities UNITER to define the interaction law between the turf and Berkovich nanoindenter. To obtain an economical 2D problem and retain the high accuracy of contact forces, we approximate the Berkovich pyramid with the equivalent conus. The cross-sectional areas of the Berkovich indenter and the rotationally symmetric conical indenter are the same at any distance from the apex of the indenter.

The FE analysis of the nanoindentation experiments on the CNT turf was performed using a rotationally symmetric mesh with linear triangular elements. A variable density mesh, shown in Figure 2.2(a), was used. The dense mesh close to the contact was required to capture the surface tractions accurately. In additional to linear elements, we have performed test runs with the identical mesh of quadratic triangular elements, modified to support constant face pressure, to ensure accuracy and mesh convergence. To avoid the influence of outer boundary conditions, the size of the domain was greater than ten times the largest contact radius (Mesarovic & Fleck, 1999). The Berkovich indenter tip was modeled as a rigid surface with the interactive forces between the turf and the indenter. To obtain the equivalent rotationally symmetric representation of the Berkovich tip which has an included angle of $142.3^\circ$ (angle between adjacent corners) and a half angle of $65.35^\circ$, we use a conical indenter with a half-angle of $70.3^\circ$. The conical indenter has an equivalent base area as a Berkovich tip at any distance from the apex.

Nanoindentation results from two different experimental setups are considered:
a) The load-controlled experiment using a Hysitron triboscope with a blunt Berkovich indenter tip. The blunt section of the indenter is represented by a spherical section with a radius of curvature of 1.8µm up to a depth of 150nm. For numerical stability, the transition from the spherical portion to the pyramidal portion of the indenter is smoothed using a fillet with a large radius of curvature.

b) The depth-controlled experiment using a Hysitron triboindenter with a sharp Berkovich indenter tip. The second indenter with a sharp tip is modeled wholly with an equivalent conical section.

Figure 2.2. (a) Axis-symmetric finite element mesh with the Berkovich indenter tip represented as a rigid surface (b) Detail of the mesh at the surface of the turf.

The adhesive contact between the diamond Berkovich tip and the CNT turf is due to the van der Waals interactions. The interaction between CNT walls is usually modeled using the Lennard-Jones type force law (Zhao & Spain, 1989):
\[ p(r) = \left( \frac{9\gamma}{2r_0} \right) \left[ \left( \frac{r_0}{r} \right)^{10} - \left( \frac{r_0}{r} \right)^{4} \right], \quad (2.10) \]

where \( p \) is the contact pressure, \( \gamma \) is the surface energy, and \( r_0 \) is the equilibrium interatomic spacing (0.34 nm). However, the contact law (2.10) is intended for interaction between static CNT walls and cannot be directly used for modeling the interacting between the turf and the indenter tip. The segments of CNTs at the surface are subject to thermal oscillations, resulting in an increased effective range of interactions. TEM observations by Treacy et al (1996) on the vibration amplitude of CNTs as function of temperature confirm their thermal origin. The root mean square of the vibration amplitude of a CNT supported at one end was computed as

\[ u^2 \approx 0.1061kTl^3/EI, \quad (2.11) \]

where \( l \) is the free standing length (7 \( \mu \)m), \( k \) is the Boltzmann constant, \( T \) is the absolute temperature (300 K), \( EI \) is the bending stiffness of a nanotube. To calculate the bending stiffness of the multiwalled nanotube we assume the elastic modulus as 0.4 TPa with tube inner and outer radii as 20 nm and 17.3 nm respectively.

**Figure 2.3** Contact law used to model the van der Waals forces between the turf and the indenter. The original curve (10) is modified to include the effects of thermal vibration of the ends of the nanotube.
Using (11), the displacement of a typical CNT at the surface of the turf is computed as 4.64 nm and this value is taken to represent the range of interactions, $r_{\text{int}}$ (Figure 4). The value $r_{\text{int}}$ is derived as the abscissa intercept of the tangent to the zero curvature point. The modified force law (10) is flattened with a reduced maximum tensile traction but with the same surface energy as the original curve (Figure 4). During the initial approach of the indenter, an unstable jump-to-contact occurs, as expected. The numerical solution for the unstable jump-to-contact and unstable pull-off requires either the arc-length algorithm, or a formulation which includes an artificial viscous damping term in addition to the contact tractions computed in (10). The developed contact algorithm was thoroughly tested and is described by Radhakrishnan & Mesarovic (2009). We ensure the validity of the solution by a negligible ratio ($<0.01$) between the energy damped by the viscous forces and the total strain energy. A fine mesh with an edge size equal to $r_0$ is required to accurately model the surface tractions between the indenter and the turf at the periphery of contact.
CHAPTER 3

FINITE ELEMENT MODEL OF A SPATIAL ELASTICA

The continuum model of the CNT turf is computationally efficient and is capable of capturing the various features seen during nanoindentation experiments by McCarter et al. (2006) and Qiu et al. (2010). The study of the mechanism of deformation of the nanotubes under external loading and the understanding of the experimental observations like coordinated buckling observed by Zbib et al. (2008), Qiu et al. (2010), Hutchens et al. (2010) and Maschmann et al. (2011) require an analysis of the interaction between the carbon nanotubes in the turf during deformation and the study of the influence of microstructural parameters like the density of the tubes and the average initial curvature of the turf on the response of the turf to external loading.

To develop the detailed computational model of the turf, we adopt a similar approach followed by Buehler (2006), Anderson et al. (2010) and Volkov and Zhigilei (2008) whereby the total energy of the turf is represented as the sum of the interaction energy between the tubes and the strain energy due to bending, torsion and stretching. These models use coarsened particle method to represent the tubes along with appropriate potentials obtained from molecular dynamic simulations to model the properties of the carbon nanotubes and the interaction between the tubes. The main distinction between the developed discrete model of the turf and the earlier models by Buehler (2006), Anderson et al. (2010) and Volkov et al. (2008) is in the discretization of the carbon nanotubes using inextensible elastica finite elements instead of a sequence of particles. The interaction between the tubes used in the discrete model is based on a
phenomenological model identical to the interaction potential used in Buehler’s model (2006). We use an explicit time integration technique to integrate the equations of motions. An inextensible elastica is a prismatic rod in a three-dimensional space which has bending and torsional stiffness. The governing equations of an elastica developed by Love (1927) are well known although the finite element implementation of an elastica in a three-dimensional setting is not frequent. Numerical modeling of elastica are usually performed using the Finite Difference technique by Nordgren (1974) and Gueron and Liron (1993) or in a restricted two-dimensional setting by Garrett (1982). In this section we describe the equations of the motion of an elastica, the development of the FE model from them and the benchmark tests to validate the developed model.

3.1 Governing Equations of an Elastica

A space curve can be defined by its position vector \( r(s) \), expressed as a function of the arc-length parameter \( s \). At any point on the curve, a set of orthonormal unit vectors can be defined: \( \hat{t} \), is the unit tangent vector, \( \hat{n} \) is the unit normal vector and \( \hat{b} \) is the unit bi-normal vector.

\[
\begin{align*}
\hat{t} &= r', \quad \hat{n} = \hat{t}'/\kappa, \quad \hat{b} = \hat{t} \times \hat{n} \\
\kappa &= \sqrt{r'' \cdot r''} 
\end{align*}
\]  

(3.1)

Here \( r' \) denotes the first derivative of the position vector with respect to the arc length parameter and \( \kappa \) is the curvature. From the classical theory of rods, the internal stress state is defined by the resultant force \( \mathbf{F} \) and the moment \( \mathbf{M} \) acting at the central axis.

