Low-temperature mean-free path of phonons in carbon nanotubes

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Abstract. The low-temperature mean-free path of phonon modes in single-wall carbon nanotubes is calculated within the relaxation time scheme using analytic expressions for the phonon dispersion relations and the specific heat capacity. We resolve the discrepancy presented by Yu et al. [Nanoletters, 5, 1842] between the length of the nanotube and their estimated mean-free path. This is explained to arise from the kinks and bends present in their sample. An analysis of our calculated radius shows that Yu et al. have studied a (9,9) single-wall nanotube.

1. Introduction
Since 1991 carbon nanotubes have been one of the most important and interesting topics in nanotechnology [1, 2]. These tubes show many exciting and unique properties not observed in bulk or other systems and, because of this, these tubes have shown several potential applications [3]. In particular, the thermal properties of carbon nanotubes (CNTs) have attracted considerable attention. These remain a topic of contention with several groups reporting both different experimental [4, 5, 6] and theoretical results [7, 8]. The mean-free path (MFP) of a phonon mode is an important thermal property normally obtained by estimate from experimental thermal conductivity results. In the low temperature regime the MFP of phonon modes in CNTs should be dominated by two processes: boundary and mass-defect (or point-defect) scattering. Three-phonon scattering events are significant only at temperatures greater than 300 K [9].

In this report we calculate the MFP of phonon modes at low temperatures (i.e. less than room temperature) when only boundary and mass-defect scattering are the main processes. We present a simple theory of boundary scattering taking into account kinks in the tube. We also derive the relaxation rate due to mass-defect scattering and show a reduced frequency dependence when compared to bulk. Using these relations we explain the recent discrepancy in the estimates of the MFP made by Yu et al. [6] and also present an estimate of the radius of the CNT used in their experiments. We also discuss the variation of the MFP with CNT radius at low temperatures.

2. Methodology
At a macroscopic level, the MFP path of phonon modes in a one-dimensional system is normally defined from

\[ \kappa(T) = \tilde{C}_v(T)\tilde{v}\tilde{\lambda}(T), \] (1)
where $\kappa$ is the thermal conductivity at temperature $T$, $\bar{C}_v$ is the mean specific heat capacity at temperature $T$, $\bar{v}$ is mean group velocity of the phonon modes and $\bar{\lambda}$ is the MFP. This expression is commonly used when performing thermal conductivity (or conductance) measurements for an experimental estimate of the MFP.

Within a microscopic approach, one can apply the single-mode relaxation time scheme [10]. Hence, the thermal conductivity, $\kappa$, for a one-dimensional system is expressed as

$$\kappa(T) = \sum_{k,s} C_v(T, k, s) v(k, s) \tau(T, k, s),$$  \hspace{1cm} (2)

where $k$ is the one-dimensional phonon wave-vector and $s$ is the polarisation. Hence, by using Eqs. (1) and (2) one can calculate the experimentally determined or mode averaged MFP. This contrasts with the average relaxation time approach where $\bar{\lambda} = \bar{v} \bar{\tau}(T)$ where $\bar{\tau}(T)$ is the average relaxation time at temperature $T$. In order to perform the calculations of $\bar{\lambda}$ and $k$, one requires two ingredients: the phonon dispersion relations and the relaxation rate of the phonon modes.

2.1. Phonon dispersion relations and specific heat capacity

Previously, Mahan [12] had developed a series of analytic expressions for the phonon dispersion relations in CNTs based upon an elastic continuum model. These relations were refined and developed further [13], and used to explain the specific heat capacity. Here, we utilise the dispersion relations expressions for the six lowest phonon branches and the density of states as described in Refs. [13, 14]. These six phonon branches are the longitudinal ($\text{LA}$), the doubly degenerate transverse ($\text{TA}$), the twist ($\text{W}$), the lowest optical ($\sigma$), and breathing branches ($\text{B}$). From the dispersion relations, the population averaged group velocity [15] of the phonon modes is determined from

$$\bar{v}(T) = \frac{\sum_{k,s} v(k, s) \bar{n}(k, s)}{\sum_{k,s} \bar{n}(k, s)},$$  \hspace{1cm} (3)

where $v(k, s)$ is the group velocity of the phonon mode $(k, s)$ and $\bar{n}(k, s)$ is the Bose-Einstein distribution function.

