Maximum thermal conductivity of aligned single wall carbon nanotubes

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Abstract

I estimate maximum thermal conductivity $\kappa$ of a perfectly aligned bundle of single wall carbon nanotubes. Each row of aligned nanotubes has a discrete structure. It consists of segments of nanotubes with length $L$. The spacing between the segments block the phonon path through the row. Only the scattering due to the finite length of the segments is taken into account. The result is that the 'effective” mean free path is of the order of $L/7$. For 1 micron tubes (10,10) we get maximum value of $\kappa \approx 300$ W/m K at room temperature. This result is in a reasonable agreement with the experiment by Hone et al. assuming that in their samples $L \approx 1\mu$m
INTRODUCTION

It is expected that a single wall carbon nanotube (SWCN) is a very promising object for creation of metamaterials with a high thermal conductivity (TC) \(^1, 2\). The first reason for this expectation is that the carbon-based materials, like diamond, have the largest known TC and the second reason is a molecular perfection \(^1\) of the (SWCN’s). However, to the best of my knowledge, the highest TC ever observed in SWCN’s bundles at room temperature is about 220 W/mK and it is ten times smaller than TC of the natural diamond \(^3\). This highest result has been reported by Hone \textit{et al.} \(^4\) for a bulk sample of magnetically aligned nanotubes. The aligned SWCN’s form a bundle where all tubes have a preferable orientation in some direction. Hone \textit{et al.} \(^4\) show that the TC of the aligned SWCN’s is strongly anisotropic with the largest value in the direction of the alignment. The enhancement of the TC due to the alignment has been observed also by Zhou \textit{et al.} \(^5\) and by Choi \textit{et al.} \(^6\), but the absolute values of the reported TC have been significantly smaller than in Ref. \(^4\). There are many theoretical works on TC of the SWCN’s. Some computational ones \(^7, 8, 9, 10\) are made by molecular dynamics simulations. The results of these simulations have different values and different \(T\)-dependences. They predict mostly very high values of the TC. We think that the main problem of all these works is a small size of an array that can be simulated. There are also some different analytical approaches to the problem \(^11, 12\) and beautiful reviews \(^13, 14, 15\).

The purpose of my work is to estimate the maximum TC value of aligned nanotubes taking into account that they consist of segments with a finite length. It is well known, that tubes in ropes are not infinitely long, but have brakes, because each method of synthesis is able to create separated tubes of only a certain length. It is believed that this length is of the order of a few \(\mu\)m (See Ref. \(^16\) and references therein) Then due to Van der Waals forces the tubes stick together and create bundles where the end of tube has no chances to make a strong chemical bond to the end of neighboring tube. There are many experiments that show, that tubes inside bundles have free ends. The idea of my work is to argue that this effect may be responsible for the relatively low TC as compared to the crystalline carbon materials.

I consider a bundle of nanotubes perfectly aligned in \(x\) direction. Each segment of a nanotube has a finite length with an average value \(L\). The nanotubes are organized in an ideal
triangular lattice with 6 nearest neighbors. The cross section in a plane perpendicular to the nanotubes is shown in Fig. 1 (a). The cuts in each line of the nanotubes have random positions. Thus, on the length of each segment there are in average six cuts of its nearest neighbors. A homogeneous interaction between infinite tubes does not cause the loss of the phonon momentum. However, a phonon flux has to overcome the openings between the segments at the termination points of each nanotube segment. I assume that this openings are so large that a jump of a flux occurs with an assistance of all six neighboring rows of the tubes as it shown in Fig. 1 (b). Slightly different mechanism of momentum scattering appears in a given nanotube (“0”) if one of the neighboring nanotubes has a termination point as shown in Fig. 1 (c).

Having in mind to get a maximum estimate of the TC, the propagation of heat flux $Q$ between the scattering points I assume to be ballistic. Quick phonon exchange at the scattering points leads to a thermalization of symmetrical parts of distribution functions of phonons with temperatures that are determined by values of effective thermal resistances between scattering points. It should be noted that my calculations cannot be applied directly to multiwall carbon nanotubes.

