Vibrations of Carbon Nanotubes: nonlinear models and energy distribution

F. Pellicano†, M. Strozzi†, L. I. Manevitch‡

† Dept. of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Modena, Italy. email: francesco.pellicano@unimore.it, matteo.strozzi@unimore.it
‡ N.N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia. email: manevitchleonid3@gmail.com

Abstract
Vibrations of Single-Walled Carbon Nanotubes for various boundary conditions are considered in the framework of the Sanders-Koiter thin shell theory. A double series expansion of displacement fields, based on the Chebyshev orthogonal polynomials and harmonic functions, is used to analyse numerically the natural frequencies of shells having free or clamped edges. A reduced form of the Sanders-Koiter theory is developed by assuming small circumferential and shear deformations; such approach allows to determine an analytical solution for the natural frequencies.
The numerical model is validated with the results of molecular dynamics and finite element analyses present in literature. The analytical model is validated by means of comparisons with the numerical approach. Nonlinear vibrations and energy distribution of carbon nanotubes are then considered.

Introduction
Carbon Nanotubes were discovered in 1991 by Iijima [1], who first analysed the synthesis of molecular carbon structures in the form of fullerenes and then reported the preparation of a new type of finite carbon structure consisting of needle-like tubes, the carbon nanotubes, described as helical microtubules of graphitic carbon.
Rao et al. [2] studied the vibrations of SWNTs by using Raman scattering experimental techniques with laser excitation wavelengths in the range of the nanometers. They observed numerous Raman peaks, which correspond to vibrational modes of the nanotubes.
Bandow et al. [3] analysed the effect of the temperature on the diameter distribution and chirality of SWNTs by comparing different experimental techniques, such as electron microscopy, X-ray diffraction and Raman spectroscopy. They studied the effect of the catalysts on the tube yield and the evolution of the tube distribution with increasing environment temperature.
Jorio et al. [4] studied the vibrations of SWNTs by resonant confocal micro-Raman spectroscopy. They developed a method to assign the carbon nanotube chirality uniquely by measuring one radial breathing mode frequency and applying the theory of resonant transitions.
Molecular dynamics (MD) simulations and finite element (FE) analyses provide good predictions of the mechanical behaviour of CNTs under external forces, with results close to the experiments. However, such techniques are not suitable for considering nonlinear effects due to their very huge computational cost.
In this paper, a semi-analytical approach is proposed for the study of carbon nanotubes vibrations; this method is computationally efficient, accurate and suitable for considering nonlinear effects.

Theory
According to the Sanders-Koiter theory, the elastic strain energy U of a cylindrical shell, neglecting both the transverse normal stress σ_z (plane stress hypothesis) and the transverse shear strains γ_{xz}, $\gamma_{\theta z}$ (Kirchhoff's hypothesis), as in the Love's "first approximation", is written in the form

$$U = \frac{1}{2} LR \int_0^1 \int_0^{2\pi} \int_{-h/2}^{h/2} \left(\sigma_x \varepsilon_x + \sigma_\theta \varepsilon_\theta + \tau_{x\theta} \gamma_{x\theta} \right) dz d\theta d\eta \qquad (1)$$

The kinetic energy T of a cylindrical shell (rotary inertia effect is neglected) is given by

$$T = \frac{1}{2}\rho hLR \int_0^1 \int_0^{2\pi} \left(\dot{u}^2 + \dot{v}^2 + \dot{w}^2\right) d\theta d\eta \tag{2}$$

Here, the three displacement fields (u, v, w) are nondimensionalized by means of the radius R of the carbon nanotube $u = R\tilde{u}$, $v = R\tilde{v}$, $w = R\tilde{w}$. A nondimensional time τ is considered by introducing a reference natural frequency ω_0 in the following form $t = \omega_0^{-1}\tau$, $\omega_0 = \sqrt{\frac{E}{(1-\nu^2)\rho R^2}}$.

