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## THERMAL CONDUCTANCE OF HELICALLY COILED CARBON NANOTUBES

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**Abstract:** Thermal conductivity is one of the most interesting physical properties of carbon nanotubes. This quantity has been extensively explored experimentally and theoretically using different approaches like: molecular dynamics simulation, Boltzmann-Peierls phonon transport equation, modified wave-vector model etc. Results of these investigations are of great interest and show that carbon-based materials, graphene and nanotubes in particular, show high values of thermal conductivity. Thus, carbon nanotubes are a good candidate for the future applications as thermal interface materials.

In this paper we present the results of thermal conductance  $\sigma$  of a model of helically coiled carbon nanotubes (HCCNTs), obtained from phonon dispersion relations. Calculation of  $\sigma$  of HCCNTs is based on the Landauer theory where phonon relaxation rate is obtained by simple Klemens-like model.

**Keywords:** helically coiled carbon nanotubes, phonon dispersions, thermal conductance, ballistic conductance.

### 1. INTRODUCTION

Since high thermal conductivity of graphite was analytically predicted by Klemens and Pedraza in 1993 [1], heat carrying of graphene and related materials has been intensively explored both theoretically and experimentally. In order to diminish heat dissipating in nanoscale elements of electronic devices, there is a great interest in thermal properties of carbon-based materials, nanotubes (NT) and graphene.

In this report we are presenting results obtained for thermal conductance of helically coiled carbon nanotubes (HCCNTs) using Landauer approach. Phonon dispersion relations of relaxed HCCNTs are calculated and intrinsic relaxation time of each phonon is found. Other phonon scattering mechanisms like boundary scattering or lattice defects are not considered in the calculations. It is found that acoustic phonons, fast moving quanta of crystal lattice vibrations, make the major contribution to the heat current.

### 2. MODEL

In our calculations we use the model of helically coiled carbon nanotubes [2,3], obtained from topological coordinate method based on graph theory [4].

Monomer of HCCNT is constructed by means of this procedure from triple connected tiling of the plane by pentagons, hexagons and heptagons. Relative mutual positions of pentagons, hexagons and heptagons in elementary cell of the plane are preserved on monomer. Elementary cells of the triple connected planes as well as corresponding monomers of the HCCNT contain pairs of pentagons and heptagons. Assignment  $(n_6, n_7, n_5, (\mathbf{b}_1, \mathbf{b}_2))$  of the HCCNT includes parameters of triple connected plane  $(n_6, n_7, n_5)$  and super-cell vectors  $(\mathbf{b}_1, \mathbf{b}_2)$  defined on it Figure 1a). Graph manipulations, used for changing the atomic structure, imply adding columns of hexagons between heptagons and pentagons  $n_6$  [5] or between pentagons  $n_5$  or between two heptagons  $n_7$  in elementary cell or adding rows of hexagons among the neighboring cells  $n_7$ . Geometry of HCCNT is described with helical geometrical parameters inclination angle  $\chi$  and helical radius  $R$  Figure 1b) and tubular geometrical parameters, tubular radius  $r$  (or tubular diameter  $d$ ) and monomer length  $a$  Figure 1d). Symmetry of thus constructed helically coiled carbon nanotube is line group [6] from the fifth family  $L = T_Q(F)D_1$ . Symmetry elements of a HCCNT's model are screw axes and rotation around X axes for  $\pi$ . Elements of screw axes are a function of geometrical parameters of HCCNTs, rotation around helix axes for  $2\pi/Q$  where  $Q = 2\pi R/a\cos\chi$ , is followed by fractional translation  $F = a\sin\chi$ . Experimentally, carbon nanocoils are of-

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ten characterized by geometrical parameters, outer diameter  $D = 2(r + R)$  and coil step  $p = 2\pi(r + R) \tan\chi$  illustrated in Figure 1c) and d). The model of HCCNT with realistic geometrical parameters has a very large

number of atoms in *symcell* (half of monomer), which makes typical calculations procedure more complex and inapplicable without the implementation of symmetry.

