Nonlocal material properties of single-walled carbon nanotubes

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Natural frequencies of single-walled carbon nanotubes (SWCNTs) obtained using a model based on Eringen’s nonlocal continuum mechanics and the Timoshenko beam theory are compared with those obtained by molecular dynamics simulations. The goal was to determine the values of the material constant, considered here as a nonlocal property, as a function of the length and the diameter of SWCNTs. The present approach has the advantage of eliminating the SWCNT thickness from the computations. A sensitivity analysis of natural frequencies to changes in the nonlocal material constant is also carried out and it shows that the influence of the nonlocal effects decreases with an increase in the SWCNT dimensions. The matching of natural frequencies shows that the nonlocal material constant varies with the natural frequency and the SWCNT length and diameter.

Keywords: nonlocal mechanics; molecular dynamics simulation; single-walled carbon nanotube; Timoshenko beam

1. Introduction

Since the paper of Ijima was published in 1991 [1], the research community has been very active in developing models to describe the behavior of carbon nanotubes. This interest is due to the exceptional mechanical, electrical and thermal properties of carbon nanotubes [2]. Carbon nanotubes exhibit a single wall of carbon atoms, which is built by rolling up a graphene sheet, or multiple walls composed of two or more nested coaxial walls of carbon atoms. The first type of nanotubes is designated by single-walled carbon nanotubes (SWCNTs), while those of the second type are designated as multi-walled carbon nanotubes (MWCNT). There are two main types of models for their analysis: atomistic models and continuum models (Figure 1). While the geometry of the atomistic model is defined by the nanotube diameter, the length of the unit vector, and the chiral angle, among others [3], the geometry of the continuum model is described by the length $L$, the outer diameter $D_0$ or the mean diameter $D$ and the thickness $h$.

Due to the computational burden of atomistic models, much interest in the development of continuum models to study the behavior of carbon nanotubes has been reported. The analysis of carbon nanotubes has been performed using several types of classical continuum theories, namely those based on beam theories, shell theories and frame models [4]. However, these theories do not account for several phenomena that appear at the nanoscale, such as atomic interactions and size effects. To overcome these classical theory
shortcomings, different types of models based on nonlocal continuum mechanics have been formulated and applied to carbon nanotubes in recent years [5–10]. These studies, based on Eringen’s nonlocal continuum mechanics [11,12], reported mainly parametric studies of nonlocal parameters and their influence on the mechanical behavior of carbon nanotubes.

This paper presents a study in which natural frequencies of SWCNTs computed using a model based on Eringen’s nonlocal continuum mechanics [11,12] along with the Timoshenko beam theory are compared with those obtained using molecular dynamics simulations [13]. In the present nonlocal beam model, the thickness of the SWCNT does not need to be specified. Since it is not well established in the literature what is the real thickness of a SWCNT [14–16], the elimination of this geometric characteristic from the formulation is one of the advantages of the present model. The nonlocal material constant of Eringen’s nonlocal continuum mechanics theory is determined by performing the described matching of natural frequencies. It was found that this nonlocal material property varies with the natural frequency, the length and the diameter and length of the SWCNT.

2. Theory

In Eringen’s nonlocal continuum mechanics [11,12] it is assumed that the stress at a point $x$ is a function of strains at all points of the body occupying the volume $V$. This leads to an integral constitutive relation [12]

$$\sigma(x) = \int_V \alpha(|x' - x|, \tau) t(x') \, dV(x'),$$

where $t(x')$ is the macroscopic (classical or local) stress tensor at point $x'$, $\sigma(x)$ is the nonlocal stress tensor and $\tau$ is a material constant depending on internal and external characteristic lengths. According to Eringen, the kernel function $\alpha(|x' - x|, \tau)$ represents the nonlocal modulus, where $|x' - x|$ is a distance measured in Euclidean norm. By defining an appropriate kernel function, it is possible to reduce the integral constitutive relation to an equivalent differential form [12]:

$$(1 - \tau^2 \hat{r}^2 \nabla^2) \sigma = t, \quad \tau = e_o \frac{a}{l},$$

where $e_0$ is a material constant, and $a$ and $l$ are internal and external characteristic lengths, respectively. As usual, the classical stress tensor $t$ at a point $x'$ is related to the strain tensor $\varepsilon$ at that point by the generalized Hooke’s law.
\[ t(x') = \lambda \text{tr}[\varepsilon(x')] I + 2G\varepsilon(x'), \] (3)

where \( \lambda \) and \( G \) are the Lamé constants and \( I \) is the identity tensor. By neglecting the nonlocal behavior in the thickness direction, the differential constitutive relation for isotropic beams reduces to

\[ \sigma_{xx} - \mu \frac{d^2\sigma_{xx}}{dx^2} = E\varepsilon_{xx}, \quad \sigma_{xz} - \mu \frac{d^2\sigma_{xz}}{dx^2} = 2G\varepsilon_{xz}, \] (4)

where \( \mu = \varepsilon_0^2 a^2 \) is the nonlocal parameter, \( E \) is the Young’s modulus and \( G \) is the shear modulus. The usual constitutive relations of the local theory of isotropic beams are recovered when \( \mu = 0 \). Using the above constitutive relations, Reddy and Pang [9] developed the equations of motion of nonlocal Euler–Bernoulli and nonlocal Timoshenko beams. These authors solved the equations for bending deflections, buckling loads and natural frequencies with various boundary conditions and used them to analyze carbon nanotubes. The solution for the \( n \)th bending natural frequency of the nonlocal Timoshenko beam, when the rotary inertia is neglected, is given by [9]:

\[ \omega_n = \alpha_n^2 \sqrt{\frac{EI}{m_0}} \left[ \frac{1}{(1 + \Omega_0\alpha_n^2)(1 + \mu\alpha_n^2)} \right]^{1/2}, \] (5)

where, for a nanotube with mean diameter \( D \), thickness \( h \), density \( \rho \), Young’s modulus \( E \), shear modulus \( G \) and shear correction factor \( K_s \), we have

\[ m_0 = \rho A, \] (6)
\[ A = \pi Dh, \] (7)
\[ I = \frac{\pi}{8}(D^3h + Dh^3), \] (8)
\[ \Omega_0 = \frac{EI}{GAK_s}, \] (9)

and where the parameter \( \alpha_n \) depends on the boundary conditions. For a nanotube acting like a cantilever beam, the parameter \( \alpha_n \) is obtained by solving the transcendental equation [9]

\[ S_{22}\beta_n^3 - S_{11}\alpha_n^3 + \alpha_n\beta_n(\alpha_n S_{22} - \beta_n S_{11}) \cos(\alpha_n L) \cosh(\beta_n L) \]
\[ - \alpha_n\beta_n(\alpha_n S_{11} + \beta_n S_{22}) \sin(\alpha_n L) \sinh(\beta_n L) = 0 \] (10)

with

\[ \beta_n = \alpha_n \left[ 1 + \frac{(\Omega + \mu)(\alpha_n L)^2}{1 + (\Omega + \mu)(\alpha_n L)^2} \right]^{1/2} \] (11)
and where

$$\Omega = \frac{\Omega_0}{L^2} = \frac{EI}{GAKsL^2} \quad \text{and} \quad \mu = \frac{\mu_0 L^2}{L^2} \quad (12)$$

are adimensional parameters, related, respectively, to the shear deformation and the nonlocal effects, and $L$ is the nanotube length. $S_{11}$ and $S_{22}$ are given respectively by

$$S_{11} = \alpha_n \left\{ \Omega \left( \beta_n L \right)^2 + \frac{\Omega \pi \left( \alpha_n L \right)^4 \left[ 1 - \Omega \left( \beta_n L \right)^2 \right]}{\left[ 1 + \Omega \left( \alpha_n L \right)^2 \right] \left[ 1 + \mu \left( \alpha_n L \right)^2 \right]} - 1 \right\}, \quad (13)$$

$$S_{22} = \beta_n \left\{ \Omega \left( \alpha_n L \right)^2 - \frac{\Omega \pi \left( \alpha_n L \right)^4 \left[ 1 + \Omega \left( \alpha_n L \right)^2 \right]}{\left[ 1 + \Omega \left( \alpha_n L \right)^2 \right] \left[ 1 + \mu \left( \alpha_n L \right)^2 \right]} + 1 \right\}. \quad (14)$$