The conservation of linear momentum is given by:

\[
\mathbf{F}' + \mathbf{q} = \rho \hat{\mathbf{w}},
\]

(3.2a)
and the conservation of angular momentum is

\[ M' + t \times F + m = 0. \] (3.2b)

We neglect the rotary inertia in (3.2b). Using Euler-Bernoulli theory for rods with equal principal stiffness, the constitutive equation is

\[ \hat{M} \hat{b} = \hat{H\alpha} + \hat{M}_b \hat{t} \] (3.3)

where \( B \) is the bending modulus and \( H = C\alpha \) is the torsional moment, with \( C \) being the torsional modulus and \( \alpha \) is the twist of the central axis. Since we are interested in inextensible rods, we now derive the constraint condition. Consider the initial position of the rod specified by the position vector of the central line \( \mathbf{r}(s) \) displaced by \( \delta\mathbf{r} \), where \( \delta\mathbf{r} \) is continuous and satisfies the boundary conditions. To maintain inextensibility the new position of the curve given by \( \mathbf{r} + \delta\mathbf{r} \) must have its arc length parameter \( s \)
unchanged. From (3.1) we can now write the magnitude of the tangent vector in the initial and displaced positions as

\[
\frac{dr}{ds} \cdot \frac{dr}{ds} = \frac{d(r + \delta r)}{ds} \cdot \frac{d(r + \delta r)}{ds} = 1. \tag{3.4}
\]

Rewriting (3.4) we obtain

\[
\frac{d(r + \delta r)}{ds} \cdot \frac{d(r + \delta r)}{ds} = \frac{dr}{ds} \cdot \frac{dr}{ds} + 2 \frac{dr}{ds} \cdot \frac{d\delta r}{ds} + \frac{d\delta r}{ds} \cdot \frac{d\delta r}{ds} = 1. \tag{3.5}
\]

In (3.5) the first term on the L.H.S is equal to the R.H.S and second and third term must vanish individually. Here we note that the continuity of \(\delta r\) permits us to interchange so that

\[
\frac{d\delta r}{ds} = \delta \left( \frac{dr}{ds} \right). \tag{3.6}
\]

Of interest is the second term which gives the desired constraint condition neglecting the constant coefficient

\[
r' \cdot \delta r' = 0 \tag{3.6}
\]

To obtain a pair of equations suitable for numerical implementation, we make use of the relations from the Serret-Frenet formulae

\[
\hat{t}' = \kappa \hat{n}, \quad \hat{n}' = \tau \hat{b} - \kappa \hat{t}, \quad \hat{b}' = -\tau \hat{n}, \quad \tau = r' \cdot \frac{r'' \times r''}{\kappa^2} \tag{3.7}
\]

We now substitute (3.7) in (3.2a)

\[
(Bk\hat{b} + H\hat{t})' + \hat{t} \times F + m = 0, \tag{3.8}
\]

and upon manipulation we get,

\[
(Bk)' \hat{b} + Bk \hat{b}' + H\hat{t}' + H\hat{t} + \hat{t} \times F + m = 0. \tag{3.9}
\]

Using (3.5) in (3.7)

\[
(Bk)' \hat{b} - \tau Bk \hat{n} + Hk \hat{n} + H\hat{t} + \hat{t} \times F + m = 0 \tag{3.10}
\]
Further manipulating (3.10), we obtain

$$ (B\kappa)'(\hat{t}\times\hat{n})+(\tau B\kappa-H\kappa)(\hat{t}\times\hat{b})+\hat{t}\times F+H\hat{t}+m = 0, $$

or

$$ \hat{t}\times\left[(B\kappa)'\hat{n}+(\tau B\kappa-H\kappa)\hat{b}+F\right]+H\hat{t}+m = 0. \quad (3.11) $$

Noting that,

$$ (B\kappa)'\hat{n}+\tau B\kappa\hat{b}=(B\kappa\hat{n})'+B\kappa^2\hat{t}, \quad (3.12) $$

we can reduce (3.11) as

$$ \hat{t}\times\left[(B\kappa\hat{n})'+B\kappa^2\hat{t}-H\kappa\hat{b}+F\right]+H\hat{t}+m = 0 \quad (3.13) $$

To obtain the equation of motion of torsion of the rod for FE implementation, we take the dot product of equation (3.13) with \( \hat{t} \)

$$ H'+m\cdot\hat{t} = 0. \quad (3.14) $$

To obtain the second equation of motion, we take the vector cross product of (3.13) with \( \hat{t} \)

$$ \hat{t}\times\left[\hat{t}\times(B\kappa\hat{n})'+H\kappa\hat{n}+\hat{t}\times F\right]+\hat{t}\times H\hat{t}+\hat{t}\times(\hat{t}\times F)+\hat{t}\times m = 0. \quad (3.15) $$

Manipulating (3.15) using (3.7), and noting that

$$ \hat{t}\times(\hat{t}\times F)=[(\hat{t}\cdot F)\hat{t}-F], \quad \hat{t}\times[\hat{t}\times(B\kappa\hat{n})']=-(B\kappa^2\hat{t}-(B\kappa\hat{n})'), \quad (3.16) $$

with the tension in the rod is given by

$$ \hat{t}\cdot F=T, \quad (3.17) $$

we obtain
\[-(B\kappa \hat{n})' - B\kappa^2 \hat{t} + \hat{T} - F + H \kappa \hat{b} + \hat{t} \times \mathbf{m} = 0.\] (3.18)

Representing in terms of the position vector of the central axis of the elastica, we obtain
\[-(B\mathbf{r}^*) - \left[ B\kappa^2 - T \right] \mathbf{r}' + H (\mathbf{r}' \times \mathbf{r}'') + \hat{t} \times \mathbf{m} = \mathbf{F}. \] (3.19)

Substituting (3.19) in (3.2a), yields the desired equation of motion.
\[-(B\mathbf{r}^*)' - \left[ \left(B\kappa^2 - T\right) \mathbf{r}' \right]' + \left[ H (\mathbf{r}' \times \mathbf{r}^*) \right]' + (\mathbf{r}' \times \mathbf{m})' + \mathbf{q} = \rho \mathbf{w}. \] (3.20)

### 3.2 Weak Form of the Governing Equations

The governing equations (3.14) and (3.20) represent the strong form of the elastica. To make them amenable to finite element implementation, we derive the equivalent weak form by taking the variations with the twist angle \(\delta\alpha\) and position \(\delta\mathbf{r}\). Multiplying equation (3.14) with the variation in the twist angle \(\delta\alpha\), and integrating over the domain we obtain,
\[\int_0^L ds \left( H' + \hat{t} \cdot \mathbf{m} \right) \delta\alpha = 0.\] (3.21)

Using integration by parts we obtain,
\[\int_0^L \left(-\delta\alpha' H + \delta\alpha (\hat{t} \cdot \mathbf{m})\right) ds = -H \delta\alpha|_0^L. \] (3.22)

