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Non-linear elastic properties of single-walled carbon nanotubes

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ABSTRACT

In this paper we have calculated the second and third order elastic constants of SWCNTs at room temperature using the interaction potential model. The approach with some modification has been established for the SWNTs nanomaterials. Further the ultrasonic properties have been determined with help of the non-linear elastic constants and other related parameters for characterization. It is observed that tube length dependent thermal conductivity is prominent reason behind the ultrasonic attenuation. Copyright © 2011 VBRI press.

Keywords: SWCNT; ultrasonic attenuation; second and third order elastic constants; debye average velocity.

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Introduction

The carbon nanotube (CNT) was discovered in 1991[**1**]. It behaves like rolled-up cylinders of graphene sheets of sp^2 bonded carbon atoms. The several studies on its physical, chemical, optical, mechanical and electrical properties have been done elsewhere [**2-5**]. It has wide applications in the fields of nano-electronics, nano-medicines, and nano-engineering due to its unique characteristics. The unusual high stiffness of CNT makes it suitable ingredients for composite materials. For practical purposes, it is essential to study the elastic properties of bulk single-walled carbon nanotubes (SWCNTs) materials. In the field of non destructive testing (NDT), ultrasonic plays an important role because it can be used not only after production but also being process of materials. The ultrasonic velocity is well related to non-linear elastic constants while ultrasonic attenuation is associated to several physical properties of materials like specific heat, thermal relaxation time, thermal energy density, acoustic coupling constant, thermal conductivity etc. We have chosen CNTs under the study due to their important features. In the present study, we proposed an approach for the calculation of second and third order elastic constants of the CNTs validating the interaction potential model. These nonlinear elastic constants have been used to calculate the ultrasonic velocity and attenuation of the CNTs for their characterization. The observed features are discussed in correlation with several physical properties.

Theory

Higher order elastic constants

The present theory for higher-order elastic constants of SWCNT has been developed with slight modification in the theory developed for higher order elastic constants for hexagonal structured materials [**6**]**.** The second (C_{IJ}) and third (C_{IJK}) order elastic constants (SOEC and TOEC) of a material are defined by following expressions.

$$\left.\begin{aligned} C_{IJ} &= \frac{\partial^2 U}{\partial e_I \partial e_J}; \qquad I \text{ or } J = 1,.....6 \\ C_{IJK} &= \frac{\partial^3 U}{\partial e_I \partial e_J \partial e_K}; I \text{ or } J \text{ or } K = 1,.....6 \end{aligned}\right\} \quad \text{-- (1)}$$

where, U is elastic energy density, $e_I = e_{ij}$ (i or j = x, y, z, I=1, …6) is component of strain tensor. The elastic energy density is related to interaction potential. In present approach, we have chosen Lennard-Jones interaction potential { $\phi(r) = -(a_0 / r^6) + (b_0 / r^7)$; where a_0, b_0 are constants} because it is a many body interaction potential. If it is assumed that the basic structure of carbon nanotube is a hexagon then equation (1) leads following six second and ten third order elastic constants.

$$\left.\begin{aligned} C_{11} &= 24.1p^4C' & C_{12} &= 5.918p^4C' \\ C_{13} &= 1.925p^6C' & C_{33} &= 3.464p^8C' \\ C_{44} &= 2.309p^4C' & C_{66} &= 9.851p^4C' \\ C_{111} &= 126.9p^2B + 8.853p^4C' & C_{112} &= 19.168p^2B - 1.61p^4C' \\ C_{113} &= 1.924p^4B + 1.155p^6C' & C_{123} &= 1.617p^4B - 1.155p^6C' \\ C_{133} &= 3.695p^6B & C_{155} &= 1.539p^4B \\ C_{144} &= 2.309p^4B & C_{344} &= 3.464p^6B \\ C_{222} &= 101.039p^2B + 9.007p^4C' & C_{333} &= 5.196p^6B \end{aligned}\right\} \quad \text{---------- (2)}$$

here $C' = \chi\ a/p^5$; $B = \psi\ a^3/p^3$; χ (harmonic parameter) $= 1/8\{7b_0/a^{11}\}$; $b_0 = 6.5 \times 10^{-79}$ J-m^7 and Ψ (anharmonic parameter) $= -\chi / (114a^2)$. The symbol 'p' (=1.66) is a proposed parameter. If l and R are interlayer separation and radius for CNT then lattice parameter (a) is equal to 2R+l [**7, 8**].

Ultrasonic velocities

The anisotropic properties of a material are related to its ultrasonic velocities as they are related to higher-order elastic constants. If ultrasonic wave is propagating along the length of the tube then there are two types of ultrasonic velocities: one longitudinal and other shear wave velocities which are given by equations (3) and (4):

$$V_L = (C_{33} / \rho)^{1/2} \quad \text{---------- (3)}$$

$$V_S = (C_{44} / \rho)^{1/2} \quad \text{---------- (4)}$$

where V_L and V_S are the longitudinal and shear wave velocities while ρ is density of material.