SCATTERING PROBLEMS

For simplicity an elastic scattering only is considered. This means that phonons generated in neighboring nanotubes not only have the same frequency, but belong to the same mode as the incident wave. It is not necessarily true but it should not lead to a big mistake due to small matrix element of the inelastic scattering. On the other hand, without this approximation the calculation of the TC would be a mess because one cannot consider each mode independently. I assume a linear dispersion law for the modes under study and argue that it is also not important if the interaction is large.

Consider a propagation of some mode along the nanotube “0” as shown in Fig. 1 (a). There are two basic scattering geometries for this mode. One of them appears at the terminational points of this very nanotube. It is shown in Fig. 1 (b). Only two neighboring nanotubes are shown, however all six are participating in the scattering. The interaction between the neighboring nanotubes is shown by springs in Fig. 1. The energy of this interaction is expected to be larger than Van der Waals interaction because $\text{div}\mathbf{P}$ at the
FIG. 1: (a) The cross-section of the bundle that show nanotube “0” and its nearest neighbors. (b) The first scattering problem. The cross-section by the plane of nanotubes 2-0-5. The wave incident from 0− reflects backward and transmits through the opening into 0+ with simultaneous excitation of the waves in all six neighboring tubes. (c) The second scattering problem. The wave incident from 0− and is scattered by the cut in tube 2. It reflects backward, transmits into 0+ and excites waves in tube 2+.

termination point might be non-zero, where $P$ is a polarization in the wave. The second scattering geometry (Fig. 1(c)) appears if one of the nearest neighbors of nanotube 0 has a terminational point. In both cases only an elastic interaction is considered.

In the first scattering problem the acoustic wave in the nanotube 0 is described by a following equation

$$L(U_\mp) = K\delta(x) \sum_{i=1}^{6}(U_i - U_\mp),$$

$$L(U) = \frac{1}{s^2} \frac{\partial^2 U}{\partial t^2} - \frac{\partial^2 U}{\partial x^2},$$

where $s$ is velocity of the mode, $K$ is a characteristic of the springs, $i = 1 \ldots 6$, $U_\mp$ is the displacement of a tube “0” at $x < -0$ and at $x > +0$ respectively, $U_i$ are displacement of the neighboring tubes. (See Fig. 1(b)).

The equations for the neighboring tubes, coupled with tube “0”, are

$$L(U_i) = K\delta(x)[(U_+ - U_i) + (U_- - U_i)],$$

One can see from the symmetry of equations that all $U_i$ are the same. In what follows I put $U_i \equiv U_1$. The solution can be found in a form

$$U_- = e^{ikx} + De^{-ikx} \ (x < 0), \quad U_+ = Ce^{ikx} \ (x > 0),$$

$$U_1^- = Ae^{-ikx} \ (x < 0), \quad U_1^+ = Ae^{ikx} \ (x > 0).$$
The time dependent factor \( \exp(-i\omega t) \) is omitted here and below. Since the forces acting on the tubes are localized near the openings and the openings are supposed to be less than the wavelength, the displacements have discontinuities at point \( x = 0 \). The boundary conditions can be obtained by integrating Eqs. (1-3) over \( x \). One gets that at \( x = 0 \)

\[
\frac{\partial U^-}{\partial x} - \frac{\partial U^+}{\partial x} = T(U_+ + U_- - 2U_1),
\]

\[
\pm \frac{\partial U_\mp}{\partial x} = 6K(U_1 - U_\mp).
\]

The solution has a form

\[
|D|^2 = \frac{k^4 + 73K^2k^2 + 36^2K^4}{(36K^2 + k^2)(49K^2 + k^2)},
\]

\[
|C|^2 = \frac{K^4}{(49K^2 + k^2)(K^2 + k^2/36)},
\]

\[
|A|^2 = \frac{36K^2}{(42^2K^2 + 36k^2)},
\]

Due to the energy conservation

\[
12A^2 + C^2 + D^2 = 1.
\]

In the case of weak interaction \( k/K \to \infty \) one gets

\[
|D|^2 = 1, |C|^2 = |A|^2 = 0,
\]

which means that the wave completely reflects from the terminational point. In the opposite case of a strong interaction \( k/K \to 0 \),

\[
|D|^2 = 36/49, |C|^2 = |A|^2 = 1/49.
\]

It will be important below that in the case of the strong interaction the structure of the operator \( L \) is irrelevant since I ignore the spatial derivatives in the boundary conditions Eq. (6). Therefore it does not matter whether or not this wave is acoustic and what spectrum it has. In fact, the numbers in Eq. (9) is determined only by the geometry of the problem.

