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Thermal conductance for single wall carbon nanotubes

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Abstract. We report a theoretical analysis of the phonon thermal conductance, $\kappa(T)$, for single wall carbon nanotubes (SWCN). In a range of low temperatues up to 100 K, $\kappa(T)$ of perfect SWCN is found to increase with temperature, approximately, in a parabolic fashion. This is qualitatively consistent with recent experimental measurements where the tube-tube interactions are negligibly weak. When the carbon-carbon bond length is slightly varied, $\kappa(T)$ is found to be qualitatively unaltered which implies that the anharmonic effect does not change the qualitative behavior of $\kappa(T)$.

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1 Introduction

Since its original discovery, carbon nanotubes [1] have received a great deal of attention due to fundamental physical interest on nano-scale systems, as well as due to nanotubes′ potential for useful industrial applications [2]. A very important recent advance has been the fabrication of high-purity crystalline bundles of nearly mono-disperse single wall carbon nanotubes [3–5]. This allows better experimental control and produces accurate data. It also provides opportunities and points to new directions for theoretical analysis of SWNT. So far, the electronic and mechanical properties of carbon nanotubes have been extensively investigated while there also exist several new measurements of thermal properties of these systems [6–9]. The purpose of this work is to present our theoretical and numerical analysis of thermal conductance of SWNT.

Of particular interest to this work is the recent experimental measurements of thermal conductance of nanotubes $\kappa(T)$ [6]. This quantity describes the thermal current induced by a temperature gradient, and we will analyze a two-terminal measurement of it. Hence, maintaining temperatures at the left and right lead to be $T_{\rm L}, T_{\rm R}$ respectively, $\kappa(T)$ is defined as $\kappa(T) \equiv \dot{Q}/\nabla T$, where $\dot{Q}$ is the thermal current flowing through the nanotube. The experimentally measured thermal conductance of carbon nanotubes indicates that the most essential contribution comes from phonons [6,7]. The data of reference [6] on aligned multiwall nanotubes suggested that at low temperature up to ∼120 K, $\kappa(T)$ can be well fit by quadratic form in T, *i.e.* $\kappa(T) \sim T^2$. On the other hand, the measurements [8] of specific heat $C(T)$, which is proportional to $\kappa(T)$, also showed a power law dependence, however with a power larger than unity but slightly less than two [8]. Finally, measurements on crystalline ropes of SWNT indicates [7] a linear temperature dependence up to 30 K and an upward bend near 30 K on the $\kappa(T)$ *versus* T curve [7]. How to interpret these experimental observations presents a challenge to theory. Indeed, although there exist a vast literature on theoretical analysis of thermal transport of both electrons and phonons in the context of mesoscopic physics [11–19], direct investigation on carbon nanotubes is rare [8,10,20].

The precise temperature power law in thermal conductance of nanotubes is expected to depend on, among other things, the detailed phonon dispersion. In this work we will calculate the dispersion for several SWNT and investigate its consequence. We neglect electrons as their contribution to $\kappa(T)$ of nanotubes can only be observed at temperature less than 1 K [10]. Our analysis of SWNT is based on the Tersoff-Brenner's empirical potential [21,22] for carbon to calculate the phonon dispersion. We then apply a Landauer-Buttiker-type formalism to compute the lattice thermal conductance in various SWNTs, for which the thermal transmission coefficient is assumed to take a Breit-Wigner form. The predicted $\kappa(T)$ shows a quadratic form in temperature for both zigzag and armchair SWNT. Using one experimental data to fix an overall shift of $\kappa(T)$, our predicted $\kappa(T)$ is consistent with the experimental data of reference [6] as the tube-tube interactions are so weak that we could compare our calculations for single wall carbon tubes with the experimental results on multiwall tubes. As pointed out in reference [7], since the tube-tube interactions are also weak, the measured $\kappa(T)$ is linear below 30 K and shows an upward bend slightly near 30 K, *i.e.* the curve appears to be also parabolic-like

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from 8 K to 100 K. When the carbon-carbon bond length is slightly varied, our results indicate that $\kappa(T)$ does not change qualitatively, implying that the anharmonic effect does not alter its qualitative behavior.

The rest of this paper is organized as follows. In the next two sections we outline the analysis of phonon dispersion and $\kappa(T)$. Section 4 presents the numerical data while a brief summary is given in the last section.