From (20), we now require the torsional moment or the twist angle to be specified at the ends of the elastica. Taking the dot product of (3.18) with \(\delta\mathbf{r}\) and integrating over the domain
\[
\int_0^l ds \left\{ -(Br'')'' - \left[ \left( Bk^2 - T \right) r' \right]' + \left[ H \left( r' \times r'' \right) \right] + \left( r' \times m \right)' + q - \rho \ddot{m} \right\} \cdot \delta r = 0. 
\]

(3.23)

Using integration by parts and considering the terms individually to identify the necessary boundary conditions we obtain:

\[
\int_0^L ds \left( -\frac{d}{ds} \right)^2 \frac{d}{ds} \cdot \delta r = -\int_0^L \delta r' \cdot \left( \frac{d}{ds} \right)^2 \frac{d}{ds} \cdot \delta r \bigg|_0^L + Br'' \cdot \delta r\bigg|_0^L, \quad \text{(3.24a)}
\]

requires the specification of the positions or the shear and slopes or the moments at the ends of the elastica.

\[
\int_0^l ds \left[ -\left( Bk^2 - T \right)r' \right]' \cdot \delta r = \int_0^l \delta r' \cdot \left( Bk^2 - T \right) r' \bigg|_0^L, \quad \text{(3.24b)}
\]

requires the specification of the thrust force or the positions at the ends.

\[
\int_0^L ds \left( H \left( r' \times r'' \right) \right)' \cdot \delta r = -\int_0^L \delta r' \cdot \left[ H \left( r' \times r'' \right) \right] ds + \int_0^L \left[ H \left( r' \times r'' \right) \right] \cdot \delta r\bigg|_0^L, \quad \text{(3.24c)}
\]

requires the specification of the torsion or the positions at the ends.

\[
\int_0^L ds \left( r' \times m \right)' \cdot \delta r = -\int_0^L \delta r' \cdot \left( r' \times m \right) ds + \left( r' \times m \right) \cdot \delta r\bigg|_0^L, \quad \text{(3.24d)}
\]

requires the specification of the torsional moment or the positions at the ends.

Now considering the equation in its entirety, we obtain the second desired equation.

\[
\int_0^L \left( -\delta r'' \cdot Br'' + \delta r' \cdot \left[ \left( Bk^2 - T \right) r' \right]' - \delta r' \cdot \left[ H \left( r' \times r'' \right) \right] - \delta r' \cdot \left( r' \times m \right) + \delta r \cdot q - \delta r \cdot \rho \ddot{m} \right) ds \\
\quad = -\left[ \left( Br'' \right)' - \left( Bk^2 - T \right) r' + H \left( r' \times r'' \right) + r' \times m \right] \cdot \delta r\bigg|_0^L - Br'' \cdot \delta r\bigg|_0^L 
\]

(3.25)
In (3.25), all the coefficients excepting the tension $T$ are known. The value of tension cannot be obtained explicitly due to the nonlinear nature of (3.25). To determine the value of tension, we make use of the constraint (3.6). Since the constraint is required to be satisfied at all points in the domain, the modified form of (3.6) is still valid

$$\lambda \cdot (r' \cdot \delta r') = 0, \tag{3.26}$$

where $\lambda = B\kappa^2 - T$. Rewriting (3.25) we obtain

$$\int_0^L \left( -\delta r'' \cdot Br'' + \delta r' \cdot [\lambda r'] - \delta r' \cdot [H (r' \times r'')] - \delta r' \cdot (r' \times m) + \delta r' \cdot q - \delta r \cdot \rho \delta r \right) ds$$

$$= \left[ -(Br'')' - \lambda r' + H (r' \times r'') + r' \times m \right] \cdot \delta r \bigg|_0^L - Br'' \cdot \delta r \bigg|_0^L$$

(3.27)

Integrating in the entire domain so that we have the resultant weak form

$$\int_0^L \delta \lambda \cdot (r' \cdot \delta r') ds = 0. \tag{3.28}$$

### 3.3 Finite Element Implementation

To develop, the finite element formulation we discretize the position vector of the central axis using cubic hermite polynomials,

$$r_i (s, t) = \sum_{J=1}^{4} N^J (s) \tilde{d}_i^J (t), \tag{3.29}$$

with $N^1 = 1 - 3\xi^2 + 2\xi^3$, $N^2 = \xi - 2\xi^2 + \xi^3$, $N^3 = 3\xi^2 - 2\xi^3$, and $N^4 = -\xi^2 + \xi^3$. Note that the shape functions are a function of the arc-length parameter $s$ with the natural
coordinate parameter $\xi = s/L$ varying between 0 and 1. The twist angle is interpolated linearly,

$$\alpha(s,t) = \sum_{J=1}^{2} A^J(s) \theta^J(t),$$

(3.30)

with $A^1 = 1 - \xi$ and $A^2 = \xi$. To determine the tension at any point on the central axis we assume the $\lambda$ to vary quadratically, and the value at any point is given by

$$\lambda(s,t) = \sum_{K=1}^{3} P^K(s) \lambda^K(t),$$

(3.31)

with $P^1 = 1 - 3\xi + 2\xi^2$, $P^2 = 4\xi (1 - \xi)$ and $P^3 = \xi (2\xi - 1)$. The element nodal dof’s are

$$U^T = \begin{bmatrix} d_1^1 & d_1^2 & d_2^1 & d_2^2 & d_3^1 & d_3^2 & \theta^1 & \lambda^1 & d_1^3 & d_2^3 & d_3^3 & \theta^2 & \lambda^2 & \lambda^3 \end{bmatrix}$$

where,

$$d_i^1 = r_i(0,t), \quad d_i^2 = L r_i'(0,t), \quad d_i^3 = r_i(L,t) \quad \text{and} \quad d_i^4 = L r_i'(L,t)$$

$$\theta^1 = \alpha(0,t) \quad \text{and} \quad \theta^2 = \alpha(L,t)$$

$$\lambda^1 = \lambda(0,t), \quad \lambda^2 = \lambda(L,t) \quad \text{and} \quad \lambda^3 = \lambda(L/2,t).$$

The elastica element has a total of 17 degrees of freedom (dof) with the two edge nodes having a total of 8 dof’s each and one central node having 1 dof.
Since (3.22), (3.27) and (3.28) are valid for any permissible $\delta U_j$, we can write the equations of motions for any element as

$$\left( F_{\text{int}} \right)_j + \left( F_{\text{ext}} \right)_j = M_{ij} \delta_{ij} , $$

$$\left( F_{\text{int}} \right)_{\text{tor}} + \left( F_{\text{ext}} \right)_{\text{tor}} = 0 \text{ and}$$

$$G = 0 .$$

with

$$M_{ij} = \int_0^L \left( N^T \rho \delta_{ij} N \right) ds , \tag{3.33}$$

$$\left( F_{\text{int}} \right)_j = \int_0^L \left( -N^*T \cdot Br_j^r + N^T \cdot \left[ \lambda r_j^r \right] - N^T \cdot \left[ H (r' \times r^r) \right] \right) ds , \tag{3.34}$$
\[
(F_{\text{ext}})_j = \int_0^L \left( -N^T \cdot (r' \times m) + N^T \cdot q_j \right) ds \\
+ \left. \left[ -\left( Br^* \right)' + \lambda r' + H (r' \times r'') + r' \times m \right] \cdot \delta r \right|_0^L + Br' \cdot \delta r|_0^L
\] 
(3.35)

\[
(F_{\text{ext}})_{\text{tor}} = \int_0^L \left( A^T (r' \cdot m) \right) ds + H \delta \alpha|_0^L,
\]
(3.36)

\[
(F_{\text{int}})_{\text{tor}} = \int_0^L \left( -A^T H \right) ds \quad \text{and}
\]
(3.37)

\[
G = -\int_0^L \left( p^T (r' \cdot \delta r') \right) ds = 0
\] 
(3.38)