The problem is analysed by means of an approach based on a double series expansion in terms of harmonic functions and polynomials followed by the application of the Rayleigh-Ritz procedure. Once the linear analysis is carried out, the displacement fields are re-expanded by means of approximate eigenfunctions; using the Lagrange equations and the potential energy with nonlinear terms, a set of nonlinear ordinary differential equations is obtained and solved numerically.

Numerical results

First of all the model is validated with experimental data present in literature [4]; the results reported in Table 1 show that the model is sufficiently accurate.

Natural frequency (THz)			Difference %
(r, s)	ESKT – Present model	RRS – Ref. [4]	
(8, 7)	6.905	7.165	3.63
(10, 5)	6.785	7.105	4.50
(11, 4)	6.669	6.865	2.85
(14, 1)	6.177	6.295	1.87
(18, 0)	5.025	5.276	4.76

Table 1. Natural frequencies of the radial breathing mode (m = 0, n = 0): comparisons between the extended Sanders-Koiter theory (ESKT) and the Resonant Raman Spectroscopy (RRS).

In order to analyse the discrete molecular carbon nanotubes as continuum thin shells, equivalent mechanical parameters (Young's modulus, Poisson's ratio, mass density, wall thickness) must be considered. These parameters are not dependent from the CNT diameter (no size effect). The carbon nanotube described in Table 2 is considered for the following computations.

Effective thickness h_0 (nm)	0.10 ÷ 0.15
Equivalent thickness h (nm)	0.066
Effective Young's modulus E_0 (TPa)	1.0 ÷ 2.0
Equivalent Young's modulus E (TPa)	5.5
Effective Poisson's ratio ν_0	0.12 ÷ 0.28
Equivalent Poisson's ratio ν	0.19
Surface density of graphite σ (kg/m^2)	7.718×10^{-7}
Equivalent mass density ρ (kg/m^3)	11700

Table 2. Effective and equivalent parameters of the Single-Walled Carbon Nanotube.

In Figure 1 the first three mode shapes of a free-free carbon nanotube are presented, such modes are then considered for the development of the semi-analytic nonlinear model of the nanotube in the re-expansion procedure. In Figure 2 the total vibration energy distribution is represented, the nanotube is unwrapped on a plane in order to allow the representation. The sequence of Figures 2(a-d) shows the development of the total energy density [Jm^{-2}] during a time period corresponding to the natural frequency of the fundamental mode; clearly, due to the presence of the nonlinearity, one can observe the absence of periodicity. It is to note that the damping is not considered here, so the total energy

should be constant (the integral of the density over the surface); a specific check is carried out, the results are omitted for the sake of brevity.

The analysis of the energy distribution over the shell shows a periodicity along the circumferential direction. This is partially expected as in the present preliminary analysis no conjugate modes are present. The energy is initially distributed non symmetrically in the axial direction, see Figure 2a, indeed here we are combining a symmetric mode (0,2) and an asymmetric mode (1,2). Then, such initial distribution is destroyed due to nonlinearity and the energy evolves in a mode more complex pattern, see Figures 2(b-e).

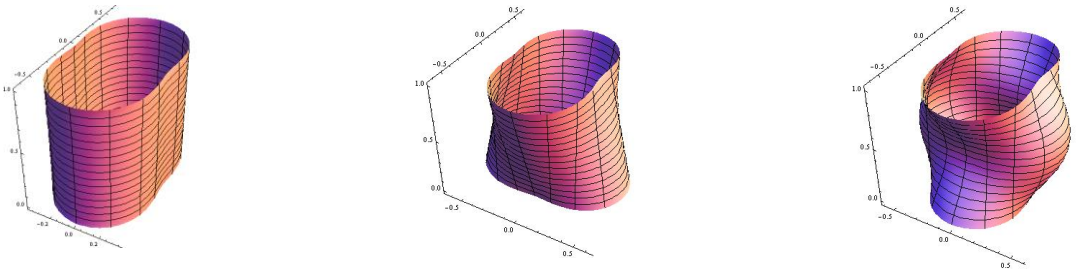

Figure 1. Mode shapes of the vibration modes (j, n). (a) Mode (0, 2). (b) Mode (1, 2). (c) Mode (2, 2).