2 Lattice thermal conductance

We start by writing down a multi-probe formula for thermal current transmission in the same spirit as the familiar Landauer-Buttiker formula [23] for electron transport. As discussed above we neglect contributions from electrons and deal with the lattice vibration as a phonon gas. The thermal current is therefore driven by a temperature gradient and carried by phonons from the probe to another. The thermal current can be written as

$$\dot{Q}^{\alpha} = \frac{1}{h}\int \mathrm{d}E\ E\ \sum_{\beta} f_{\beta}(E)\ A_{\alpha\beta}(E) \tag{1}$$

where α, β label the leads, h is the Planck constant, E is the phonon energy, and $f_{\beta}(E)=1/(\mathrm{e}^{\frac{E}{k_{\mathrm{B}}T_{\beta}}}-1)$, is the phonon distribution function with temperature T_{β} at lead β. The thermal transmission function $A_{\alpha\beta}(E)$ is defined as

$$A_{\alpha\beta}(E) = \delta_{\alpha\beta} - S^{\dagger}_{\alpha\beta}(E)S_{\alpha\beta}(E), \tag{2}$$

where $S_{\alpha\beta}$ is the scattering matrix for phonons. Equations (1, 2) are similar to the Landauer-Buttiker formula [23] for electron transport. Let the energy of the sth branch of phonon be $\hbar\omega_s$. The thermal current can be rewritten as

$$\dot{Q}^{\alpha} = \frac{1}{2\pi}\sum_{s}\int \mathrm{d}\omega_s\ \hbar\omega_s\ \sum_{\beta} f_{\beta}(\hbar\omega_s)\ A_{\alpha\beta}(\hbar\omega_s) \tag{3}$$

or

$$\dot{Q}^{\alpha}=\frac{1}{2\pi}\sum_{s}\int_0^{\infty} \mathrm{d}\mathbf{q}\cdot\mathbf{v}_s(\mathbf{q})\ \hbar\omega_s(\mathbf{q})\ \sum_{\beta} f_{\beta}(\mathbf{q})\ A_{\alpha\beta}(\mathbf{q}), \tag{4}$$

where $\mathbf{v}_s(\mathbf{q}) = \nabla_{\mathbf{q}}\omega_s(\mathbf{q})$ is the group velocity.

For the special case of two probe measurement in one dimension, one can easily confirm that equation (4) is reduced to the form which has been used to study the quantized thermal conductance of dielectric quantum wires [24]. We have

$$\dot{Q} = \sum_{s}\int_0^{\infty}\frac{\mathrm{d}k}{2\pi}\hbar\omega_s(k)v_s(k)(f_{\mathrm{R}}-f_{\mathrm{L}})\zeta_s(k), \tag{5}$$

where $\omega_s(k)$ and $v_s(k)=\frac{\partial\omega_s(k)}{\partial k}$ are the frequency and the velocity of normal mode s of the wire with wave vector k, respectively, $\zeta_s(k)$ is the phonon transmission probability through the wire, and f_{α} is the phonon distribution function at the right or left lead indicated by $\alpha\ (=\mathrm{R},\mathrm{L})$. We refer interested readers to references [25,26] for more details about the present formulation. For the SWNT the thermal conductance, $\kappa = \dot{Q}/\nabla T$, can be numerically computed through the following form

$$\kappa = \frac{\Delta L}{2\pi}\sum_{s}\int_{\omega_s(0)}^{\omega_{\max}}\mathrm{d}\omega\hbar\omega(f_{\mathrm{R}}(\omega)-f_{\mathrm{L}}(\omega))\zeta_s(\omega)/\Delta T. \tag{6}$$