It should be noted that the derivatives of the shape functions are with respect to the arc-length parameter \( s \) and those in (3.34), (3.35) and (3.37) are expressed in terms of the natural coordinate parameter \( \xi \). In (3.32), the coefficients \( B \) and \( \lambda \) are matrices with the bending stiffness acting in the normal and binormal directions and the stiffness in tension acting in the tangential direction. We use the updated Lagrangian formulation – the position vector of the central axis and hence the orthonormal set of vectors in (3.1) is updated at the end of each time increment or iteration depending on the procedure, the bending and tension stiffness components are rotated to account for the change in the position of the elastica element. This requires the specifying of the direction of two of the three orthonormal vectors in the undeformed (straight) configuration.
3.4 Static Conditions

We develop the static formulation to verify developed finite element formulation with closed form solutions of an elastica under external loading. In static problems, we neglect the inertial terms in (3.32) giving the equilibrium equations

\[(F_{\text{int}})_j + (F_{\text{ext}})_j = 0,\]

\[(F_{\text{int}})_{\text{tor}} + (F_{\text{ext}})_{\text{tor}} = 0 \text{ and } G = 0.\]  

(3.39)

The nonlinearity of equation (3.38) requires an iterative procedure as in the Newton’s method leading to the following equations.

\[(F_{\text{int}})_j^{n+1} = (F_{\text{int}})_j^n - \frac{\partial (F_{\text{int}})_j}{\partial \lambda^I} \Delta \lambda^I - \frac{\partial (F_{\text{int}})_j}{\partial \lambda^K} \Delta \lambda^K,\]  

(3.40)

\[(F_{\text{ext}})_j^{n+1} = (F_{\text{ext}})_j^n - \frac{\partial (F_{\text{ext}})_j}{\partial \lambda^I} \Delta \lambda^I,\]  

(3.41)

\[(F_{\text{int}})_{\text{tor}}^{n+1} = (F_{\text{int}})_{\text{tor}}^n - \frac{\partial (F_{\text{int}})_{\text{tor}}}{\partial \theta^J} \Delta \theta^J,\]  

(3.42)

\[(F_{\text{ext}})_{\text{tor}}^{n+1} = (F_{\text{ext}})_{\text{tor}}^n - \frac{\partial (F_{\text{ext}})_{\text{tor}}}{\partial \theta^J} \Delta \theta^J \text{ and } G^{n+1} = G^n - \frac{\partial G}{\partial d^I} \Delta d^I.\]  

(3.43)

(3.44)

Here the superscript \(n\) indicates the iteration number. Substitution of (3.49) – (3.44) in (3.39) along the specified boundary conditions defines the iterative procedure. The static solution is obtained using an increment procedure to account for degree of nonlinearity. The problem is divided into (load) increments and the size of the increment is dependent
of the number of iterations required to obtain a convergent solution in the previous increment. The solution is accepted if the ratio of the unbalanced energy (dot product of the unbalanced force and displacement correction) to the total energy increment in the step is less than the specified tolerance (ratio chosen as $10^{-5}$).

3.5 Dynamic Conditions

The deformation of the nanotubes here are quasi-static under external loading with negligible inertial effects. The typical procedure is to use the equations (3.37) – (3.41) to solve the problem. However, the deformation of the nanotubes in the CNT turf is nonlinear due to the van der Waals interaction with the neighboring tubes and large rotations. Further in the turf model we intend to model a large number of tubes ranging from 50 to 500 tubes in each periodic cell with 100 elements in each tube. Using a static solver in such cases would result in a completely coupled system stiffness matrix with the order $10^5$ degrees of freedom. Inverting the system stiffness matrix would be cumbersome and the number of iterations required to obtain equilibrium would be large. It is further expected that any instabilities in the system would lead to an ill-conditioned stiffness matrix making the Newton-Raphson scheme unsuitable. In such cases, an explicit time integration technique to solve for the differential equations of motion in (3.39) is preferable – the change in the nodal positions $\mathbf{U}(t)$ to $\mathbf{U}(t + \Delta t)$ is dependent on the forces acting at time $t$. The method is conditionally stable requiring a sufficiently small value of $\Delta t$ and is dependent on the highest natural frequency of the elastica element used to discretize the turf. Further the method permits parallelization of the code as the equations of each tube can be solved individually.
The Verlet explicit integration technique is attractive as the Hamiltonian is conserved but is restrictive in problems where velocity dependent forces (damping forces) are present and when accurate values of velocities are desired. In the current case an accurate measurement of the velocities at time $\Delta t$ due to the nature of the constraints and the damping forces. We use a modification of the Verlet technique referred to as the Half-step Leapfrog Verlet used by Fraige (2004) where the velocities at each half-step are calculated.

\[
U\left(t + \frac{\Delta t}{2}\right) = U\left(t - \frac{\Delta t}{2}\right) + \frac{\Delta t}{2} \dot{U}(t).
\]

The velocities at time $t + \Delta t$ are calculated using

\[
U(t + \Delta t) = U(t) + \frac{\Delta t}{2} \dot{U}(t).
\]

The integration technique must be modified as there is no evolution equation for computing the tension $T(s,t)$ in the central axis. Similar problems have been solved by using constraint algorithms like the SHAKE algorithm developed by Ryckaert et al. (1977) in molecular dynamics simulations.

As in the SHAKE algorithm, each increment in time is composed of two steps: In the first step, the equations of motion are integrated from time $t$ to time $t + \Delta t$ without taking into account the $\lambda$ (or constraint force in a general case) to obtain the unconstrained position of the nodes $\mathbf{U}(t + \Delta t)$. In the second step the value of $\lambda$ at time $t$ is calculated so that the constraints are satisfied at time $t + \Delta t$ with the resulting positions $\mathbf{U}(t + \Delta t)$. The calculation of the value of $\lambda$ to satisfy the constraints is
performed using an iterative procedure and involves the computation of the jacobian. At
the end of each iteration, the unconstrained positions of the nodes $\mathbf{U}(t + \Delta t)$ are
corrected till the constraint conditions are satisfied. Note that, it is assumed that the
constraints are satisfied at time $t$. The rate form of the constraint equation (3.7) is given
by
$$\mathbf{r}' \cdot \mathbf{\lambda} = 0. \quad (3.48)$$

The weak form the constraint equation now becomes

$$G(s, t) = -\int_0^L \left( P^T (\mathbf{r}' \cdot \mathbf{\lambda}) \right) ds = 0 \quad (3.49)$$

We now list the steps involved in integrating the equations of motion (3.39).