2.2. Relaxation rate

In the low temperature regime, the total relaxation time of phonon mode $\omega(k, s)$ (where $\omega$ is the frequency) is calculated from Mathiessen’s rule and by considering mass-defect and boundary scattering. The common definition of the relaxation time due to boundary scattering is

$$\tau(\text{BS}, k, s) = \frac{L_0}{v(k, s)},$$  \hspace{1cm} (4)

where $L_0$ is the length of the tube. Recent evidence [16] has shown that CNTs act as waveguides. This means that the boundary mean-free path is unaffected by the tube’s curvature except in extreme cases. However, the effective length $L_0$ between boundary scattering events is reduced if the CNT has any sharp kinks [17]. In figure 2 of Ref. [6], a kink in the CNT can be observed at approximately 0.4-0.5 $\mu$m. This value can also be calculated from the gradient of the thermal conductivity results from Yu et al. Hence in this work $L_0$ is set to 0.46 $\mu$m.

The theory of phonon scattering by isotropic mass defects in three-dimensional solids has been discussed by Klemens [18]. We adopt that theory for CNTs in the form of a one-dimensional system. Accordingly, the relaxation time due to mass-defect scattering can be expressed as

$$\tau_m^{-1}(\omega, \text{md}) = \frac{\pi G_{\text{md}}}{2} \left| \frac{T}{L_0} \right| \sum_{s'} g_{s'}(\omega(s)) \omega^2(s).$$  \hspace{1cm} (5)
Figure 1. The population-averaged phonon velocity $\bar{v}$ as a function of temperature for a (10,10) carbon nanotube.

Figure 2. The mean-free path $\bar{\lambda}$ of phonon modes in a (10,10) carbon nanotube as a function of temperature.

where $\mathbf{T}$ is the translation vector of the tube, $g_{s'}(\omega(s))$ is the density of states of phonon branch $s'$ at the frequency $\omega(k, s)$, $G_{md} = \sum_i f_i \left( \frac{\Delta M_i}{M} \right)$. $M$ is the average mass, $f_i$ is the fraction of atoms with mass $M_i$ and and $\Delta M_i = M_i - M$. In nature, carbon-13 provides a natural isotope in CNTs and occurs in a 1:1000 ratio, resulting in $G_{md} = 6.5 \times 10^{-6}$.

3. Results

The average group velocity of a phonon mode as a function of temperature is shown in figure 1. As expected, at low temperatures the result is in approximate agreement with the Debye expression over four acoustic branches of $4\bar{v}^{-3} = \sum_s v(s)^{-3}$, yielding $\bar{v} = 11.82 \text{km/s}$. However, as the temperature increases and the optical modes become increasingly populated, the average group velocity of the phonon modes decreases.

The MFP of a phonon mode as a function of temperature is shown in figure 2. The most striking result is the decrease in the MFP as the temperature decreases below 300 K. This is contrary to the traditionally expected result (i.e. a constant) for the MFP of a phonon due to boundary scattering. The reason for the deviation is threefold: (i) the change in the mean velocity of the phonon mode, (ii) the deviation from linear temperature dependence in the specific heat capacity at low temperatures [13], and (iii) the difference between the expressions in Eqs. (1) and (2).

The latter of these reasons (i.e. (iii)) is easily explained as being a result of the simplistic macroscopic theory of Eq. (1) against the microscopic expression in Eq. (2), which is more rigorous and does not average over values within the summation. In particular, as different phonon modes have different population weightings at various temperatures, the simple definition breaks down. Hence, the effect of taking an average value for each of the terms ($C_v$ and $\bar{v}$) in Eq. (1) is to underestimate the MFP of the phonon mode. The variation in velocity dominates the change in behaviour of the MFP distance at low temperatures. The average velocity (as seen in figure 1) increases with a decrease in temperature at low temperatures. Because of this, the MFP starts to increase with a decrease in temperature for temperatures less than 70 K. The point of inflexion is a result of this effect and the low temperature deviation from linear behaviour in the specific heat capacity.