where $\Delta T = T_{\mathrm{R}} - T_{\mathrm{L}}$ is the temperature difference between the two leads, ΔL is the length of the SWNT, and $\omega_{\max}$ is the maximum of phonon modes in SWCNs, which was investigated elsewhere [27]. To proceed, it is clear that the phonon frequencies of SWNT at Γ point and the transmission function $\zeta_s(\omega)$ are required. There are a number of methods which can be applied to obtain the phonon frequencies, and we will present our calculation of this quantity in the next section. On the other hand, it is rather complicated to accurately determine the phonon transmission function. For a perfect infinite harmonic lattice the thermal conductivity diverges because every mode transmits perfectly. The contacts play an important role as in case of electron transport. Even for perfect phonon transmission, the thermal conductance is finite due to the contact resistance. Defects, boundary scatterings, phonon-phonon interactions and other scattering mechanisms in the conductor inevitably introduce thermal resistances. The transmission function $\zeta_s(\omega)$ is contributed by lattice imperfection and conductor boundary, and the anharmonic effect due to interactions can be included in terms of the renormalized temperature-dependent dispersion relation. To obtain $\zeta_s(\omega)$ for SWNT one should in principle solve the scattering of a phonon wave by the atoms of the nanotube which is a nontrivial problem not solved so far. However if the length of a conductor is much larger than its cross-section size, $\zeta_s(\omega)$ can be approximately obtained by solving linear elastic equations assuming the conductor to be an uniform elastic medium [24]. In 1D, the continuum mechanics results indicate [24] that $\zeta_s(\omega)$ is dominated by sharp resonances reminiscent of a resonance transmission of phonon modes: $\zeta_s(\omega) = 1$ at resonant energies and sharply becomes much smaller for other energies. Guided by this observation and for simplicity of analysis, we shall investigate the consequence of such a resonance transmission of phonon modes for carbon nanotubes by parameterizing ζ_s into a Breit-Wigner form,

$$\zeta(E) = \frac{D^2}{(E-E_0)^2+D^2}, \tag{7}$$

where D and E_0 are the width of the resonance and position of a resonance. Both of these parameters are closely related to the effects of defects and boundary scatterings. Furthermore, instead of directly considering anharmonic effects, we will investigate its consequence by simply varying the carbon-carbon bond length to observe how much the thermal conductance can vary.

3 Lattice vibrations

To calculate the phonon spectra ω_s at the Γ point for armchair and zigzag carbon nanotubes, we shall make

	$R_{ij}^{(e)}$Å	$D_{ij}^{(e)}$eV	$\beta_{ij}/$Å	S_{ij}	δ_i	$R_{ij}^{(1)}$Å	$R_{ij}^{(2)}$Å	α_0	c_0	d_0
1st	1.315	6.325	1.5	1.29	0.80469	1.7	2.0	0.011304	19.0	2.5
2nd	1.39	6.0	2.1	1.22	0.5	1.7	2.0	2.0813×10^{-4}	330	3.5

use of the Tersoff-Brenner empirical potentia [21,22] for carbon. Although this empirical potential only gives an approximation to the vibration frequency of nanotubes, it does capture the basic and qualitative characteristics of their phonon spectra. Tersoff-Brenner's potential is also numerically efficient to allow investigations of large systems which is required for our study. The parameters for this potential have been determined before and there are two sets of them which have been widely used [22] for structure analysis of carbon:

see Table above

The meaning of the symbols refers to reference [22]. We have checked that for SWNT the second set of Brenner's parameters gave results closer to those obtained by using Tersoff parameter [21]. We shall use in our calculations the second set values shown in the table. In addition, experimental measurements have shown that phonon modes of SWNT have frequencies up to 1700 cm^{-1}. We have numerically confirmed that if the equilibrium distance parameter $R_{ij}^{(\mathrm{e})} = 1.33$ Å, which is a value in between the first and second Brenners's parameter sets (see table), the obtained vibration frequencies at Γ point is consistent with experimental data [28]. On the other hand, all the parameter sets give similar total binding energy. For instance, for the armchair (4,4) nanotube, the binding energy per atom is found to be -6.8920, -7.0881, -6.9993 and -7.0456 eV using Tersoff's potential, the first Brenner's potential, the second Brenner's potential and our modified second Brenner's potential, respectively. Figure 1 presents a comparison between these empirical potentials. In all subsequent numerical analysis we shall utilize the revised value of $R_{ij}^{(\mathrm{e})}$.

The lattice vibration frequencies of the SWCN at Γ point can be obtained by diagonalizing the dynamical matrix given by

$$D_{\alpha\beta}(k,lk') = \frac{1}{M}\sum_{l} \Phi_{\alpha\beta}\left(0k,lk'\right) \mathrm{e}^{\mathrm{i}\mathbf{q}\cdot(\mathbf{R}(0k)-\mathbf{R}(lk')}, \quad (8)$$

where $\mathbf{q}$ is the wave vector, the perturbation of $R_\alpha(lk)$ is taken to be 0.001 Å, and

$$\Phi_{\alpha\beta}\left(lk,l'k'\right) = \frac{\partial^2 E_b}{\partial R_\alpha\left(lk\right)\partial R_\beta\left(l'k'\right)}.$$