**Step 1:**

Compute the unconstrained nodal values $\mathbf{U}(t + \Delta t)$ using (3.46) and (3.47), where:

$$M_{ij}^{-1} \left[ (\mathbf{F}_{\text{int}})_j + (\mathbf{F}_{\text{ext}})_j \right] \quad (3.50)$$

and

$$(\mathbf{F}_{\text{int}})_{\text{tor}} + (\mathbf{F}_{\text{ext}})_{\text{tor}} = 0. \quad (3.51)$$

It should be noted that now in the computation of the internal forces, we neglect the term
associated with the $\lambda$

$$(\mathbf{F}_{\text{int}})_j = \int_0^L \left( -N^n T \cdot B \mathbf{r}'_j - N'T \cdot \left[ H (\mathbf{r}' \times \mathbf{r}'^n) \right] \right) ds \quad (3.52)$$
Step 2:

We now begin the iterative procedure using the computed value of the constraint equation at time \( t + \Delta t \) using (3.49). To evaluate (3.49), it must be noted that the order of differentiation can be interchanged as the length of the elastica element must remain unchanged i.e.

\[
\frac{d}{dt} \left( \frac{dr}{ds} \right) = \frac{d}{ds} \left( \frac{dr}{dt} \right).
\]  

(3.53)

So that,

\[
G^{n+1}(s, t + \Delta t) = -\int_{0}^{L} P^T \left( N^{T} \hat{\mathcal{G}}^{n+1} \right)^T N^{T} \hat{\mathcal{G}}^{n+1} ds.
\]  

(3.54)

In (3.54), we use (3.47) to compute the velocities \( \dot{\mathcal{G}} \). Here

\[
\hat{\mathcal{G}}_{i}^{n+1} = \hat{\mathcal{G}}_{i}^{n} - \frac{\Delta t^2}{M_{ij}} \int_{0}^{L} \left( N_{i}^{T} \Delta \lambda^{n} N_{j} \right) ds,
\]  

(3.55)

where \( \Delta \lambda^{n} \) represents the increment in the value of the \( \lambda \) computed at the \( n \) iteration.

To compute \( \Delta \lambda^{n+1} \), we compute the jacobian by substituting (3.54) in (3.55) and using the following equation

\[
\Delta \lambda^{n+1} = \frac{-G^{n}}{\partial G^{n}/\partial \lambda}.
\]  

(3.56)

Note that in the first iteration in the first time increment, we assume the tension to be zero. In the subsequent time increments, the change in the value of \( \lambda \) from time \( t \) to \( t + \Delta t \) is small so that the efficiency of the Newton-Raphson technique can be improved by using converged value of \( \lambda \) in the previous time step in (3.52) to obtain
The subsequent change in $\lambda$ in that time increment is then computed using (3.56). The iterations converge when the displacement correction in (3.55) goes to zero. We use the quasi-Newton method here – the Jacobian is calculated in the first iteration and in the subsequent iterations, the same is used for computational efficiency.

### 3.6 Benchmark: Static Conditions

<table>
<thead>
<tr>
<th>P/Pc</th>
<th>Error in $\phi$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.02</td>
<td>0.085</td>
</tr>
<tr>
<td>2.54</td>
<td>0.083</td>
</tr>
<tr>
<td>9.11</td>
<td>0.065</td>
</tr>
</tbody>
</table>

**Figure 3.3** Buckling of a prismatic column under an end thrust load. The error in the angle made by the free end with the vertical axis is compared with analytical solutions. The finite element model is discretized using 10 elastica elements.

To benchmark the developed finite element for an elastica, we consider the post-buckling behavior of an elastica under the I mode. An elastica column under thrust load from one end is considered. The FE solutions are compared with the values from the exact solution to gauge the validity of the code and the magnitude of the error. The good agreement between the computed values and the analytical solution seen in Figure 3.4 helps validate the updated Lagrangian formulation used in the FE algorithm.
One disadvantage of using cubic hermite polynomials as the shape functions for the position vector is the inability to accurately represent conic shapes, e.g. circular arcs and ellipses. The drawback is approached by using multiple hermite segments to approximately describe a conic shape. The problem is of interest as the shape of an elastica subjected to a couple at the ends is a circular segment. In the next part we seek to determine the error introduced due to the inherent flaw in the shape functions. We consider a single elastica finite element subjected to an end couple $M$ and compare the shape and the associated error in the normalized strain energy with respect to the analytical results. In Figure 3.4 the normalized deformed shapes are plotted against the analytical results. The shapes are for different values of the normalized moment $\frac{ML}{EI}$.

**Figure 3.4** Normalized deflected shape of a single elastica element subjected to an end couple. The solid lines with open circles are the numerical results and solid black lines are the analytical results plotted for different values of $ML/EI$. 
3.6 Benchmark: Dynamic Conditions

To verify the explicit algorithm we perform benchmark tests simulating the oscillatory motion of a rigid rod acting as a pendulum under body forces. The solution to the problem is invariant of the mass of the rod and allows us to verify if the Hamiltonian is indeed conserved. We assume a pendulum with bending modulus of $1. \times 10^{11}$ consistent units and of unit length. The pendulum is homogenous and has unit density (mass per length). The size of the time step was determined based on the speed of the longitudinal wave in the element. In the current analysis, the time step chosen was $0.6 \times 10^{-7}$ seconds (about one-sixteenth of the time taken by the longitudinal wave to pass through an element). Subsequent runs of increasing density were performed to verify the independence of the solution with respect to the mass of the pendulum. The solutions were obtained over multiple time periods and the amplitude of the pendulum was seen to be constant (within the numerical tolerance) and no loss of energy was seen after $10^9$ time increments. The time period was normalized with the theoretical value computed using the infinite series expression given by Nelson and Olosson (1987).

![Graph](image)

**Figure 3.5** The angle of the pendulum with respect to the horizontal. The pendulum was initially placed horizontally with gravity acting perpendicular to the initial tangent vector of the pendulum.
CHAPTER 4
A DISCRETE FINITE ELEMENT MODEL OF THE CNT TURF

Using the elastica finite element developed in the previous section, we now describe the details of the discrete model of the CNT turf.

4.1 Constrained Random Walk Algorithm

The SEM images of the turf in Figure 1.1 show the typical initial microstructure of the turf sample. The carbon nanotubes are grown from the substrate are nominally straight tubes with prebuckled segments enabling the tubes to make contacts with the neighboring tubes. To generate a representative model of the turf sample, we use a constrained random walk algorithm. The constraints are used to ensure that the tubes generally grow in the vertical direction (z-direction) but are allowed leeway to traverse sideways (x and y-direction) depending on the required average initial curvature. The nanotubes are modeled to grow from a square periodic substrate of predetermined dimensions and the growth site locations \((x_0, y_0, z_0)\) are assumed to be randomly distributed on the substrate with the minimum allowable distance between any two growth sites specified. The number of growth sites per periodic cell can be adjusted to obtain the desired density of the turf. The tubes are grown vertically in the z direction by using random walk points with distance of each step \(L\) specified. The growth direction of each step was determined using randomly computed angles \(\theta\) and \(\phi\). The position of a point at the end of the \(n^{th}\) random step \((x_n, y_n, z_n)\) is given by:

\[
x_n = x_{n-1} + L \cdot \cos \theta \cdot \sin \phi,
\]
\[ y_n = y_{n-1} + L \cdot \sin \theta \sin \phi, \quad (4.1) \]

\[ z_n = z_{n-1} + L \cdot \cos \phi, \]

with \(-\pi < \theta < \pi\) and \(-\alpha/2 < \phi < \alpha/2\), where \(\alpha\) is the cone angle specified by the user.