For the geometry of Fig. (c), the equations of waves are

\[
L(U) = K\delta(x)(U_2^- + U_2^+ - 2U),
\]

\[
L(U_2^\pm) = K\delta(x)(U - U_2^\pm),
\]
where $U$ is displacement of tube 0, $U_2^+$ and $U_2^-$ are displacements of tube 2 at $x > 0$ and $x < 0$ respectively. The solutions have a form

$$U^- = e^{ikx} + D_1e^{-ikx}, \quad U^+ = C_1e^{ikx}, \quad (12)$$

$$U_2^- = A_1e^{-ikx}, \quad U_2^+ = A_1e^{ikx}. \quad (13)$$

The boundary conditions at $x = 0$ are

$$\frac{\partial U^-}{\partial x} - \frac{\partial U^+}{\partial x} = K(U_2^- + U_2^+ - 2U), \quad (14)$$

$$\pm \frac{\partial U_2^\mp}{\partial x} = K(U - U_2^\mp). \quad (15)$$

Then

$$|D_1|^2 = |A_1|^2 = \frac{K^2}{4K^2 + k^2}, \quad |C_1|^2 = \frac{K^2 + k^2}{4K^2 + k^2}. \quad (16)$$

Due to the energy conservation $2|A_1|^2 + |D_1|^2 + |C_1|^2 = 1$. For the weak interaction $K \ll k$ one gets

$$|C_1|^2 = 1, |A_1|^2 = |D_1|^2 = 0. \quad (17)$$

In this case the wave is transmitted without any scattering. In the opposite case $K \gg k$ one gets

$$|D_1|^2 = |A_1|^2 = |C_1|^2 = 1/4. \quad (18)$$

As in the previous case the result for the strong interaction is independent of the form of the operator $L$.

**THERMAL CONDUCTIVITY**

Let us now calculate the TC of the perfectly aligned nanotubes. In the approximation of elastic scattering the heat flux $Q$ along each row of the aligned nanotube conserves because the waves generated in neighboring nanotubes due to scattering have zero total momentum. This leads to a conservation of $Q$ along the row because in the theory of phonon thermal conductivity any relaxation of $Q$ is the result of momentum loss. It is important, however, that at the points of scattering of both types, considered above, the numbers of phonons in each mode changes. Therefore the symmetric parts of the distribution functions in these points can be considered as in equilibrium with different temperatures for each point. Finally, I assume that between the scattering points of both types the propagation is ballistic.
FIG. 2: Part of the row of nanotubes with two cuts. Dotted lines in the nanotubes correspond to the cuts of the neighboring nanotubes. The regions between them are considered as ballistic.

In average every section of a nanotube can be divided into seven ballistic regions such that each boundary of the region corresponds to a cut in one of the six neighboring rows of the nanotubes. The part of one row is shown in Fig. 2. Since the energy flux is the same along the row, but the scattering is different the temperature intervals between neighboring boundaries are also different. To calculate the TC, I find the total temperature difference through all the nanotube at a given flux $Q$.

Consider a region $i$ of one nanotube and assume that each end of a region perfectly matches a thermal bath. The temperature difference of the left and right boundaries of the region is $t_i$. Thermal flux produced in this region is $Q = G(T)t_i$, where the function $G(T)$ is called thermal conductance. It can be written in a form:

$$G(T) = \frac{k_B^2 T}{h} \sum_{\alpha} \int_{z_{\alpha 1}}^{z_{\alpha 2}} dx \frac{x^2 \exp(x)}{\left(\exp(x) - 1\right)^2},$$  \hspace{1cm} (19)

where $z = \hbar \omega / k_B T$, and the sum is over all monotonously increasing segments of spectrum $\omega_s(k)$, $z_{\alpha 1}$ and $z_{\alpha 2}$ being the lower and upper boundaries of such segments. Here $k_B$ and $h$ are the Boltzmann and the Plank constants respectively. To calculate the above integrals one should know the vibration spectra of nanotubes. They have been calculated previously within different frameworks such as an empirical force constant model, \textit{ab initio} studies, and tight-binding molecular dynamics. I use here the function $G(T)$ calculated by Yu. Gartstein. His results for phonon spectra does not differ much from the previous ones though he used some original method.