Once the phonon modes are obtained, we are able to calculate thermal conductance by equation (6). Here we would like to point out that although there have been a number of studies dedicated to the lattice vibrations of carbon nanotubes so far [2], it is not suitable for us to adopt directly the phonon data in literature. This is because in our situation we need frequency data for different sizes of carbon nanotubes as well as the data of frequencies when the carbon-carbon bond length is simply varied in order to retrieve the anharmonic effects. In principle, we can use *ab initio* molecular dynamics method to get the frequencies if the system is not too big. Since in the present case the system contains hundreds of atoms, it is not easy to obtain useful data on the basis of *ab initio* simulations, and for a practical purpose it is better to invoke an empirical potential to compute the phonon spectra of SWNCs with larger sizes.

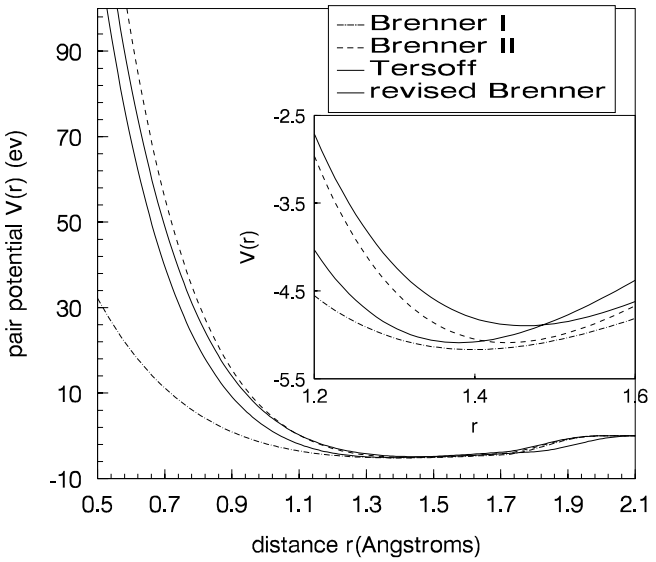

Fig. 1. The carbon-carbon two-body empirical potential as a function of the bond length for four sets of parameters. Our numerical analysis is based on the modified Brenner II potential.

4 Results

As discussed in the introduction, we are investigating long SWCNs such that the left end is at temperature T_{L} and the right end is at temperature T_{R}. Let us first consider the basic characteristic of $\kappa(T)$. At very low temperatures where only the massless modes (*i.e.* $\omega_s(0) = 0$) are relevant, κ/T is simply a constant independent of temperature. At slightly higher temperature, the high frequency modes set in because a SWNT is a quasi-one dimensional system in which each unit cell contains so many atoms that there are many modes with nonzero cutoff frequencies. Therefore κ/T will deviate from the constant behavior when temperature is increased.

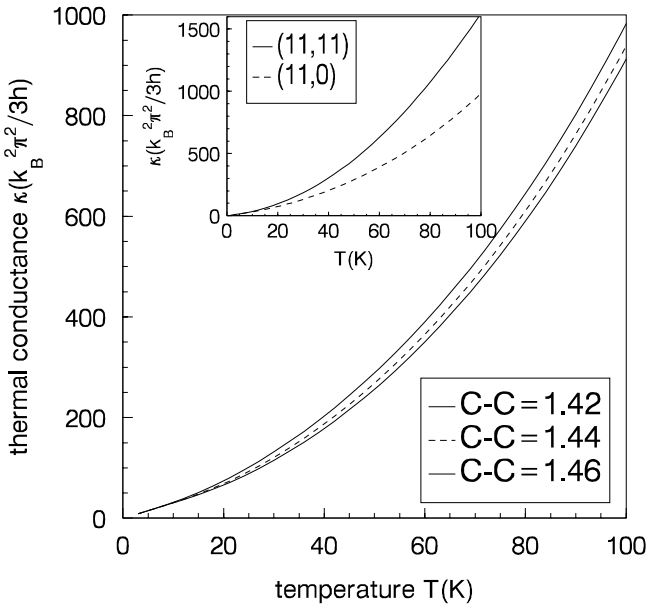

Fig. 2. Thermal conductance κ *versus* temperature for different C-C bond lengths for zigzag (11,0) SWCN assuming perfect phonon transmission. Inset: The temperature-dependence of the thermal conductance for armchair (11,11) and zigzag (11,0).