Ultrasonic attenuation and allied parameters

The predominant causes of ultrasonic attenuation in a solid at room temperature are phonon-phonon interaction (Akhieser type loss) and thermoelastic relaxation mechanisms [**6**]. The ultrasonic attenuation coefficient, $(\alpha)_{Akh}$, due to phonon-phonon interaction mechanism is given by equation (5):

$$(\alpha / f^2)_{Akh} = 4\pi^2 (3E_0 < (\gamma_i^j)^2 > - < \gamma_i^j >^2 C_V T)\tau / 2\rho V^3 \quad \text{----- (5)}$$

where f is the frequency of the ultrasonic wave; V is the velocity for longitudinal and shear waves as defined in the equations (3) and (4); E_0 is the thermal energy density and C_V is the specific heat per unit volume of the material; T is the temperature and γ is the Grüneisen number. The Grüneisen number is a direct consequence of the SOECs and TOECs. The acoustic coupling constants 'D' is the measure of the acoustic energy converted into thermal energy and is given by equation (6):

$$D = 3(3E_0 < (\gamma_i^j)^2 > - < \gamma_i^j >^2 C_V T) / E_0 \quad \text{----- (6)}$$

When an ultrasonic wave propagates through a crystalline material, the equilibrium of phonon distribution is disturbed. The time taken for re-establishment of equilibrium of the thermal phonons is called the thermal relaxation time 'τ' and is given by equation (7):

$$\tau = \tau_S = \tau_L / 2 = 3K / C_V V_D^2 \quad \text{----- (7)}$$

where τ_L is the thermal relaxation time for the longitudinal wave; τ_S is the thermal relaxation time for the shear wave; and K is the thermal conductivity; V_D is the Debye average velocity given by equation (8):

$$V_D = \left[\frac{1}{3}\left(\frac{1}{V_1^3} + \frac{1}{V_2^3} + \frac{1}{V_3^3}\right)\right]^{-1/3} \quad \text{----- (8)}$$

The propagation of the longitudinal ultrasonic wave creates compression and rarefaction throughout the tube. The rarefied regions are colder than the compressed regions. Thus there is a flow of heat between these two regions and results in the thermoelastic loss. The thermoelastic loss '$(\alpha)_{Th}$' is given by the equation (9):

$$(\alpha / f^2)_{Th} = 4\pi^2 < \gamma_i^j >^2 KT / 2\rho V_L^5 \quad \text{----- (9)}$$

The thermoelastic loss for the shear wave has no physical significance because the average of the Grüneisen number for each mode and direction of propagation is equal to zero for the shear wave .Only the longitudinal wave is responsible for thermoelastic loss because it causes

variation in entropy along the direction of propagation. The total ultrasonic attenuation is given by the equation (10):

$$(\alpha / f^2)_{Total} = (\alpha / f^2)_{Th} + (\alpha / f^2)_L + (\alpha / f^2)_S \quad \text{-----} \quad (10)$$

where $(\alpha/f^2)_L$ is the ultrasonic attenuation coefficient for the longitudinal wave and $(\alpha/f^2)_S$ is the ultrasonic attenuation coefficient for the shear wave .The dominant mechanism for total attenuation is phonon-phonon interaction. The attenuation due to phonon-phonon interaction is directly related to the acoustic coupling constant and thermal relaxation time.

Results and discussion

The parameters l and R for SWCNT (10, 10) are 3.38 Å and 6.78 Å respectively [**7, 8**]. Hence the lattice parameter 'a' becomes equal to 16.94 Å. The SOECs and TOECs of SWCNT are calculated using lattice parameter and set of equations (2). The results are visualized in **Table 1.** Further we have also determined the Bulk modulus ($B = [2(C_{11} + C_{12}) + 4C_{13} + C_{33}]/9$), shear modulus ($G = [C_{11} + C_{12} + 2C_{33} - 4C_{13} + 12(C_{44} + C_{66})]/30$), Young modulus ($Y = 9BG/(3B+G)$) and poission's ratio ($\nu = (3B-2G)/2(3B-G)$) using second order elastic constants, which are listed **Table 1**.

Table 1. SOECs (GPa) and TOECs (GPa) of SWCNT at room temperature.

C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B	G	Y	ν
42.43	10.42	9.34	46.31	11.20	16.64	21.04	14.74	35.85	0.34
42*	35*	13*	-	-	-				0.15#
C_{111}	C_{112}	C_{113}	C_{123}	C_{133}	C_{344}	C_{144}	C_{155}	C_{222}	C_{333}
-691.94	-109.71	-23.96	-30.45	-156.43	-146.65	-35.47	-23.64	-547.48	-60.62

*: Ref. [11] and #: Ref. [12]

The density (ρ) has value $1.33 \times 10^3 Kgm^{-3}$ for SWCNT (10, 10) [**8**]. The longitudinal, shear and Debye average velocities of ultrasonic wave propagating along the length of the SWCNT are calculated using (3), (4), and (8) at room temperature that are shown in **Table 2**. Specific heat per unit volume 'C_V' and energy density 'E_0' are determined with help of V_D and literature [**9**], which are presented in **Table 2**.