By increasing the value of \(\alpha\), we can obtain turfs with increasing initial average curvature. The generated random walk points are connected using Hermite curves (cubic polynomials). These curves ensure first and second order continuity at the connecting (random walk) points. The simplest parametric equation of the third order is given by

\[ P(u) = a_0 + a_1 \xi + a_2 \xi^2 + a_3 \xi^3, \quad 0 \leq \xi \leq 1 \quad (4.2) \]

where the coefficients are the vector coefficients of the parametric equation. To determine these coefficients, we use the known values of the position and slopes (still to be determined) at the random walk points. Replacing the coefficients with these known values we can rewrite (3.2)

\[
\begin{bmatrix}
P_0 \\
P_1 \\
\end{bmatrix} = \begin{bmatrix}
1 - 3\xi^2 + 2\xi^3 & 3\xi^2 - 2\xi^3 & \xi - 2\xi^2 + \xi^3 & -\xi^2 + \xi^3
\end{bmatrix} \begin{bmatrix}
P_0 \\
P_1 \\
\end{bmatrix} \quad (4.3)
\]

To determine the values of the slopes at the random walk points, we assume zero curvature at the free end of the tube and a random slope enforced at the substrate.

Enforcing these conditions we can then arrive at the equation relating the positions with the slopes.
Thus using the random walk points generated in the previous step, we can determine the coefficients of the equation of all the segments to form the nanotubes. The nanotubes are then discretized using the desire number of elastica elements.

4.2 Interaction Model

During the course of relaxation and deformation of the turf, the segments of the tube interact with the adjacent neighbors due the Van der Waals forces. We assume that there are no covalent bonds between two distinct tubes. The interaction model used in the
discrete model is based on the Lennard Jones force law and was developed by Buehler (2006). The model was developed to describe the interactions between tubes modeled as particles and is extended here to describe for a continuum model. The model assumes that there no multi-body interactions and the pair wise interaction between a point on a tube and a segment of an adjacent tube is only determined by the shortest distance between them and acts along that direction. The total interacting force on a node is obtained summing the interacting forces acting on that node based on the shortest distance to all other elements forming the turf. The process is computationally intensive and the technique is optimized using the convex hull method to avoid computing the interacting forces when tubes are distant. The potential to describe the interaction is given by:

$$\phi = 4\varepsilon \left( \frac{\rho}{r} \right)^{12} - \left( \frac{\rho}{r} \right)^{6}, \quad \text{(4.5)}$$

where $\varepsilon$ is the depth of the potential well, $\rho$ is the distance parameter proportional to the equilibrium distance between the tubes and $r$ is the distance between the outer walls of the tube. From (4.5), the force acting at the node due to a segment is computed as

$$P(r) = \frac{24\varepsilon}{\rho} \left( -2 \left( \frac{\rho}{r} \right)^{13} + \left( \frac{\rho}{r} \right)^{7} \right) \quad \text{(4.6)}$$

The interacting force at point A due to a segment calculated from (4.6) acts along $\hat{a}_1$, the direction of shortest distance from the segment at point B to A. In addition to the normal interacting force, a frictional component which resists the sliding motion between the interacting segments and acting in the direction of $\hat{a}_2$ is computed. The direction of $\hat{a}_2$ is computed such that the relative velocity between points A and B is given by
\[ V_{AB} = V_1 \hat{a}_1 + V_2 \hat{a}_2, \quad (4.7) \]

where \( V_1 \) is the component of velocity along \( \hat{a}_1 \) and \( V_2 \) is the component lying in the plane perpendicular to \( \hat{a}_2 \). The frictional force acting on point A along the direction \( \hat{a}_2 \) is calculated by

\[ P_{fric} = -\mu P_f (r) \left( \frac{V_2}{V_{ref}} \right)^{1/10}, \quad (4.8) \]

where \( \mu \) is the frictional coefficient, \( P_f (r) \) is shown in Figure 4.3(c) and \( V_{ref} \) is the reference velocity.

**Figure 4.2** (a) Interacting force on point A due to a neighboring segment (b) Normalized force vs Normalized distance. \( r_0 \) is the distance where the adhesive force is maximum and \( r_1 \) is the distance where \( P^* = 0 \) (c) Frictional force vs Normalized distance
5.1 Results from the Continuum Turf Model

To define the behavior of the turf, the values of the initial shear modulus $\mu_0$, $\alpha$ and the relaxation properties $\tau$ and $\mu$ are specified. From Figure 2.1(a), it is observed that the initial tangent modulus of the turf varies between 0.6-0.2 GPa thereby giving an estimate of the initial shear modulus. In all the measurements, the ratio of the initial tangent modulus to that at moderate strains is 10. Suitable values of $\alpha$ are used in the FE analysis to ensure that this ratio is consistent with this observation. The appropriate values $\mu_0$ and $\alpha$ are determined by fitting the FE results with the initial load-depth curves from experiments (segments a-b in Figures 5.1(a) and 6.1(a)). The characteristic relaxation time $\tau$ is calculated in Figure 2.1(b) as 2.3 seconds. The value of $\mu$ is determined from the relaxation behavior of the turf by fitting the magnitude of relaxation from the FE results with the constant load / depth portion in experiments (segments b-c and d-e in Figure 5.1(a) and 5.2(a)).

The actual loading mechanism of the Hysitron Triboscope is described McCarter et al (2006) and its schematic is illustrated in Figure 5.1(c), with Figure 5.1(b) showing the loading history used in experiments. A Hysitron triboscope was used for the load-controlled experiments and the Hysitron Triboindenter for the depth-controlled experiments. The indenter mechanism in both cases was replicated in the finite element model using spring elements. Net repulsive forces between the indenter and the turf are shown as positive.
As in the experiments, we discard the initial jump-to-contact portion in the numerical results and the measurements start when there is zero net force between the turf and the indenter. The best fit with experimental data was obtained with the initial shear modulus $\mu_0$ equal to 230 MPa and $\alpha$ as 18.8. The fit between computational and experimental results in Figure 5.1(a) is satisfactory, including the loading, visco-elastic relaxation, unloading and adhesive pull-off. The differences between the experiments and the model during unloading can be attributed to the differences between the equivalent cone and the blunt Berkovich indenter.