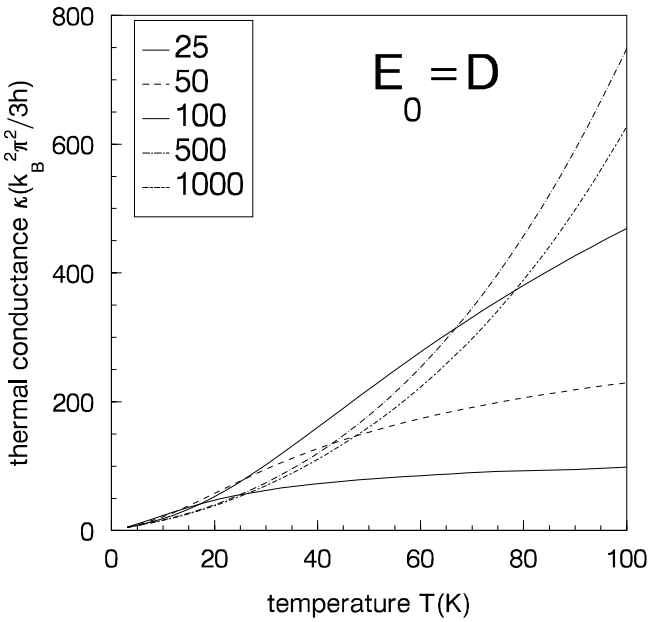

Fig. 3. Thermal conductance κ *versus* temperature for different resonance width (D) fixing $D = E_0$ in unit of cm^{-1}.

The inset of Figure 2 shows the temperature dependence of thermal conductance for the armchair (11,11) and the zigzag (11,0) carbon nanotubes when the transmission is perfect, *i.e.,* by setting $\varsigma_s = 1$ for all the phonon modes. For these cases our results indicate that $\kappa(T)$ increases, approximately, in a parabolic fashion as a function of temperature. We found that anharmonic effect has only a slight influence on the temperature dependence of $\kappa(T)$, and this is shown by calculating $\kappa(T)$ for different values of carbon-carbon bond length which generates different phonon spectra at the Γ point. Figure 2 shows $\kappa(T)$ for three different bond lengths 1.42 Å, 1.44 Å and 1.46 Å for a zigzag (11,0) system. This result clearly shows that the basic shape of $\kappa(T)$ is not changed qualitatively by varying the bond length. The magnitude of $\kappa(T)$ is however dependent on bond length as expected: the longer the bond length the lower the thermal conductance value.

In a real SWNT system the flow of thermal current is not perfect due to scattering of phonons by various lattice imperfections. It is thus inevitable that $\varsigma_s < 1$ in general and only at resonances [24] do we have $\varsigma_s = 1$ (see Eq. (7)). Nevertheless, as long as the transmission resonances are sharp for a large number of modes, which is the case shown by previous numerical calculations for various one-dimensional wires [24], we do not expect qualitative changes of behavior from that shown in Figure 2. On the other hand, it is interesting to examine the opposite situation, namely the transmission is dominated by a single resonance, *i.e.* the transmission coefficient ς_s is centered at a single mode E_0 with a resonance width D (see Eq. (7)). Therefore for a small D only very few terms in the summation of equation (6) have substantial contribution to $\kappa(T)$, while a large D should give a similar result as those of Figure 2. Figure 3 shows this behavior for a number of values of D by fixing $E_0 = D$ for simplicity. Indeed, a large D which essentially gives $\varsigma_s = 1$ for a wide range of modes, gives a parabolic temperature dependence for $\kappa(T)$. For small values of D , on the other hand, not only the value of κ is reduced because only a few modes contribute, but also the temperature dependence changes qualitatively. This exercise indicates the importance of the quality of phonon wave transmission.

