OPEN ISSUES IN CONTINUUM MODELING OF CARBON NANOTUBES

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Keywords: *carbon nanotubes, anisotropy, nonlocality, van der Waals interactions*

ABSTRACT

Introduction
Carbon nanotubes (CNTs) were discovered in 1991 inside NEC Corporation laboratories by S. Iijima, who studied the synthesis of fullerenes and first prepared a new type of carbon structures, referred to as CNTs, which were described as "helical microtubules of graphitic carbon" [1].
Since CNTs have very high Young's modulus and tensile strength, together with very small diameter, then they can reach natural frequencies of the THz order and therefore can be used as high sensitivity resonators in several nano-electro-mechanical devices, such as sensors, charge detectors and oscillators.
In addition, the extremely high electric and thermal conductivity of CNTs makes them very promising candidates for innovative applications that include heat exchangers and energy conversion systems, with the role of advanced catalyst supports or electrodes in solar and fuel cells, respectively.
CNTs are divided into two main classes: single-walled carbon nanotubes (SWNTs), which are composed by graphene sheets rolled into cylinders, and multi-walled carbon nanotubes (MWNTs), which are given by concentric SWNTs, where the cylinders are connected by van der Waals interaction forces.
Due to their relevant applications in several mechanical components, vibrations of CNTs have been attracted much attention from researchers. Specifically, CNT vibrations have been studied by means of experimental, atomistic mechanics and continuum mechanics methods.
Resonant Raman spectroscopy (RRS), starting from the experimental measurement of CNT diameter by means of atomic force microscopy, investigates atomic structure, chirality and natural frequencies of CNTs. However, due to their high technological complexity and costs, experimental methods cannot be considered as efficient approaches to study the vibrational behaviour of CNTs.
Molecular dynamics (MD) simulations consider CNT atoms as interacting point-like masses, where the vibrations of the free atoms are recorded for a certain time duration at a fixed temperature. However, due to their high computational effort, atomistic mechanics methods cannot be easily applied to perform the vibrational simulation of CNTs, specially MWCNTs, which incorporate a large number of carbon atoms.

Since theoretical models based on continuum mechanics are computationally more efficient than MD simulations and do not present the technological complexity and high costs of RRS, then the continuous elastic models are the most commonly adopted methods for the study of CNT vibrations. In these models, it is assumed that the effective discrete structure of CNTs can be replaced by means of an equivalent homogeneous elastic structure with a continuous distribution of mass and stiffness, not considering their intrinsic atomic nature and therefore reducing the number of degrees of freedom.

Description of open issues

In order to carefully investigate the validity of the continuum mechanics approaches for CNT vibrations, in the case when the actual lattice structure of CNTs is modelled with a continuous circular cylindrical shell, some very important open issues should be properly considered and correctly faced.

The first relevant issue to be considered in the modelling of CNTs as continuous elastic shells is given by anisotropy. CNTs are usually modelled as isotropic elastic shells; however, they present a chirality-induced anisotropic behavior due to their discrete helical nature that cannot be captured by using an isotropic shell model.

To this aim, Chang et al. [2] developed a molecular mechanics approach, called "stick-spiral model", able to correctly predict the chirality and size-dependent elastic properties of CNTs. They obtained the explicit expressions for longitudinal Young's modulus and Poisson's ratio, circumferential Young's modulus and Poisson's ratio, and longitudinal shear modulus in case of chiral SWCNTs. This molecular based anisotropic elastic shell model including chirality effects was validated via comparisons with RRS and MD data, proving that the classical relationship of isotropic elastic continuum mechanics between Young's and shear modulus is not valid for SWCNTs.

In Figure 1, based on the anisotropic model developed by Chang, the surface elastic constants versus the diameter of SWCNTs with different chiralities are shown. It can be seen that, with increase in the tube diameter, the values of the surface elastic constants increase or decrease, and their limit values approach those for graphite when the tube diameter is relatively large: in this case, an isotropic elastic shell model should be accurate enough.