If we consider the thickness much smaller than the mean diameter, one may take $h^3 \approx 0$ and then

$$I = \frac{\pi}{8} D^3 h, \quad (15)$$

$$I \frac{A}{A} = \frac{D^2}{8} \quad (16)$$

and the adimensional shear deformation parameter $\Omega$ is given by

$$\Omega = \frac{\Omega_0}{L^2} = \frac{ED^2}{8GKsL^2}. \quad (17)$$

By inserting Equations (15)–(17) in (5), the $n$th bending natural frequency is obtained as a function of the Young’s and shear moduli, $E$ and $G$, the mean diameter $D$, the length $L$, and the density $\rho$:

$$\omega_n = \alpha_n^2 \sqrt{\frac{ED^2}{8\rho} \left[ \frac{1}{\left( 1 + \Omega_0 \alpha_n^2 \right) \left( 1 + \mu \alpha_n^2 \right)} \right]}^{1/2}. \quad (18)$$

From Equation (18) we see that the natural frequencies are independent of the thickness. Therefore, with the present model one does not need to specify the value of the SWCNT thickness. The assumption that $h^3 \approx 0$ is also admissible since by neglecting the rotary inertia $\rho \pi D h^3 / 12$ we are assuming that $h^3 \approx 0$.

Note that the nonlocal material constant $e_0$ is present in Equation (18) through the parameter $\alpha_n$ and the nonlocal parameter $\mu = e_0^2 a^2$, i.e. $\omega_n = \omega_n (e_0)$ and $\alpha_n = \alpha_n (e_0)$. The computation of the natural frequencies for a certain value of $e_0$ is, therefore, performed by solving the transcendental Equation (10) and then replacing the parameter $\alpha_n$ in Equation (18).
3. Application

In this work, the mass density of the SWCNT is assumed to be the same as that of graphitized carbon, \( \rho = 2250 \text{ kg/m}^3 \), and the Poisson’s ratio \( \nu = 0.19 \) [4]. For consistency, the shear modulus is given by \( G = E/[2(1 + \nu)] \). As in other works found in the literature [6,7], in this study the internal length \( a \) is taken equal to the carbon bond length (0.1421 nm). In order to study the influence of the Young’s modulus \( E \) in the evaluation of the nonlocal material constant, two values of this elastic constant were considered: 1 TPa and 1.2 TPa. The shear correction factor \( K_s \) of a beam with a cross-section with inner diameter \( D_i \) and outer diameter \( D_0 \) is given by [17]

\[
K_s = \frac{6(1 + \nu)(1 + m^2)^2}{(7 + 6\nu)(1 + m^2)^2 + (20 + 12\nu)m^2}, \quad \text{with } m = \frac{D_i}{D_0}.
\]  

(19)

For a SWCNT with a large diameter to thickness ratio, we may take \( D_i \approx D_0 \) and Equation (19) becomes

\[
K_s = \frac{2(1 + \nu)}{4 + 3\nu}.
\]  

(20)

3.1. Sensitivities of natural frequencies

Figure 2 shows the dependence of the first and second natural frequencies on the nonlocal material constant of a SWCNT with a mean diameter of 2 nm and a length of 20 nm. It is clear that the natural frequencies with \( e_0 \neq 0 \) are lower than the ones obtained with the local (classical) continuum mechanics theory, i.e. \( e_0 = 0 \), and decrease with the increase in the nonlocal material constant. This is in accordance with previous comparisons of local and nonlocal natural frequencies of Timoshenko beams (see, for example, [18]).