Suppose that the temperature decreases from left to right and the flux oriented in the same direction. The flux coming from the section 0 to section 1 is $Q|C|^2$, where $|C|^2$ is the transmission coefficient of the first scattering problem. Ballistic flux generated in the region 1 is $-Gt_1$, where $G$ is ballistic conductance given by Eq. (19) and $t_1$ is the negative temperature difference between boundaries 0-1 and 1-2 in Fig.2. To get the total flux in the region 1 one should take into account reflection at the boundary 1-2. Simple calculations show that multiple reflections inside the same region do not change the result substantially.
Finally, in the region 1

\[ Q = (Q|C|^2 - Gt_1)(1 - |D_1|^2). \]  

(20)

Thus I can find the change of the temperature \( t_1 \) in the first region

\[ -t_1 = \frac{Q}{G} \left( \frac{1}{1 - |D_1|^2} - |C|^2 \right). \]  

(21)

In the same way I find

\[ -t_2 = \frac{Q}{G} \left( \frac{1}{1 - |D_1|^2} - |C_1|^2 \right) = -t_3 = \ldots = -t_6, \]  

(22)

while

\[ -t_0 = \frac{Q}{G} \left( \frac{1}{1 - |D|^2} - |C_1|^2 \right). \]  

(23)

The total change of the temperature \( \Delta T \) through the segment can be calculated as

\[ \Delta T = \sum_{i=0}^{6} t_i = -QB/G(T), \]  

(24)

where

\[ B = \left( \frac{6}{1 - |D_1|^2} + \frac{1}{1 - |D|^2} - 6|C_1|^2 - |C|^2 \right). \]  

(25)

Since I suppose that the interaction is strong, coefficients in \( B \) are independent of the frequency. As a result I can express the TC \( \kappa \) through \( G(T) \).

Flux per m\(^2\) is \( Q_T = QN \), where \( N \) is the number of tubes in the bundle per m\(^2\). Assuming triangular lattice it is easy to get \( N = 4 \times 10^{17} \text{m}^{-2} \) for (10,10) nanotubes \[13, 17\]. Using equation \( \Delta T = LdT/dx \), definition of TC \( Q_T = -\kappa dT/dx \), and Eq. (24) one gets

\[ \kappa = NLG(T)/B. \]  

(26)

One can see from Eq. (8) and Eq. (17) that in the case of the weak interaction \( B \to \infty \) and \( \kappa \to 0 \). That is because the jump of the wave through the cut is a bottleneck of the problem. Thus, assuming that interaction is strong, I get a maximum estimate for the TC.

From Eqs. (9,18) one can find that \( 1/B = 0.0976 \), and Eq. (26) leads to the final result

\[ \kappa = 0.0976G(T)LN. \]  

(27)

where \( L \) is the length of one nanotube.

Fig. 3 shows the results of Eq. (27) at \( L = 1, 0.87, 0.7 \mu \) together with the results by Hone at al. [4]. One can see that the theory reflects well enough both the magnitude and the temperature behavior. In fact, the only parameter here is the average length of a nanotube.

The deviation at high temperatures is probably related to Umklapp processes.
FIG. 3: Thermal conductivity as calculated from Eq. (27) for the (10,10) tube with $L = 0.7$ (dashed line), 0.87 (solid) and 1.0 (dotted) micron. The experimental data of Ref. 4 are shown by diamonds.

CONCLUSIONS

Finally, I present the maximum estimate of the TC of perfectly aligned nanotubes taking into account the scattering of phonons by the terminational points of the nanotubes. This estimate gives a quantitatively correct description of the thermal conductivity of aligned nanotubes as obtained experimentally by Hone et al. [4] assuming that the length of segments is of the order of 1 $\mu$m. It follows from my results that the way to make thermal conductivity of the aligned nanotubes at room temperature larger than about 300 W/m K is to increase their lengths. Of course the TC will not increase indefinitely with $L$, as it follows from Eq. (27), because sooner or later the mean free path due to other scattering processes will be smaller than $L/7$. However, some additional gain may be achieved with increasing $L$.

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