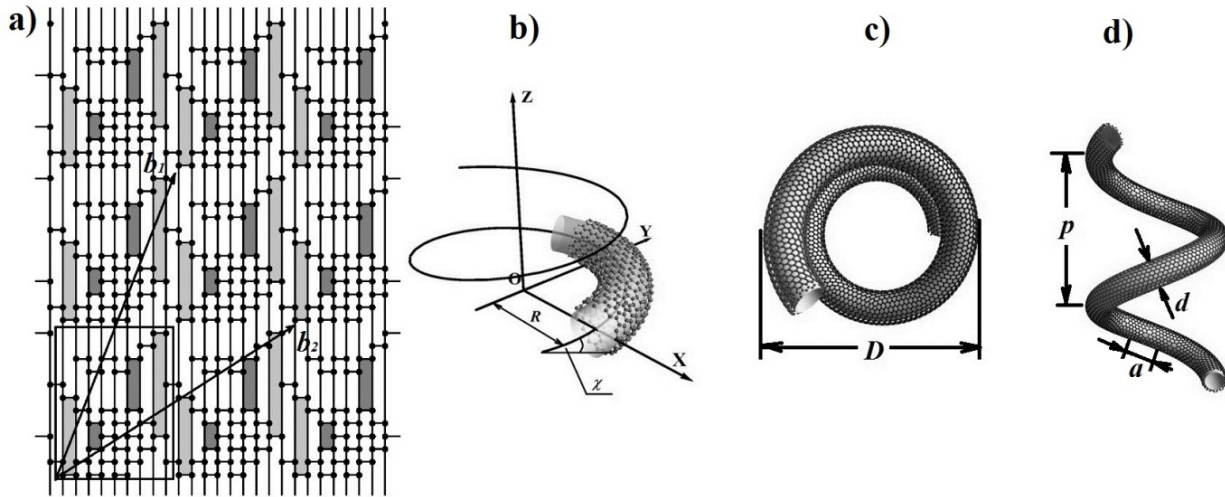


Figure 1. a) Triple connected graph tiled by pentagons (dark gray), hexagons (white) and heptagons (gray). Black rectangle denotes the elementary cell of the plane with super-cell vectors  $(\mathbf{b}_1, \mathbf{b}_2) = ((2, 1), (1, 2))$ . b) Part of HCCNT pulled on helix with geometrical parameter of helix inclination angle  $\chi$  and helical radius  $R$ . c) Top view of HCCNT with outer diameter  $D$ . d) Front view of HCCNT with geometrical parameters helical step  $p$ , tubular diameter  $d$  and monomer length  $a$ .

### 3. PHONON DISPERSIONS

Dynamical sub-matrices of each atom in *symcell* of relaxed HCCNTs are obtained numerically. Every force constant is evaluated by changing Brenner's interatomic potential energy [7] during variation of spatial coordinates of carbon atom [8,9].

Helically coiled carbon nanotubes contain large number of atoms in monomers and are mostly not translationally periodic. Even periodic HCCNT has too many atoms in elementary cell. Despite periodicity, it is easier to present phonon branches in helical quantum numbers representation [6]. Longitudinal (LA) and twisting (TW) acoustic phonons are at  $\Gamma$  point ( $k = 0$ ), and they have linear dispersion Figure 2a). The lowest energy phonon branch contains transversal acoustic phonons (TA) at  $k = 2\pi/Q$ , with quadratic dispersion indicated with an arrow in Figure 2a). The model of the coiled nanotubes is not rotationally symmetric, so that the angular quantum number disappears ( $m = 0$  of all bands).

Acoustic velocities ( $v_{ac}$ ) of SWCNTs weakly depend on tubular radius or chirality, and group velocities of optical phonons  $v_s(k) = d\omega_s/dk$  are significantly lower than the speed of the sound. Consequently, acoustical phonons have a major contribution in heat conduction of NTs and graphene. We have found that acoustic velocities of HCCNTs are highly correlated within the geometrical parameters

of the tube, and are generally lower than acoustic velocities of SWCNTs. LA, TW and TA branches of (7, 2) SWCNT and two lowest phonon branches of two HCCNTs are presented in Figure 2b). Longitudinal and twisting modes of helical nanotube have equal speed of sound ( $v_{LA} = v_{TW}$ ), and along the helix of (1, 2, 0, 2, ((1, 0), (0, 5))) ( $D = 2.7$  nm,  $p = 1.5$  nm) and (1, 2, 0, 2, ((1, 4), (0, 5))) ( $D = 1.3$  nm,  $p = 5.5$  nm) HCCNTs,  $v_{ac}$  amounts to 11000 m/s and 9700 m/s respectively. The given NTs have similar tubular geometrical parameters, the same number of atoms in a monomer (68) but different helical geometrical parameters. It is verified that the shape of phonons branches as well as phonon group velocities depend of geometrical parameters of HCCNT.