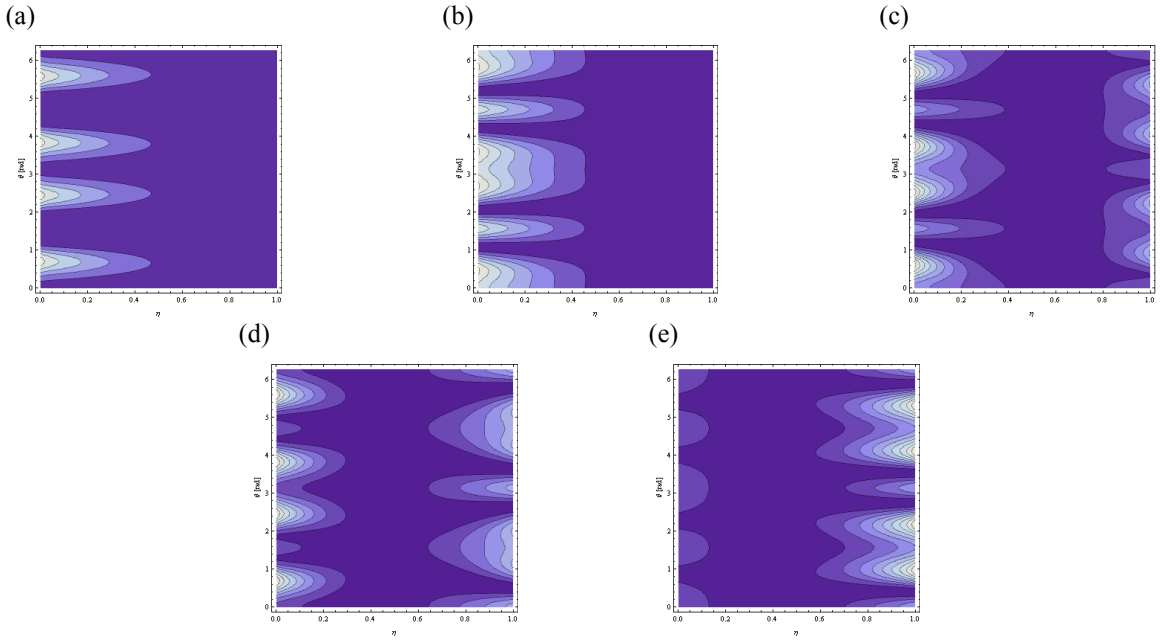

Figure 2. Contour plots of the total energy distribution $\tilde{E}(\eta, \theta, \tau)$. Combination of the vibration modes (0, 2) and (1, 2). (a) Time $\tau = 0$. (b) Time $\tau = 1/4$. (c) Time $\tau = 1/2$. (d) Time $\tau = 3/4$. (e) Time $\tau = 1$.

References

[1] Iijima S. Helical microtubules of graphitic carbon. *Nature* 354 (1991) 56-58.

[2] Rao AM, Richter E, Bandow S, Chase B, Eklund PC, Williams KA, Fang S. Diameter-Selective Raman Scattering from Vibrational Modes in Carbon Nanotubes. *Science* 275 (1997) 187-191.

[3] Bandow S, Asaka S, Saito Y. Effect of the Growth Temperature on the Diameter Distribution and Chirality of Single-Wall Carbon Nanotubes. *Physical Review Letters* 80 (1998) 3779-82.

[4] Jorio A, Saito R, Hafner J, Lieber CM. Structural Determination of Isolated Single-Wall Carbon Nanotubes by Resonant Raman Scattering. *Physical Review Letters* 86 (2001) 1118-21.