Artsiom PRANEUSKI[1], Mikhail TIVANOV[1], Karolina CZARNACKA[2], Konrad KIERCZYNSKI[3]

Belarusian State University, Minsk, Belarus (1), University of Life Sciences in Lublin, Lublin, Poland (2), Lublin University of Technology, Lublin, Poland (3)

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Two-dimensional thermal conductivity of defect-free single-walled carbon nanotubes

Abstract. *Based on the known Debye's model for heat capacity and on the kinetic model for the phonon heat transfer taking into account the length of nanotube and also of the contribution made by phonon-phonon scattering, a heat conduction model of defect-free single-wall carbon nanotube was proposed. Based on this model, the dependences of the two-dimensional thermal conductivity of defect-free single-wall carbon nanotubes on their length and temperature were defined.*

Streszczenie. *Na podstawie modelu pojemności cieplnej Debaye'a oraz modelu cieplnego transferu fononów, biorąc pod uwagę długość nanorurki a także wkład rozpraszania fonon-fonon, zaproponowano model przewodzenia ciepła jednościennych nanorurek węglowych bez defektów. Bazując na tym modelu zdefiniowano zależności dwuwymiarowego przewodnictwa cieplnego jednościennych nanorurek węglowych bez defektów od ich długości. (**Dwuwymiarowa przewodność cieplna jednościennych nanorurek węglowych bez defektów**).*

Keywords: carbon nanotube, thermal conductivity.
Słowa kluczowe: nanorurki węglowe, przewodność cieplna.

Introduction

Due to its good electrical and heat conductivity [1], high values of chemical, thermic and mechanical stability [1, 2], carbon nanotubes (CNTs) are one of the most promising objects of nanoelectronics [1-5].

Despite the huge potential of CNTs application in nano-electronics as a part of heat-removing devices, known models for calculation of its thermal conductivity provide different results [6-11]. The values of CNTs thermal conductivity determined experimentally also vary significantly [12-14]. A possible reason for this discrepancy is incorrect application of three-dimensional representations of the thermal conductivity and other physical phenomena in two-dimensional structures [15].

We have developed a heat conduction model of defect-free single-wall carbon nanotube (SWCNT). This model is based on the known Debye's model for heat capacity and on the kinetic model for the phonon heat transfer that takes into account the length of SWCNTs due to clarifying of Debye's model for the case of nanoscale structures and also of the contribution made by phonon-phonon scattering on the basis of Clemens's formula. The length is considered in the context of parameterization of the lower integration frequency in the Debye formula.

The model of thermal conductivity of defect-free SWCNTs

Considering SWCNTs as a sheet of graphene rolled into a cylinder – a two-dimensional object - we will regard SWCNTs as two-dimensional objects as well. We apply to SWCNTs the Fourier's law in its two-dimensional form [12], where two-dimensional thermal conductivity has a *W/K* dimension.

According to the elementary heat transport theory, the coefficient of two-dimensional thermal conductivity can be expressed as [15]

$$k = \frac{1}{2}\rho v c_V L_B = \frac{1}{2s_2}\frac{C_2}{\mu} v^2 \tau_B, \tag{1}$$

where v is the phonon group velocity, as it is related directly to the transfer of energy; ρ is the two-dimensional density of the material; L_B is the phonon mean free path; τ_B is the phonon relaxation time (ballistic time); c_V is the specific heat; C_2 is the a two-dimensional molar heat capacity; $\mu = 12\ {}^{g}\!/_{mol}$ is the molar (atomic) weight of carbon; $s_2 = \rho^{-1} = 2.63 \cdot 10^6\ {}^{m^2}\!/_{kg}$ is the specific surface [15].

Thus, expressions for the specific heat, the relaxation time and group velocities need to be found in order to determine the coefficient of the two-dimensional thermal conductivity of SWNT.

To calculate the heat capacity we use the well-known Debye model, which considers only the long-wavelength acoustic phonons with a linear dispersion law.

Since the object of the study is nano-scale, the lower limit of integration over frequency must be different from zero due to the fact that in an extreme case a half-wave of elastic vibrations fits in the length of the structure, thus indicating that the lower limit of integration over frequency depends on the length of the nanostructure [16]. By doing such assumption, we get an expression which differs from the calculation formula obtained by the authors [15], as it takes into account the length of the considered two-dimensional nanostructure:

$$C_2(T,L) = \frac{4R}{\Theta_D^2 - \Theta_{\min}^2} \times \tag{2}$$
$$\times \left\{ \int_{\frac{\Theta_{\min}}{T}}^{\frac{\Theta_D}{T}} \frac{3T^2 z^2 dz}{\exp(z) - 1} + \frac{\Theta_{\min}^3 / T}{\exp\left(\Theta_{\min}/T\right) - 1} - \frac{\Theta_D^3 / T}{\exp\left(\Theta_D/T\right) - 1} \right\},$$

where $\Theta_{\min} = {}^{h\upsilon}\!/_{2Lk_B}$ is a "minimum" temperature corresponding to the lowest possible phonon frequency, introduced by analogy with Θ_D (Debye temperature); L is the length of SWCNTs; k_B is the Boltzmann constant; R is the universal gas constant.