### 4. THERMAL CONDUCTANCE

Phonons have a major contribution as heat carriers in carbon-based systems. Thermal conduction of nanotubes or graphene at all temperature is dominated by acoustic phonons, regardless of their metal properties [10]. This is caused by low anharmonicity of crystal lattice and high speed of acoustic waves in carbon-based materials. We have applied Landauer formalism to solving heat quantum transport problem of HCCNTs and SWCNTs [10,12].

The formula used for calculation of thermal conductance ( $\sigma$ ) is derived from the definition as a ratio of phonon thermal current and temperature difference of the heat baths connected to NT  $\sigma = J_{ph}/\Delta T$ . Assuming that temperature difference  $\Delta T = T_2 - T_1$  is much lower than the average temperature of the system  $T = (T_1 + T_2)/2$ ,  $\Delta T \ll T$  ( $T_1, T_2$  are temperatures of contacts of nanodevice), the resulting formula of thermal conductance is

$$\sigma = \sum_s \int_{\omega_{max}} \frac{d\omega_s}{2\pi} \hbar \omega_s \frac{\partial f_B}{\partial T} \mathcal{T}_s(\omega)$$

where,  $f_B$  is Bose-Einstein equilibrium distribution function at temperature  $T$ . Approximation of effective transmission function  $\mathcal{T}_s(\omega)$  of the phonon ( $s, \omega$ ) through a nanodevice [11,13] is given by rela-

tion  $\mathcal{T}_s(\omega) = \lambda_s(\omega)/(L + \lambda_s(\omega))$ , where  $L$  is conductor length (for HCCNTs  $L$  is measured along helix) and  $\lambda_s(\omega) = v_s(\omega)\tau_s(\omega)$  is phonon mean free path and  $v_s(\omega)$  is ( $s, \omega$ ) phonon group velocity. Intrinsic relaxation time for the three-phonon Umklapp scattering process is obtained from a simple model [1,10] based on Klemens-like expression

$$\tau_s(\omega) = \frac{1}{\gamma_s^2} \frac{M \bar{v}_s^2}{k_B T} \frac{\omega_{s,max}}{\omega^2}$$

Umklapp scattering rates depend on Grünesen parameter  $\gamma$  which determines the degree of lattice anharmonicity. Grünesen parameter of an individual phonon is defined as  $\gamma_s(k) = -\partial(\ln\omega_s(k))/\partial(\ln V)$ , while  $\bar{\gamma}_s^2$  is obtained from the averaged over whole branch  $s$  [1].

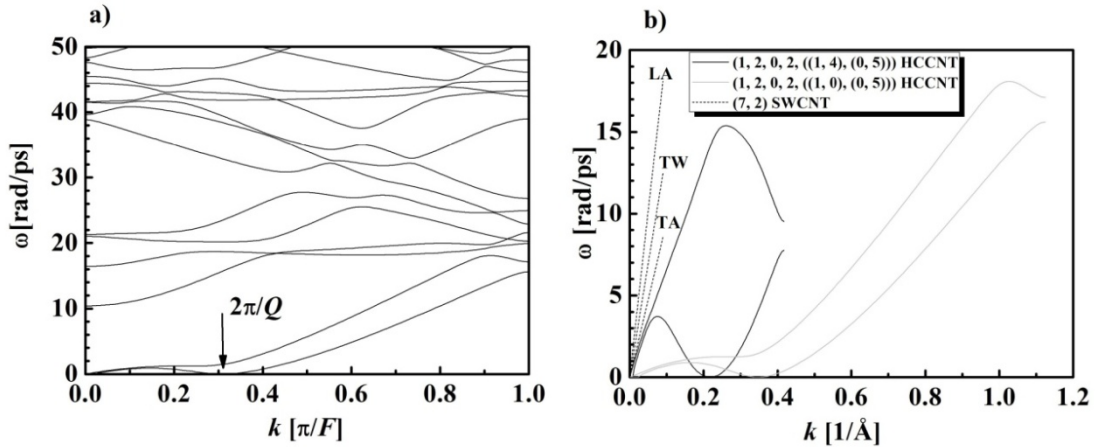


Figure 2. a) Phonon dispersion in the low energy range of  $(1, 2, 0, 2, ((1, 0), (0, 5)))$  HCCNT. The arrow indicates transversal acoustic phonons at  $\kappa$  point, b) Acoustic branches of straight  $(7, 2)$  SWCNT (dashed line) and two lowest phonons branches containing acoustic phonons of  $(1, 2, 0, 2, ((1, 0), (0, 5)))$  (light gray line) and  $(1, 2, 0, 2, ((1, 4), (0, 5)))$  (dark gray line) HCCNTs