In addition to anisotropy, another very relevant issue in the modelling of CNTs as continuous elastic shells is given by nonlocality. Classical continuum mechanics models assume that the stress state at a given point of the body is uniquely dependent on the strain state at that point, and they do not admit any intrinsic size dependence within the elastic constitutive equations: therefore, they are not able to identify the small-scale effects on CNT mechanical behavior.

On the other hand, Eringen's nonlocal elasticity theory assumes that the stress tensor σ at a reference point $\mathbf{x}$ in a body depends not only on the strain tensor ε at the point $\mathbf{x}$, but also on the strain tensor at all the other points $\mathbf{x}'$ of the body, in the form:

$$\sigma(\mathbf{x}) = \int_V K(|\mathbf{x}-\mathbf{x}'|,\tau)\mathbf{C}\varepsilon(\mathbf{x}')dV(\mathbf{x}'), \quad \forall \mathbf{x} \in V \tag{1}$$

where $\mathbf{C}$ is the elastic modulus tensor in macroscopic isotropic elasticity, $K(|\mathbf{x}-\mathbf{x}'|,\tau)$ is the nonlocal modulus or attenuation function, which incorporates the nonlocal effects, $\tau = e_0 a/l$ is a dimensionless constant where e_0 is the dimensionless nonlocal parameter to be calibrated, a is the C-C bond length and l is the wavelength.

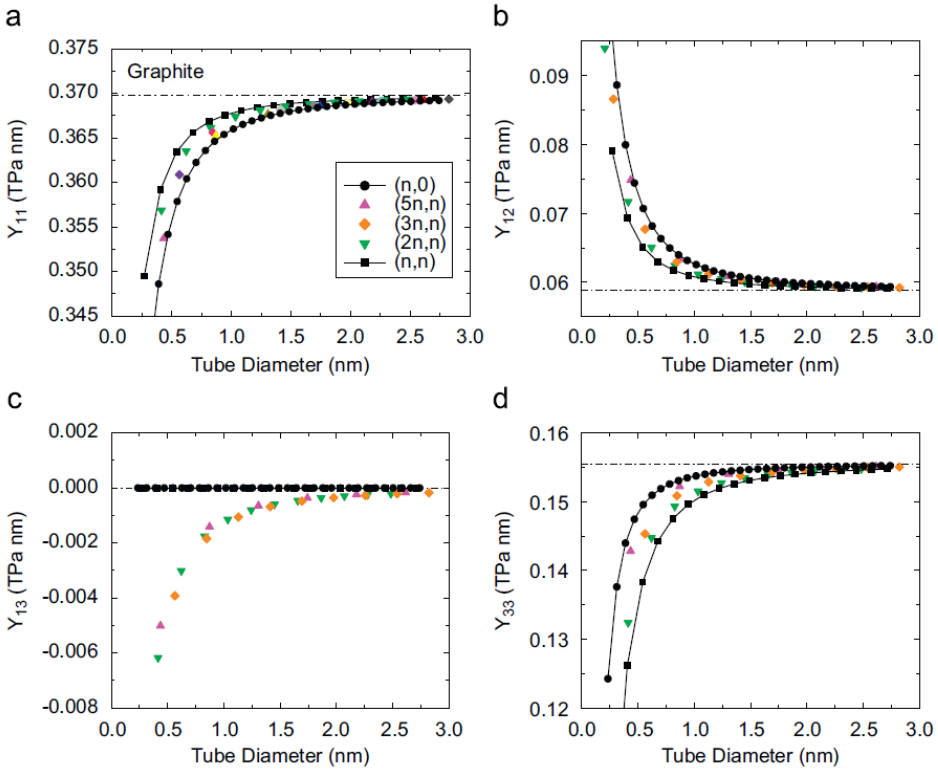

Figure 1. Size D and chirality (n, m) dependent anisotropic elastic constants Y_{ij} of zigzag and armchair SWCNTs. (a) $Y_{11} = Y_{22}$. (b) $Y_{12} = Y_{21}$. (c) $Y_{13} = Y_{23} = Y_{31} = Y_{32}$. (d) Y_{33}.