Recently the thermal conductance of the carbon nanotubes has been experimentally measured [6,7]. In both experiments, the results show clearly that the tube-tube interactions are quite weak, implying that it would be reasonable at some extent that is also capable of comparing the measured results for multi-wall carbon nanotubes with the calculated ones for single wall tubes without generating qualitative deviations, as it indeed is. Our result is found to be qualitatively consistent with the experimental data [6] as shown in Figure 4 where the circles are the measured data and the dotted and dashed lines are our calculated results. The solid line is a least square fit to the experimental data in the range of 10 K to 120 K which gives $\kappa = 0.00089\, T^{1.97}(\mathrm{WK}^{-1}\mathrm{M}^{-1})$. Hence the experimental data indicate a parabolic dependence on temperature. Surprisingly, our calculated value of κ is even quantitatively reasonable considering the various approximation used in our analysis: since the Lorentz number $\frac{k_B^2\pi^2}{3h} \sim 10^{-12}(\mathrm{JK}^{-2}\mathrm{S}^{-1})$, the size of nanotube is on the order of $nm \sim 10^{-9}(\mathrm{M})$, and at $T = 100$ K our calculated $\kappa \sim 100$ in units of Lorenz number (*e.g.* Fig. 2), gives the same order of magnitudes as the measured data. To plot our calculated curves in Figure 4, we have used one experimental data point at $T = 120$ K to fix the scale

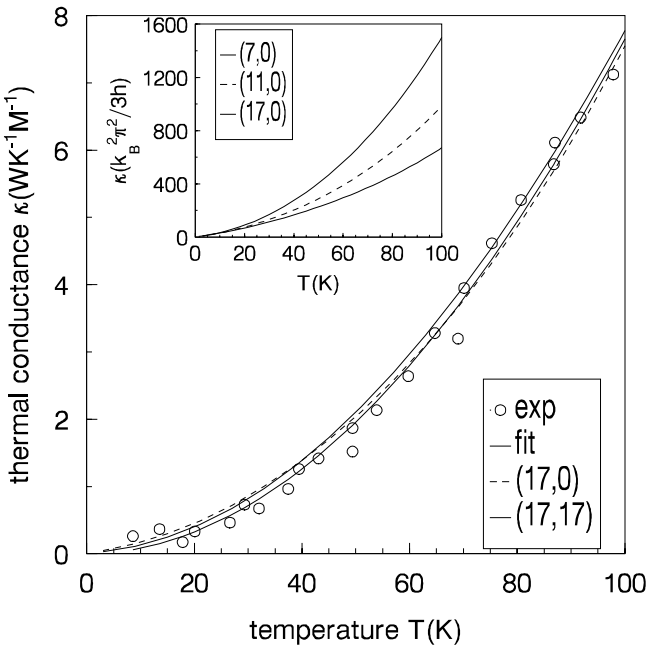

Fig. 4. Comparison of theoretical and experimental results.

of κ. It is clear that for both zigzag and armchair tubes, the predicted curves qualitatively agree with the measured data quite reasonably. In reference [7], the measured $\kappa(T)$ is linear below 30 K and an upward bend slightly near 30 K, *i.e.* the curve appears also to be parabolic-like from 8 K to 100 K. The linear dependence below 30 K in reference [7] may be the results of particular phonon scattering mechanisms or the imperfection phonon transmission. As a result, our results appear to suggest that the thermal transport in nanotubes might primarily be mediated by lattice vibrations, and the electron contribution is less important.

5 Summary

We have studied the properties of the thermal conductance of single-walled carbon nanotubes by means of a Landauer-Buttiker-like thermal conductance formalism using a modified Tersoff-Brenner potential. We found that the thermal conductance of the SWCN increases almost parabolically with increasing temperature at perfect transmission at low temperature. Our results are qualitatively consistent and quantitatively on the same order of magnitude as the measured data [6,7] because the tube-tube interactions in these carbon nanotubes are weak. This allows us to suggest that in the experimental device the phonon transmission is quite ideal, which is consistent with the fact that the high quality of the nanotubes [6,7] was ensured in the measurements. It also suggests that it is the phonon contribution which gave, to a large extent, the observed behavior of temperature dependence of the thermal transport in SWCNs. In addition, our results suggest that the anharmonic contribution to the thermal conductance of SWCN is only quantitative but not qualitative.

Although the simple analysis presented in this paper has given a qualitative understanding of the experimental data of references [6,7], a number of further improvements to theory are desirable. An extremely difficult subject is the calculation of phonon transmission function for carbon nanotubes. Our choice in this work is the phenomenological Breit-Wigner formula motivated by one-dimensional theory of linear elasticity. For realistic nanotube devices, especially those with lattice imperfections, it will be useful to accurately compute the transmission coefficient. Another improvement to the present work involves a more accurate analysis of the phonon frequency, perhaps from first principle methods. Finally, since experimental measurements are usually performed for a bundle of carbon nanotubes, if the tube-tube interaction is not weak it is also interesting to investigate the effect of inclusion of tube-tube interactions [29].

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