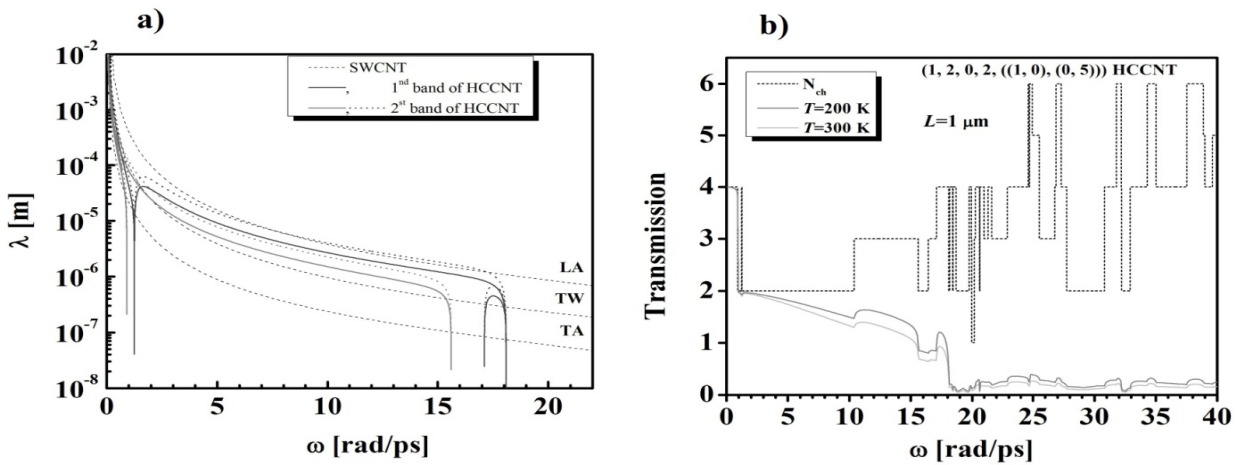


Figure 3. a) Mean free path as the function of frequency of LA, TW and TA phonons for straight  $(7, 1)$  SWCNT (dashed lines) and for the first two phonon branches of  $(1, 2, 0, 2, ((1, 0), (0, 5)))$  HCCNT at 200 K (dotted lines) and 300 K (solid lines), b) Frequency dependence of effective transmission function of phonon frequency for  $(1, 2, 0, 2, ((1, 0), (0, 5)))$  HCCNT at 200 K (dark gray solid line) and 300 K (light gray solid line) with number of conductive channels  $N_{ch}$  (dashed line)

In Figure 3a) mean free path (MFP) is shown as the function of frequency for low energy part of acoustical phonon branches of (7, 1) SWCNT at room temperature and MFP for the first two phonon branches of (1, 2, 0, 2, ((1, 0), (0, 5))) HCCNT at different temperature. The mean free path decreases with the temperature for all phonons. Over the entire range of frequencies, solid lines are below the dotted lines of the same color, they have a similar shape, and denote MFP of HCCNT obtained for 200 K and 300 K, respectively. Peaks of the acoustic branches of HCCNT correspond to the phonons with zero group velocity and do not contribute to heat conduction. The effective transmission function dependence of frequency for 1  $\mu\text{m}$  long HCCNT at 300 K and 200 K, respectively, marked with light and dark gray solid line is shown in Fig. 3 b). At low frequencies the effective transmission function approaches the dashed line, which corresponds to the number of conduction channels  $N_{ch}$ . The frequency bandwidth that satisfies  $N_{ch} \sim \mathcal{T}_s(\omega)$  is determined by temperature ( $T$ ) and the length of conductor ( $L$ ).