The sensitivities of natural frequencies \( f_n(e_0) = \omega_n(e_0)/(2\pi) \) to changes in the nonlocal material constant \( e_0 \) are computed using a finite difference:

\[
\frac{df_n(e_0)}{de_0} = \frac{f_n(e_0 + \Delta e_0) - f_n(e_0)}{\Delta e_0},
\]  

(21)

where \( \Delta = 0.1 \). Figure 3 shows the sensitivities of the first and second natural frequencies presented in Figure 2. It is noticeable that the second frequency is much more sensitive to changes in the nonlocal material constant than the first one. This shows that the nonlocal effects are more important at higher frequencies. Also, these sensitivities are not monotonic, exhibiting maximum absolute values. This trend is also observed in SWCNTs with other geometric characteristics. However, the maximum absolute value of sensitivities changes with the SWCNT length and diameter.

Figure 4a shows the maximum absolute value of sensitivities of the first natural frequency of SWCNTs with varying aspect ratio \( L/D \) and constant mean diameters \( D \). It can be seen that the sensitivities decrease steeply with the increase in the SWCNT length and are lower for larger diameters. As shown in Figure 4b, the nonlocal material constant where the maximum absolute value of sensitivities is observed increases linearly with an increase in the SWCNT length. From this analysis we can conclude that the influence of the nonlocal effects decreases with an increase in the SWCNT dimensions.
3.2. Matching of natural frequencies

The matching of natural frequencies obtained with molecular dynamics simulations $\omega_n^{MDS}$ to those obtained with the present nonlocal continuum mechanics Timoshenko beam model $\omega_n^{NLCM}$ is performed in order to obtain a value of the nonlocal material constant $e_0^*$ such that $\omega_n^{MDS} = \omega_n^{NLCM}(e_0^*)$. The natural frequencies of nine cantilever SWCNT, with different mean diameters $D$ and lengths $L$, were computed using molecular dynamics simulations by Agrawal et al. [13] and are listed in Table 1. These molecular dynamics simulations
Figure 4. Sensitivity analysis of first frequency of SWCNT with varying aspect ratio $L/D$ and constant mean diameters $D$: (a) maximum absolute value of sensitivities; (b) nonlocal material constant $e_0^*$ for which the absolute value of sensitivities are maximum.

are based on a combination of a second generation reactive empirical bond order potential developed by Brenner et al. [19] and van de Waals interactions [13].

The first study carried out relates the values of the nonlocal material constant $e_0^*$, obtained by matching the first natural frequencies of SWCNT with the same mean diameter $D$, to the aspect ratio $L/D$ and different Young’s modulus. As can be seen in Figures 5 and 6, the nonlocal material constant increases in a linear fashion with the increase of the aspect ratio $L/D$. It is interesting to note that with a Young’s modulus of 1 TPa (Figure 5), the SWCNT with a mean diameter of 1.9 nm and aspect ratio of 3.1 exhibits a value of zero for the nonlocal material constant. This means that for this particular SWCNT and Young’s modulus, the nonlocal effect is not important and can be neglected. However, it can be seen
Table 1. Natural frequencies of cantilever SWCNT computed by molecular dynamics simulations.

| Diameter $D$ (nm) | Length $L$ (nm) | Aspect ratio $L/D$ | 1st frequency (GHz) | 2nd frequency (GHz) |
|-------------------|----------------|-------------------|---------------------|---------------------|
| 1.90              | 5.88           | 3.1               | 172.69              | –                   |
| 1.90              | 11.88          | 6.25              | 47.04               | –                   |
| 1.90              | 28.42          | 14.95             | 8.04                | 52.26               |
| 1.22              | 7.59           | 6.25              | 74.49               | –                   |
| 1.22              | 15.19          | 12.45             | 19.29               | 114.78              |
| 1.22              | 21.32          | 17.45             | 9.65                | 60.93               |
| 0.95              | 5.88           | 6.25              | 99.63               | –                   |
| 0.95              | 14.20          | 14.95             | 17.46               | 107.06              |
| 0.95              | 17.15          | 18.05             | 11.97               | 75.02               |