Starting from Eringen's nonlocal elasticity theory, Fazelzadeh and Ghavanloo [3] developed a refined nonlocal anisotropic elastic shell model by calibrating the value of the nonlocal parameter with the results of MD simulations in order to obtain linear vibrations and natural frequencies of CNTs with different chiralities, geometries and boundary conditions.
Besides anisotropy and nonlocality, in the specific case of MWCNTs, a third relevant issue to be taken into consideration in the continuous modelling is given by van der Waals (vdW) interaction forces between the concentric SWCNTs.
Ru [4] proposed a relationship between pressure due to van der Waals interactions and radial displacement for the buckling and vibration analysis of MWCNTs in which the interaction coefficient is constant, i.e., it is not dependent on the radius of the individual SWCNT.
However, it is clear that this first simplified formulation is not accurate in the modelling of van der Waals interactions.
In order to accurately describe van der Waals interaction forces in MWCNTs, He et al. [5] proposed a relationship where the interaction coefficient is radius dependent. By using this refined formulation, natural frequencies of MWCNTs were analyzed for different geometries and chiralities, obtaining an excellent agreement with the results derived by performing MD simulations.

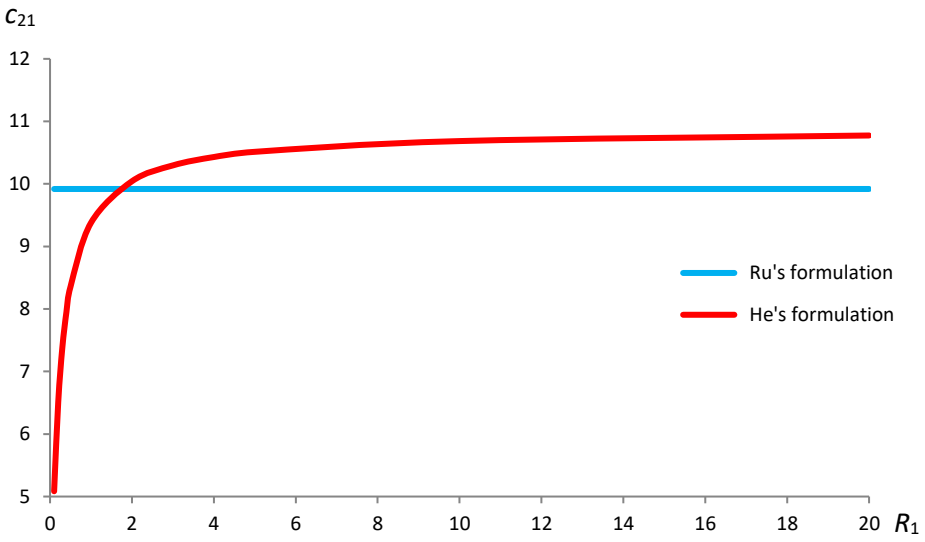

Figure 2. Effect of DWCNT inner radius R_1 (10^{-9} m) on the value of vdW interaction coefficient c_{21} (10^{19} N/m^3). Comparison between Ru's and He's formulations.

In Figure 2, the effect of DWCNT inner radius R_1 on the value of van der Waals interaction coefficient c_{21} obtained by considering Ru's and He's formulations is shown. It can be noted that, for relatively low inner radius, when the nonlocal anisotropic elastic shell model should be adopted, the difference between the two formulations results very high, and van der Waals interaction coefficient from He's formulation is demonstrated to be more accurate.

Conclusions

In order to obtain a proper continuum modelling of CNTs, able to capture their actual discrete behavior derived from experiments and MD simulations, refined models should be adopted, taking into account anisotropy, nonlocality and radius dependent vdW interaction forces.

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