Figure 5.1  (a) Comparison between FE and nanoindentation experimental results. (b) Loading history. The constant load segment during unloading (d-e) is at twenty percent of the maximum load. (c) The loading mechanism of the Hysitron Triboscope used in the FE model.
In the second experimental setup, a sharp Berkovich tip was used and the experiment was performed using a Hysitron Triboindenter that was capable of utilizing a feedback loop to carry out depth controlled indentation. The values of the shear modulus as 0.05 GPa and $\alpha$ as 9.1 are determined by fitting the FE results with the experiments. The results shown in Figure 5.2(a) indicate a satisfactory fit. In Figure 5.2(a), the sharp change in the slope at $c^1$ of the computational load-depth curve during the initial stage of unloading characterized as an elbow is a result of neglecting contact creep between the turf and indenter. We assume that the creep is small enough and constant surface energy

![Figure 5.2. (a) Comparison between FE and nanoindentation experimental results. (b) Contact radius as a function of indentation depth (c) Depth history and the loading mechanism of the Triboindenter used in the FE model.](image-url)
used in (10) is sufficient enough to describe the relaxation behavior. In the numerical model this leads to a constant contact area during the initial stages of unloading (segment c-c\textsuperscript{1} in Figure 5.2(b)). We define the radius of contact as the radial distance at which we have the maximum tensile traction. During the initial stages of unloading in regime c-c\textsuperscript{1}, the contact radius remains constant but the size of the region under tensile tractions increases leading to sharp drop in the indenter load. With further unloading, the turf begins peeling-off from the indenter and is seen by a smaller slope of the load-depth curve. In actual experiments, the curve appears smooth due to weakening of the surface energy between turf and the indenter.

5.2 Results from the Discrete CNT Turf model

The initial structure of the turf is generated by using the random walk algorithm. Here we consider 50 nanotubes in the periodic cell. The total dimensions of the periodic cell are 1μm x 1μm. This gives a density of 50 tubes in each 1μm\textsuperscript{2} matching those reported by Qiu (2011). Each nanotube is assumed to discretized using 100 elastica elements each of approximately 1000nm in length. The total height of the turf is approximately 10μm. The minimum distance between any two growth sites of the CNTs at the substrate are specified to be 200 nm. This ensures that there is a sufficient distance between the tubes at the start of the analysis preventing the possibility of the penetration of the tubes. Periodic boundary conditions are used on each of the 4 faces of the periodic cell in the x and y direction with the z direction being the general orientation of the tubes. The ends of the CNTs at the substrate have their displacements and rotations completely fixed.
The elastic modulus of single wall CNT determined by Yakobson et al. (1996) using ab initio calculations is estimated around 3.9 TPa. In this analysis we use 4 TPa as the elastic modulus. From the SEM images the diameter of the tubes is estimated around 20nm. The tubes are multiwalled and are assumed to have 10 coaxial tubes. To determine the inner diameter we assume the thickness of each CNT wall to be equal to that of the graphene sheet (0.34nm) giving the tube an inner diameter of 16.6nm. Using the classical beam model we then calculate the CNT bending stiffness $B$, using the relation

$$B = EI = E \frac{\pi}{4} \left[ \left( R + \frac{h}{2} \right)^4 - \left( R - \frac{h}{2} \right)^4 \right].$$

(5.1)

This gives us a bending stiffness of $1.65 \times 10^{-21} \text{N.m}^2$. Here using the relation 5.1, we assume that the multiwalled carbon nanotube can be treated as a solid homogenous rod neglecting the atomic nature of each CNT wall. To determine the mass of the CNT we use the upper estimate of mass density (2.1g/cm$^3$) given by Kim et al. (2009). This gives the mass per unit length of $8.21 \times 10^{-22} \text{kg/nm}$.

To determine the parameters in the interaction law in (4.6) and (4.8), we scale the parameters used in the original model by Buehler (2006). For a single walled (5,5) CNT, Buehler estimated the value of $\varepsilon/\sigma$ in (4.6) from molecular dynamics simulation results as $1.122 \times 10^{-10} \text{N}$. The diameter of the (5,5) CNT is 6.78Å giving it a surface area per unit length of $1.07 \text{nm}^2/\text{nm}$. The 20nm diameter tube used in the discrete model has roughly 30 times the surface area per unit length when compared to the CNTs in the Buehler model. Linearly scaling the value of $\varepsilon/\sigma$ for a 20nm CNT would give it a value of $33.66 \times 10^{-10} \text{N}$. Accounting for the multiwalled nature of the CNTs we use the value of
50x10^{-10}N in our model. The value of \( \sigma \) is still retained as 1.163 in our model and the distance is computed as the distance between the outer walls of the CNTs rather than the center-center distance as in the Buehler model. We assume a coefficient of friction of 1.0 in (4.8) with the reference velocity \( V_{ref} \) taken as 1m/s based on the average strain rate during loading of the turf.

We model three turf samples shown in Figure 5.3(a), Figure 5.4(a) and Figure 5.5(a) generated using different angles in the random walk algorithm

i) Turf A with \( \alpha = \pi/8 \),

ii) Turf B with \( \alpha = \pi/4 \) and

iii) Turf C with \( \alpha = \pi/3 \).

The average curvature of the turf is measured using the relation

\[
\kappa_{avg} = \frac{\int_0^L |\kappa(s)| ds}{L} \tag{5.2}
\]

The average curvature of all the tubes at the start of the analysis was 1.82x10^{-4}nm^{-1}, 3.36x10^{-4}nm^{-1} and 4.43x10^{-4}nm^{-1} respectively. We also include mass proportional damping in the model to damp the high frequency vibration due to the Lennard Jones interaction model between the tubes. However, the damping ratio is kept small (<0.05) to ensure the validity of the solution. The analysis was performed in two steps i) initial relaxation of the turf ii) Flat punch indentation of the turf. During the initial relaxation period, the initial structure of the turf is allowed to relax due on the interaction of the CNTs with the neighboring tubes. There are two opposing forces (2.1), the elastic restoring forces which tends to reduce strain energy of the tubes by straightening them.
and the van der Waals forces causing the tubes to adhere with each and thus resulting in an decrease in the surface energy. Note that the decrease in the surface energy requires the tubes to be bent and thus resulting in the competing nature of the elastic and surface energies.

![Figure 5.3](image)

**Figure 5.3** (a) Side view of the initial structure of the CNT turf generate using random walk method with $\alpha = \pi/8$ (b) Relaxed structure of the CNT turf (c) Energy plots during relaxation

![Figure 5.4](image)

**Figure 5.4** (a) Side view of the initial structure of the CNT turf generate using random walk method with $\alpha = \pi/4$ (b) Relaxed structure of the CNT turf (c) Energy plots during relaxation
Runs with no frictional component in the interaction model showed that the contacts between the tubes are not stable tending to straighten the CNTs completely in contrast with the SEM images in Figure 1.1 and experimental observation by Qiu (2011) indicating stable contacts. The system tends to approach a quasi-equilibrium state where the kinetic energy and the strain energy remain constant with time. The samples of the turf were relaxed for 0.2 µs. At the end of relaxation the tubes formed stable contacts with neighboring segments and the free segments tended to straighten out causing a reduction in the average curvature of the turf. The average curvature of the relaxed turfs in Figure 5.3(b) was 1.29x10^{-4} nm^{-1}, 2.17x10^{4} nm^{-1} in Figure 5.4(b) and 2.71x10^{4} nm^{-1} in Figure 5.5(b).
We then analyze the flat punch indentation of the turf sample under a constant strain rate of 3m/s. The flat punch is assumed to be rigid and the interaction between the tubes and punch is calculated using (4.6). The reaction force at the punch is determined by summing the total interacting force between the tubes and flat punch. The deformed configuration of the turf is plotted in Figure 5.6, Figure 5.7 and Figure 5.8. The neighboring periodic cells are also shown to show the deformed configuration clearly.