We note that the length of SWCNT is limited. This fact automatically suggests the dependence of Debye temperature on the length of the SWNTs, which is parameterized by the number of atoms per unit length of SWCNTs.

The number of atoms per unit length N/L is determined by the geometry of the SWCNTs. Thus, based on simple geometrical considerations, for *zigzag* and *armchair* types of SWCNTs we have respectively

$$(3) \qquad \left(N/L\right)_{zigzag} = \frac{38\sqrt{3}\pi d}{87a^2};\ \left(N/L\right)_{armchair} = \frac{4\sqrt{3}\pi d}{9a^2}.$$

where d is CNTs diameter; $a = 0.142\,nm$ is the distance between the nearest atoms in a graphene unit cell.

At room temperature and lower concentration of free charge carriers in graphene and CNTs is low, therefore electron-phonon scattering can be neglected compared to the phonon-phonon scattering and scattering by defects [17, 18]. Since in our case the object of the study is presented by defect-free SWCNTs, ballistic time τ_B is determined by phonon-phonon scattering only.

The following formula was obtained for the ballistic time of the long-wave phonon in graphene in Umklapp-process, considering the three-phonon scattering of the second order of perturbation theory (for temperatures much lower than the Debye temperature that is about 2000 K for graphene [19]) [20, 21]:

$$(4) \qquad \frac{1}{\tau_B(\omega)} \cong \gamma^2 \frac{k_B T}{Mv^2}\left[2\frac{\omega^2}{\omega_D} + \gamma^2 \frac{k_B T}{Mv^2}\omega_D\right].$$

where γ is the Grüneisen parameter; $M = 4\cdot 10^{-26}\ kg$ is the mass of the unit cell of graphene.

We apply this expression to SWCNTs. We take the Grüneisen parameter equal to $\gamma = 1.24$, the value obtained in paper [22], which is definitely a certain value averaged over all the phonon branches, as the Grüneisen parameter for graphene, as well as the group velocity, has a dispersion and it's different for different phonon branches [19].

For the group velocity we take Debye average velocity $< u >_D$ (elastic continuum model), i.e. averaged over the Debye model velocity of sound waves (longitudinal v_L and transverse v_T) determined for graphene in [23]:

$$(5) \quad v = < u >_D = \sqrt{2}\left(1/v_L^2 + 1/v_T^2\right)^{-1/2} = 16.2\cdot 10^3\ m/sec.$$

According to formula (1) we calculate the coefficient of two-dimensional thermal conductivity of defect-free SWCNTs based on the expression for the heat capacity (2), the relaxation time (4) and speed (5) of the phonons.

Results and Discussion

We use formula (1) to evaluate the dependence of the thermal conductivity of SWCNT on its temperature and length.

Within the framework of the kinetic model of the phonon heat transfer, the maximum can be expected in the plot of the dependence of thermal conductivity on the temperature. In fact, the rise in temperature is accompanied by growth in the number of phonons contributing to the heat transfer, which corresponds to an increase in thermal conductivity of the structure under consideration. However, the phonon-phonon scattering that contributes to the thermal resistance (Umklapp-scattering processes) intensifies with increasing temperature, which corresponds to a decrease in thermal conductivity. It is evident that the peak in the plot of the dependence of thermal conductivity on the temperature corresponds to a certain balance between increase in thermal conductivity due to the increase in the number of phonons and decrease of the thermal conductivity due to the intensification of the phonon-phonon scattering (without considering scattering by electrons and lattice defects).

In other words, within this model, an increase in thermal conductivity with the temperature rising to a certain value, and then decrease in thermal conductivity with further rise in temperature - is to be expected. This, in our view, determines the effective temperature range of use of CNTs and graphene as heat sink elements in nanoelectronic devices, i.e. the temperature range in which the thermal conductivity of the considered nanostructures is maximum.

In Fig. 1 there are presented calculated dependences of two-dimensional thermal conductivity of SWCNTs of *zigzag* or *armchair* types on the temperature for nanotubes of different lengths (curves obtained for the two types of nanotubes are virtually identical). As expected, these curves have a peak - a superposition of processes of thermal conductivity increase due to the rise in number of phonons with increasing temperature and decreasing thermal conductivity due to the intensification of Umklapp-scattering processes with increasing temperature. This behavior of the thermal conductivity was reported in papers [6, 7, 12].