Table 2. Specific heat, Energy density, Ultrasonic velocity, Debye average velocity of SWCNT at room temperature

T (K)	C_v ($x10^6 JK^{-1}m^{-3}$)	E_0 ($x10^8 Jm^{-3}$)	V_L ($x\ 10^3 ms^{-1}$)	V_S ($x\ 10^3 ms^{-1}$)	V_D ($x\ 10^3 ms^{-1}$)
300	4.4967	7.0210	5.90	2.90	3.22

Calculated coupling constants using equation (6) and Grüneisen numbers are given in the **Table 3**. Thermal conductivities of the SWCNT at various lengths are taken from literature [**10**]. The length dependent thermal relaxation time and total ultrasonic attenuation coefficients are evaluated using equations (7) and (10) respectively that are listed in **Table 4** and their variation with tube length is shown in **Fig. 1**.

It is clear from the **Table 1** that the present second order elastic constants have good agreement with others [**11, 12**]. Thus our theoretical approach for the calculation of non-linear elastic constants is justified. The negative values of third order elastic constants are justified with literature [**6**] and indicate that the internal stress of tube supports the deforming force. The higher value of acoustic coupling constant for longitudinal wave than the shear wave (**Table 3)** implies that the conversion of acoustical energy to thermal energy will be large for longitudinal wave. The pico-second order of thermal relaxation time justifies its basic structure to be hexagon.

Table 3. Grüniesen numbers and Acoustic coupling constants at room temperature.

$\langle\gamma_i^j\rangle_L$	$\langle(\gamma_i^j)^2\rangle_L$	$\langle\gamma_i^j\rangle^2_L$	$\langle\gamma_i^j\rangle_S$	$\langle(\gamma_i^j)^2\rangle_S$	$\langle\gamma_i^j\rangle^2_S$	D_L	D_S
-0.6896	5.9647	0.4756	0	0.1953	0	50.941	1.758

Table 4. Thermal conductivity, Thermal relaxation time and Total ultrasonic attenuation of SWCNT Vs length of SWCNT

L (nm)	K ($Wm^{-1}K^{-1}$)	τ ($x\ 10^{-12}s$)	$(\alpha/f^2)_{Total}$ ($x10^{-15}Nps^2m^{-1}$)
50	35	2.255	8.896
100	60	3.866	15.250
150	80	5.155	20.334
200	88	5.670	22.367
250	100	6.443	25.417

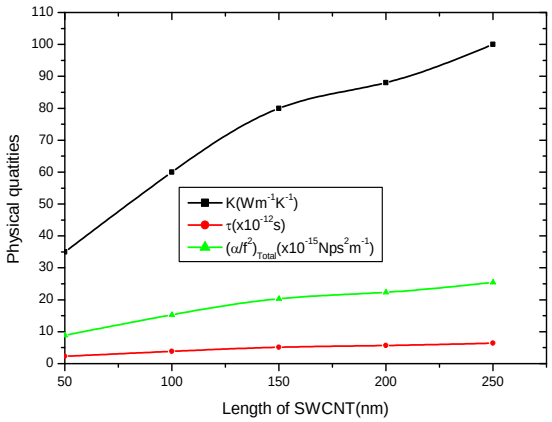

Fig. 1. Thermal conductivity, Thermal relaxation time, Total ultrasonic attenuation Vs Length of SWCNT

The length dependent variation of total ultrasonic attenuation coefficient over frequency square (**Fig.1**) defines that the thermal conductivity is dominating factor to the attenuation with length of SWCNTs. A few works have been reported in literature regarding size dependent ultrasonic attenuation [**13-14**]. In these, it is also observed that thermal conductivity is affecting factor to the attenuation. So, it seems that our finding for SWCNT is justified. If the experimental data of length dependent thermal conductivity and ultrasonic attenuation for SWCNT is available in future then our prediction about attenuation will be verified.

Conclusion

- The anisotropic properties of SWCNTs are well related with the ultrasonic velocities as well as with the higher order elastic constants.
- The predominant causes of ultrasonic attenuation in SWCNTs are phonon-phonon interaction mechanism (Akhieser type loss) and thermoelastic loss. The thermoelastic loss for the shear wave has no physical significance because average of the Grüneisen number for each mode and direction of propagation is equal to zero for the shear wave. Only the longitudinal wave is responsible for thermoelastic loss because it causes variation in entropy along the direction of propagation.
- The length dependent ultrasonic attenuation of the SWCNTs over frequency square is mainly affected by the length dependent thermal conductivity of the tubes. Therefore, variation of the ultrasonic attenuation with length of tube is correlated to the variation of thermal conductivity of tube with its length.

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