During the initial stages of the flat punch indentation, the tubes which are initially aligned in different directions tend to coalesce together. With increasing deformation there is sharp rise in the nominal stress is followed by state where the nominal stress is constant with increasing nominal strain at the onset of the first buckle. The tubes generally buckle in the same direction as in the coordinated buckling seen in experiments by Cao et al. (2005), Zbib et al. (2008) and Maschmann et al. (2011). We wish to emphasize the conditions under which we see this behavior. Only when the free ends of the CNTs at the surface of the turf are constrained to prevent slipping when in contact with the flat punch, the coordinated buckling occurs. In the finite element model we constrain the displacements and rotations at the free end of the tubes when the distance between the flat punch and the free end is less than 2nm. Further the frictional component in the tube-tube interaction model in (4.8) is critical in ensuring that the sliding between the neighboring tubes is prevented enabling them to coalesce and deform in the same general direction.
Figure 5.6 (a) Side view of the deformed configuration of Turf A at different nominal strains and simulation times. (b) Energy plots during relaxation (<0.2 µs) and loading (>0.2 µs). (c) Nominal stress-strain curve during loading.
Figure 5.7 (a) Side view of the deformed configuration of Turf B at different nominal strains and simulation times. (b) Energy plots during relaxation (<0.2 µs) and loading (>0.2 µs) (c) Nominal stress-strain curve during loading
Figure 5.8 (a) Side view of the deformed configuration of Turf C at different nominal strains and simulation times. (b) Energy plots during relaxation (<0.2 µs) and loading (>0.2 µs) (c) Nominal stress-strain curve during loading.
The initial time of 0.2 µs is used to relax the turf structure followed by a flat punch indentation at a constant loading rate of 3 m/s. The energy plots confirm the quasi-static nature of the loading during the analysis. The average kinetic energy of the relaxed turf and that during major portion of loading remains unchanged. There are two distinct time spans where we see a spike in the total kinetic energy of the system. During the initial stages of loading (around 0.2 µs) there is a spike in the kinetic energy and its magnitude is comparable to strain energy. This is due to rapid rearrangement of the orientation of the CNTs near the surface at the start of loading. This enables the tubes to coalesce and at increasing strains we see the first buckle appear near the surface.

At the appearance of the first buckle there is a drop in the strain energy. This is followed by a state of constant nominal stress with increasing nominal strain during which we see an increase and drop in the strain energy at the appearance of each buckle. At nominal strains >0.3 we see rapid densification of the turf near the indenter surface. This causes a sharp rise in the nominal stress for a small increase in the nominal strains. We also begin to see a rapid rise in the kinetic energy due to close proximity of the tubes in the region below the punch. The nominal stress-strain plots are in qualitative agreement with experimental observations by Zbib et al. (2008) and Maschmann et al. (2011) where we see a foam-like behavior of the turfs.
In Figure 5.9, the deformed configuration of the turf samples at the same state of nominal strain shows that the wavelength of the buckles is inversely proportional to the average initial curvatures. We calculate the wavelength as the distance between a complete wave with the start and ending points as approximate locations where the tangent of the tubes is vertical. We also note that the location of the buckles is consistent.

**Figure 5.9** Approximate wavelength of the buckles for the three turf samples at the same state of nominal strain.
with the results from Maschmann et al (2011). Their shortest turfs which are of 35mm height, exhibited coordinated buckling nearest to the indenter surface with the buckles propagating towards the substrate with increasing deformation. Further the nominal stress-strain plots are consistent with the experimental results reported by Zbib et al. (2008) and Maschmann et al. (2011).
CHAPTER 6

CONCLUSIONS

The deformation of CNT turfs are studied through two computational models; a continuum model of the turf and a detailed discrete model. The continuum model is computationally convenient but observation of the nonlocal deformation in experiments requires a detailed model.

The experimental results also reveal the turf to exhibit highly compressible foam-like behavior under compression and the deformation is shown to be reversible under moderate strains. The isotropic hyperfoam material model with a Kelvin-Voigt relaxation component serves as a first continuum approximation for the turf. The time dependent relaxation behavior seen in experiments is due to the thermally activated sliding of contacts between the tubes in the turf and contact creep between the turf and the indenter. We model only the material relaxation using a Kelvin-Voigt model and neglect the contact creep. The parameters in the hyperfoam model and the Kelvin-Voigt model are determined from experimental observations and by fitting the FE results with the nanoindentation experiments. The Berkovich indenter tip is modeled with an equivalent conical indenter and the interaction between the turf and indenter is represented using Lennard-Jones type of contact law. The contact law is modified to account for the increased range of the interactive forces due to thermal vibrations. The contact algorithm also includes negligible damping forces to resolve the unstable jump-to-contact and pull-off between the interacting surfaces. The finite element results demonstrate that a continuum model of the nanotube turf is capable of capturing the
mechanical behavior under moderate strains seen in both the load-controlled and depth-controlled experiments. The minor differences during the unloading portion are due to the absence of contact creep in the FE model.

In the detailed discrete model of the turf, we discretized the CNTs using inextensible elastica finite elements and use an explicit integration technique to integrate the equations of motion. An ad hoc Lennard-Jones type force law is used to model the interaction between neighboring segments and with the indenter surface. Periodic boundary conditions are used to mimic infinitely wide turf samples. The material properties of the elastica are inferred from MD simulations. A representative structure of the turf is generated using a controlled random walk to manage the average curvature of the tubes. The initial structure is relaxed followed by compression at a constant loading rate using a flat punch whereby we monitor the deformation and nominal-stress strain response. The energy plots show the quasi-static nature of the loading in simulations. During the initial stages of deformation, the tubes at the periphery of the surface tend to align themselves together rapidly followed by bending till the onset of the first buckle. This is characterized by a sharp drop in the rapidly increasing strain energy and state of constant nominal stress with increasing nominal strain. Further compression enables the buckles to propagate towards the bottom of the substrate and in general the tubes buckle in the same direction akin to the coordinated buckling seen in experiments. At large compressive strains (>0.3), we begin to rapid densification of the turf underneath the indenter surface causing a rapid rise in the nominal stress with a small increase in the nominal strains. The nominal stress-strain response is in good qualitative agreement with
the foam-like behavior seen in experiments. The wavelength of the buckles are seen to be inversely proportional to the relaxed average curvature of the turf.

6.1 Future work

a) The interaction model in the continuum turf model ignores contact creep and this leads to the discrepancy between the numerical results and the experiments. Further the model assumes homogenous isotropic behavior while the turf is orthotropic and experiments indicate varying behavior at different locations. The continuum model would need to address these issues and also investigations on the relation between the material parameters and measurable micromechanical parameters like average curvature, density and number of contacts between neighboring segments is needed.

b) The discrete model employs inextensible elastica elements as the primary mechanism of deformation of slender CNTs is bending with negligible bending. Ignoring axial strains also permit larger time increments in the explicit integration technique. However the determining the Lagrange multipliers to enforce the inextensibility constraint is expensive requiring additional computational time negating any advantage gained by taking larger time increments. We are making efforts to address this issue by using a computationally cheap penalty based approach.
REFERENCES