Figure 5. Variation of the nonlocal material constant $e_0^*$ with the aspect ratio $L/D$ ($E = 1$ TPa).

that for a higher value of Young’s modulus there is an increase in the nonlocal material constant for all the SWCNTs considered in this work (Figure 6). A calibration of the nonlocal material constant performed by Duan et al. [7] for cantilever (5,5) SWCNT, using the first frequency shows a similar variation of $e_0^*$ with the aspect ratio $L/D$ to the one reported here. These authors also applied the nonlocal formulation of Eringen and the Timoshenko beam theory. However, they neglected the nonlocal effect on the shear-strain relation of the Timoshenko beam theory, i.e. they took the local constitutive relation $\sigma_{xz} = 2G\varepsilon_{xz}$ instead of the differential one in the second expression of equation (4). Moreover, these authors considered a Young’s modulus of 5.5 TPa, a Poisson’s ratio of 0.19, and considered that the SWCNT have a thickness of 0.066 nm [20]. Duan et al. [7] also used the carbon bond length as the internal characteristic length.

A study of matching first natural frequencies of SWCNT with constant aspect ratio $L/D$ but varying mean diameter $D$ was also performed. As can be seen in Figures 7 and 8, the larger the diameter, the higher the nonlocal material constant. The variation of $e_0^*$ with the mean diameter is not linear as is the variation of $e_0^*$ with the aspect ratio $L/D$.
Figure 6. Variation of the nonlocal material constant $e_0^*$ with the aspect ratio $L/D$ ($E = 1.2$ TPa).

(Figures 5 and 6). By comparing Figure 7 and 8, we observe that the nonlocal material constant is higher for higher values of the Young’s modulus.

The two studies reported above lead to the conclusion that the results are somehow physically inconsistent, since smaller SWCNTs exhibit lower values of the nonlocal material constant. Another inconsistency is also observed after matching the first and second natural frequencies. As shown in Table 2, the second natural frequencies exhibit nonlocal material constants which are lower than the ones obtained for the first natural frequency. We may assume that there will be a certain natural frequency and subsequent ones for which the nonlocal effects are negligible, since $e_0^*$ will be zero in such cases. Therefore,
for higher natural frequencies the local (classical) continuum mechanics will suffice to
describe the dynamic behavior of the SWCNT. These inconsistencies may be related to
the failure of the differential constitutive relation in Equation (2) to cope with the com-
plex lattice dynamics of SWCNT, as described in a very recent paper by Sundararaghavan
and Waas [21]. These authors proposed a more elaborate kernel function that changes sign
close to the inflection point of the interatomic potential, contrary to the kernel function
used by Eringen [12] in the formulation of the differential constitutive relation.

4. Conclusions
The results reported in this paper show that the nonlocal material properties of a model
based on Eringen’s nonlocal continuum mechanics and the Timoshenko beam theory for
free vibration analysis of single-walled carbon nanotubes is natural frequency, length and
diameter dependent. Moreover, and contrary to what was expected, the nonlocal material
constant increases as the length or diameter increases. For short single-walled carbon nan-
otubes and certain values of the Young’s modulus, the nonlocal material constant is zero,
i.e. the nonlocal theory reduces to the local (classical) theory. Also, for higher natural frequencies we obtain nonlocal material constants with smaller values. The present results suggest that further studies are needed to fully comprehend the mechanical behavior of single-walled carbon nanotubes in the context of nonlocal theories.