Traditionally, when performing MFP calculations, the optical modes are ignored due to their low group velocity, and their short lifetimes (when compared to the acoustic modes). In CNTs low-lying optical modes are created due to zone-folding. Two of these low-lying...
branches are particularly significant, the $B$ and $\sigma$ branches. These low-lying phonon modes have group velocities comparable to the acoustic modes, and their frequencies are also comparable. Figure 3 shows the contributions from different phonon modes to the total MFP as a function of temperature. As expected, the MFP is dominated by the acoustic modes at low temperatures (the $LA$, $TA$ and $W$ branches), but at high temperatures the contribution from the $B$ and the $\sigma$ mode (and their associative branches) are highly significant. If one ignores the contribution of these two branches to the total MFP then one would underestimate the MFP of the phonon modes and the resultant estimate would be half of the correct value.

Our calculations show that the difference that mass-defect scattering makes to the total MFP is less than 5%. At 250 K the MFP with only boundary scattering is 719 nm, whereas if both boundary and mass-defect scattering are included, the total MFP is 703 nm. If one artificially increases the magnitude of $G_{nd}$ by a factor of ten, which represents a sample with an abnormally large amount of impurities, the MFP is reduced to approximately 85% of its original value. However, such a system is unrealistic. The decrease in the strength of mass-defect scattering is caused by a reduction in the power law for the frequency dependence of the density of states; i.e. changing from $\omega^2$ for three-dimensions to $\omega^0$ for one-dimension. This reduces the significance of the mass defect scattering rate when compared to the boundary scattering as the latter does not change with dimensionality. This shows that the thermal conductivity and MFP properties of CNTs (in general) are relatively unaffected by mass defects within the tube. By considering the ineffectiveness of mass defect scattering and Eq. (4) we can now show that the initial discrepancy between the reduced MFP observed by Yu et al. and the length of their tube is a direct result of a kink within their sample.
Figure 4 shows the mode averaged MFP as a function of chiral number \((n)\) \cite{19} for a \((n,n)\) CNT. As can be seen, the thinner the tube, the shorter this MFP will be. This is because the higher velocity phonon modes have a larger contribution to the total population in thinner tubes and this affects Eqs. (1) and (2) differently. Yu et al. \cite{6} have measured the thermal conductance at 300 K of a CNT of unknown radius and used this to estimate three different MFPs of the phonon mode which are dependent on the tube’s radius. Yu et al. estimated the MFP, assuming the radius of the CNT to be 1 nm, 2 nm, and 3 nm, to be 750 nm, 375 nm and 350 nm, respectively. Using figure 4, we can now show that the diameter of the CNT used by Yu et al. is 1.2 nm. This corresponds to the (9,9) CNT, and fits well with their SEM image.

4. Conclusion
In summary, we have presented a theory and results for the mean-free path of phonon modes in single-wall carbon nanotubes at low temperatures. We have included the effects of boundary and mass-defect scattering and have shown that in CNTs the effect of mass-defect scattering is almost insignificant, when compared to boundary scattering, due to the 1D nature and the small isotopic concentration. We have shown that kinks in a CNT reduce the commonly perceived length for boundary scattering is not necessarily the same as the total length of the tube, and have shown this is in agreement with the measurements of Yu et al. We have shown that the discrepancy between their CNT length and the MFP is a result of a kink found within their sample. We have shown that the measured MFP is both a function of temperature and of tube radius, and used this feature to calculate the radius of the CNT used by Yu et al. for their experimental measurements. We believe these results provide the much needed clarity for future measurements of MFP in future as well as suggest a mechanism (kink formation) by which one could control the thermal conductivity of CNTs.

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