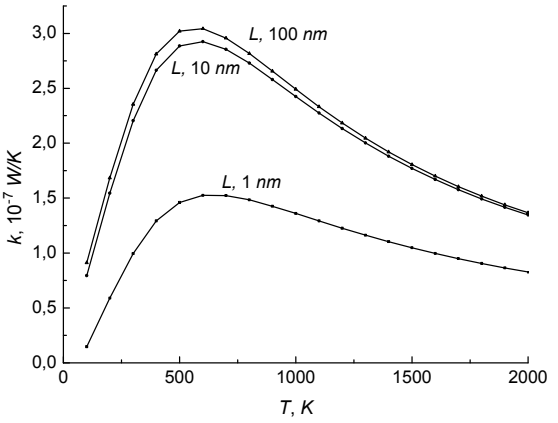

Fig.1. Dependencies of two-dimensional thermal conductivity on temperature for SWCNTs of zigzag or armchair type with a certain length.

The values obtained are consistent with those in paper [15]. At the same time the difference in thermal conductivities of SWNTs with chirality of *armchair* and *zigzag* types is extremely small, the dependence plot of two-dimensional thermal conductivity on temperature is therefore built for *zigzag* type SWCNTs. For example, at a temperature of 300 K within this model two-dimensional thermal conductivity coefficient for *armchair* type SWCNTs with length of 50 nm is equal to $2.29\cdot 10^{-7}$ *W/K*, and for *zigzag* type SWCNTs it equals to $2.35\cdot 10^{-7}$ *W/K*. Within this model thermal conductivity coefficient of *zigzag* type SWCNTs exceeds that of *armchair* type SWNTs, which is consistent with the results presented in papers [24-26].

If we take the distance between the adjacent layers in the graphite equal to 0.34 *nm* as the value of the conditional thickness of considered SWCNTs (e.g. such an approach is proposed in paper [15]), then at the temperature of 300 K equivalent volumetric thermal conductivity for *armchair* SWCNTs of 50 nm length equals to 674 *W/*(*m K*) and to 691 *W/*(*m K*) for *zigzag* SWCNTs of the same length. The calculated values fit into the interval of possible values of the thermal conductivity coefficient obtained for SWCNT in papers [6-11].

Calculated dependences of the maximum value of two-dimensional thermal conductivity coefficient of the considered SWCNTs on their length are presented in Fig. 2. Moreover saturation can be seen at this plot as well. Similar dependences of the thermal conductivity of SWCNTs on their length are reported in other papers [11, 12, 15, 23].

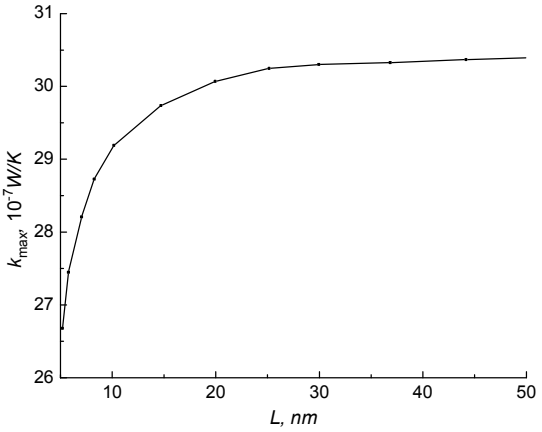

Fig.2. Dependence plot of the maximum value of two-dimensional thermal conductivity on the length of *zigzag* or *armchair* SWCNTs.

Conclusion

A model of thermal conductivity of defect-free SWNTs has been developed. The proposed model is based on the known Debye model for heat capacity and on the kinetic model of the phonon heat transfer. It takes into account the length of SWCNTs due to redetermine of Debye's model for the case of nanoscale structures and also of the contribution made by phonon-phonon scattering on the basis of Clemens's formula. This model was used to determine dependencies of two-dimensional thermal conductivity coefficient of defect-free SWNTs with chirality *zigzag* and *armchair* on their length and temperature.

It was found that the temperature dependences of the two-dimensional thermal conductivity of defect-free SWCNTs have an obvious maximum slightly shifted on the temperature axis to higher temperatures with an increase in the length of SWCNTs. The absolute value of a maximum at the curve for the two-dimensional thermal conductivity as a function of temperature is increased with the SWCNT length, gradually reaching saturation.

***Authors**: PhD Mikhail Tivanov, Belarusian State University, Physics Faculty, 4, Nezavisimosti av., 220030 Minsk, Belarus, e-mail: tivanov@bsu.by; M.Sc. Artsiom Praneuski, Belarusian State University, Physics Faculty, 4, Nezavisimosti av., 220030 Minsk, Belarus, e-mail: artem.pronevskiy@gmail.com, M.Sc. Karolina Czarnacka, Department of Technology Fundamentals, University of Life Sciences in Lublin, 28, Gleboka Str., 20-612 Lublin, Poland, M.Sc. Konrad Kierczynski, Lublin University of Technology, 38a, Nadbystrzycka Str., 20-618 Lublin, Poland*

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