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References
[1] S. Iijima, *Helical microtubules of graphitic carbon*, Nature 354 (1991), pp. 56–58.
[2] M. Endo, M.S. Strano, and P.M. Ajayan, *Potential applications of carbon nanotubes*, Top. Appl. Phys. 111 (2008), pp. 13–62.
[3] M.S. Dresselhaus, G. Dresselhaus, and R. Saito, *Physics of carbon nanotubes*, Carbon 33 (1995), pp. 883–891.
[4] J.V. Araújo dos Santos, *Effective elastic moduli evaluation of single walled carbon nanotubes using flexural vibrations*, Mech. Adv. Mater. Struct. 18 (2011), pp. 262–271.
[5] Y.Q. Zhang, G.R. Liu, and X.Y. Xie, *Free transverse vibrations of double-walled carbon nanotubes using a theory of nonlocal elasticity*, Phys. Rev. B 71 (2005), 195404.
[6] Q. Wang and V.K. Varadan, *Vibration of carbon nanotubes studied using nonlocal continuum mechanics*, Smart Mater. Struct. 15 (2006), pp. 659–666.
[7] W.H. Duan, C.M. Wang, and Y.Y. Zhang, *Calibration of nonlocal scaling effect parameter for free vibration of carbon nanotubes by molecular dynamics*, J. Appl. Phys. (2007), 024305.
[8] P. Lu, H.P. Lee, C. Lu, and P.Q. Zhang, *Application of nonlocal beam models for carbon nanotubes*, Int. J. Solid Struct. 44 (2007), pp. 5289–5300.
[9] J.N. Reddy and S.D. Pang, *Nonlocal continuum theories of beams for the analysis of carbon nanotubes*, J. Appl. Phys. 103 (2008), 023511.
[10] S. Adali, *Variational principles for multi-walled carbon nanotubes undergoing buckling based on nonlocal elasticity theory*, Phys. Lett. A 372 (2008), pp. 5701–5705.
[11] A.C. Eringen and D.G.B. Edelen, *On nonlocal elasticity*, Int. J. Eng. Sci. 10 (1972), pp. 233–248.
[12] A.C. Eringen, *On differential equations of nonlocal elasticity and solutions of screw dislocations and surface waves*, J. Appl. Phys. 54 (1983), pp. 4703–4710.
[13] P.M. Agrawal, B.S. Sudalayandi, L.M. Raff, and R. Komanduri, *A comparison of different methods of Young’s modulus determination for single-wall carbon nanotubes (SWCNT) using molecular dynamics (MD) simulations*, Comput. Mater. Sci. 38 (2006), pp. 271–281.
[14] T. Vodenitcharova and L.C. Zhang, *Effective wall thickness of a single-walled carbon nanotube*, Phys. Rev. B 68 (2003), 165401.
[15] J. Peng, J. Wu, K.C. Hwang, J. Song, and Y. Huang, *Can a single-wall carbon nanotube be modeled as a thin shell?,* J. Mech. Phys. Solid 56 (2008), pp. 2213–2224.
[16] C.Y. Wang and L.C Zhang, *A critical assessment of the elastic properties and effective wall thickness of single-walled carbon nanotubes*, Nanotechnology 19 (2008), 075705.
[17] S.M. Han, H. Benaroya, and T. Wei, *Dynamics of transversely vibrating beams using four engineering theories*, J. Sound Vib. 225 (1999), pp. 935–988.
[18] J.V. Araújo dos Santos and J.N. Reddy, *Vibration of Timoshenko beams using non-classical elasticity theories*, Shock Vib. 18 (2011), DOI 10.3233/SAV-2011-0627 (in press).
[19] D.W. Brenner, O.A. Shenderova, J.A. Harrison, S.I. Stuart, B. Ni, and S.B. Sinnott, *A second-generation reactive empirical bond order (REBO) potential energy expression for hydrocarbons*, J. Phys.: Condens. Matter 14 (2002), p. 783–802.
[20] B.I. Yakobson, C.J. Brabec, and J. Bernholc, *Nanomechanics of carbon tubes: instabilities beyond linear response*, Phys. Rev. Lett. 76 (1996), pp. 2511–2514.
[21] V. Sundararaghavan and A. Waas, *Non-local continuum modeling of carbon nanotubes: Physical interpretation of non-local kernels using atomistic simulations*, J. Mech. Phys. Solid 59 (2011), pp. 1191–1203.