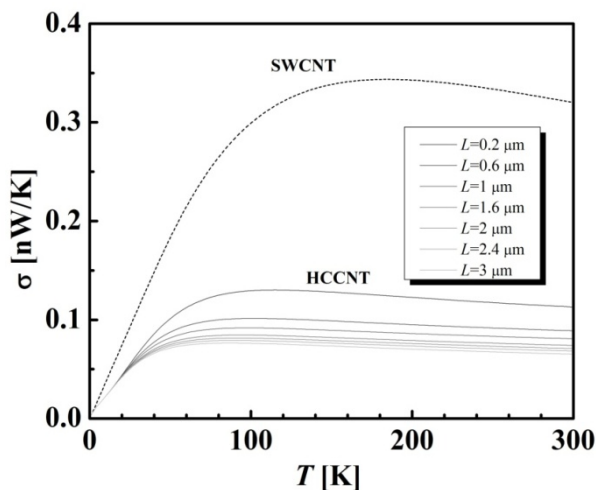


Figure 4. Thermal conductance as a function of temperature for different coil length  $L$  of (1, 2, 0, 2, ((1, 0), (0, 5))) HCCNT (solid lines) and 2  $\mu\text{m}$  long (7, 1) SWCNT (dashed line)

Ballistic conductance regime, independent of the length of the conductor, is obtained for SWCNTs and HCCNTs at cryogenic temperature. Heat flow in NT at low temperature is characterized by quantized thermal conductance which linearly increases with  $T$  Fig.4. Straight nanotubes have universal quantized thermal conductance  $4\sigma_0$  [14], where each acoustic phonon mode has an equal contribution that is  $\sigma_0 = T\pi^2 k_B^2 / 3h$ . In the case of HCCNTs, conductance is linear at low temperature but it is not integer multiple of  $\sigma_0$  and increases more slowly with  $T$  than at SWCNT (approximately doubly). At higher tem-

perature  $\sigma$  of HCCNTs and SWCNTs reach maximal values depending on the length of the conductor. Further, a temperature increase causes decreasing of MFP and transmission function of the conductor with length  $L$  and as a result, the conductance regime becomes diffusive. In Fig. 4 is presented conductance of (1, 2, 0, 2, ((1, 0), (0, 5))) HCCNT for several coil length (solid lines) and 3  $\mu\text{m}$  long (7, 1) SWCNT (dashed line). A decrease of the coil length is indicated with variable colors from dark gray to light gray line which corresponds to 0.2  $\mu\text{m}$  and 3  $\mu\text{m}$  respectively.

## 5. CONCLUSION

We calculated thermal conductance for different lengths of SWCNTs and HCCNTs at a wide range of temperature within the Landauer theory of conductivity. Klemens-like approach was used in order to obtain intrinsic relaxation rate, which includes only phonon-phonon scatterings caused by anharmonic effect. We found a difference between temperature dependences of conductance at cryogenic temperature of HCCNTs and SWCNTs. HCCNT has lower conductance than SWCNT of the same length over the entire range of temperature due to a slower increase of  $\sigma$  from zero temperature, the narrow phonon optical gap and low group velocity that caused short phonon mean free path. Combined elastic and thermal properties of HCCNTs makes them a good candidate for thermal management applications.

## 6. ACKNOWLEDGEMENTS

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#### ТЕРМАЛНА КОНДУКТАНСА ХЕЛИКАЛНИХ УГЉЕНИЧНИХ НАНОТУБА

**Сажетак:** Термална проводност је једна од најзначајнијих особина угљеничних нанотуба. Ова величина је детаљно истражена експериментално али и теоријским методама као што су: молекуларна динамика, Болцман-Пајерлс фононске транспортне једначине, метод модификованих таласних вектора итд. Резултати ових истраживања су од великог значаја и указују да материјали на бази угљеника, посебно графен и нанотубе, имају велику топлотну проводност. Због тога су угљеничне нанотубе добри кандидати за примјену као интерфејс материјали за одвођење топлоте.

Топлотна кондуктанса  $\sigma$  модела хеликалних угљеничних нанотуба (ХУНТа), добијена је из фононских дисперзионих релација. Рачунање топлотне кондуктансе ХУНТа засновано је на Ландауеровој теорији, а вријеме релаксације фонона добијено је примјеном простог Клеменсовог модела.

**Кључне ријечи:** хеликалне угљеничне нанотубе, фононске дисперзије, термална кондуктанса, балистичка проводност.

