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LETTER TO THE EDITOR

Three-phonon Umklapp process in zigzag single-walled carbon nanotubes

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Abstract
The rate of relaxation of zigzag single-walled carbon nanotubes is calculated by consideration of three-phonon Umklapp process. The results show that the relaxation rate increases exponentially with phonon frequency at low frequency. The linear dependence of the relaxation rate on temperature is obtained. It is shown that the value of the phonon mean free path reaches a few micrometres, which is consistent with the estimated experimental result.

Continuous improvement of the fabrication of carbon nanotubes (CNTs) has attracted extensive research interest both experimentally and theoretically since their discovery [1, 2]. The unique electronic properties originating from their unique structures have stimulated calculations of their electronic structures involving developing some analytical [3] and numerical schemes [4–6]. This research suggests that CNTs have bright prospects for applications: they can be used to fabricate field emission devices, tips for scanning probe microscopy instruments, and constituents of nanoelectronic devices [7–9]. Like the electronic properties, the thermal properties of CNTs, such as thermal conductivity, have been proposed as attractive for thermal transport management in ultralarge-scale-integration chips due to the high heat flow along the axis of CNTs [10–13]. Berber *et al* [14] predicted CNTs to have an unusually high thermal conductivity κ associated with a large phonon mean free path l by virtue of molecular dynamics simulations. Using a self-heating 3ω method [15], κ for aligned multi-walled carbon nanotubes (MWCNs) is found to follow an almost quadratic T-dependence up to 120 K, corresponding to a nearly linear decrease of l with T. Taking advantage of the fast progress in fabrication technology of CNTs, Kim *et al* [16] has measured the thermal conductivity of an isolated MWCN with diameter $d = 14$ nm using a microfabricated suspended device. The measurement shows a nearly T^2-dependence of κ on temperature for $T < 100$ K, while there

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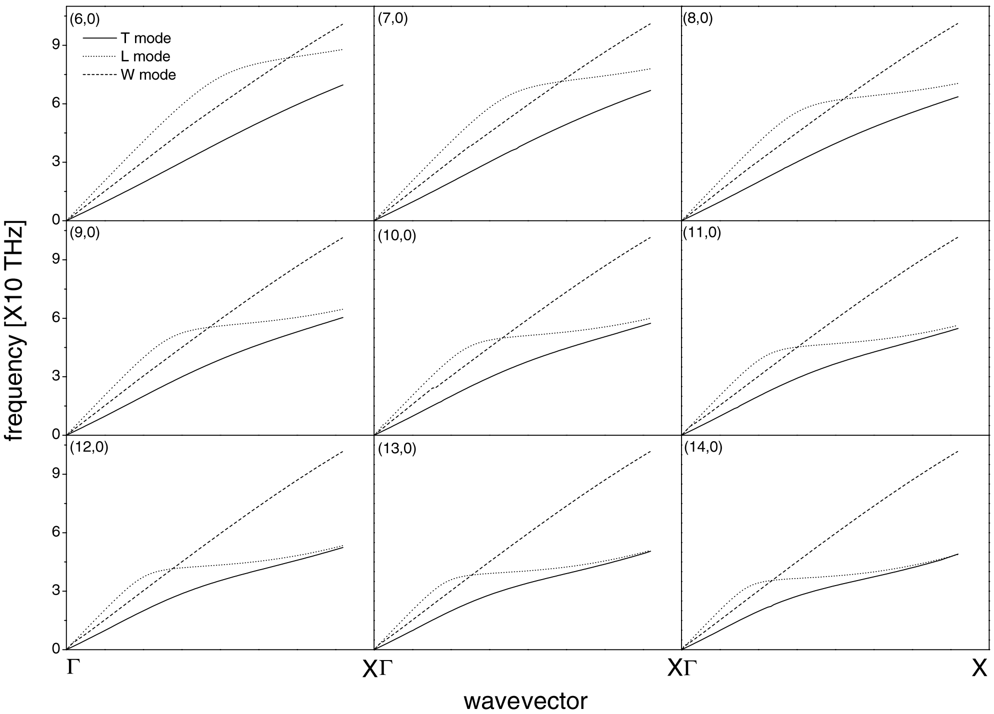

Figure 1. The acoustic phonon dispersion relation for $(n, 0)$ SWCNs, $n = 6$–14.

is a deviation from quadratic temperature dependence for $T > 100$ K due to the onset of the Umklapp process. Although this research has provided considerable insight into the thermal conductivity, it is necessary theoretically to find the intrinsic phonon scattering mechanisms in CNTs. In this letter, we present a rigorous calculation of the three-phonon Umklapp relaxation rate $1/\tau_U$ of zigzag single-walled carbon nanotubes (SWCNs) based on first-order perturbation theory, which has been used to study Umklapp process in Si nanowires [17]. We limit our consideration to the acoustic three-phonon Umklapp process due to it making the main contribution to the thermal resistance in CNTs.

In order to take into account the specific features of phonon transport in isolated zigzag SWCNs, we investigated the phonon dispersion relation within the force-constant model [18]. In this model, only four (3×3) force-constant matrices are required to generate the dynamical matrix $D(\boldsymbol{k})$ of SWCNs. The force-constant matrix of any two atoms on a cylinder can be given by rotating the bond from the two-dimensional plane of graphite to the three-dimensional cylindrical coordinate system of a SWCN. To obtain the eigenvalues for $D(\boldsymbol{k})$ and the nontrivial eigenvectors $\boldsymbol{u}$, we solve the secular equation $\det |D(\boldsymbol{k})| = 0$ for a given $\boldsymbol{k}$-vector.

The phonon dispersion relations of zigzag SWCNs are shown in figure 1, where only acoustic phonon modes are adopted. One can see that there are four acoustic modes: the transverse mode (T, doubly degenerate), the longitudinal mode (L), and the twist mode (W); of these, the T mode would lie below the L and W modes throughout the whole Brillouin zones. For the $(6, 0)$ SWCN, the frequency of the T mode is roughly proportional to the wavevector. With increasing diameter, the T mode at high frequency deviates from showing linear dependence because of the weakening of the one-dimensional quantization confinement. As for the L mode, a similar slope appears at low frequency. At high frequency, the slope

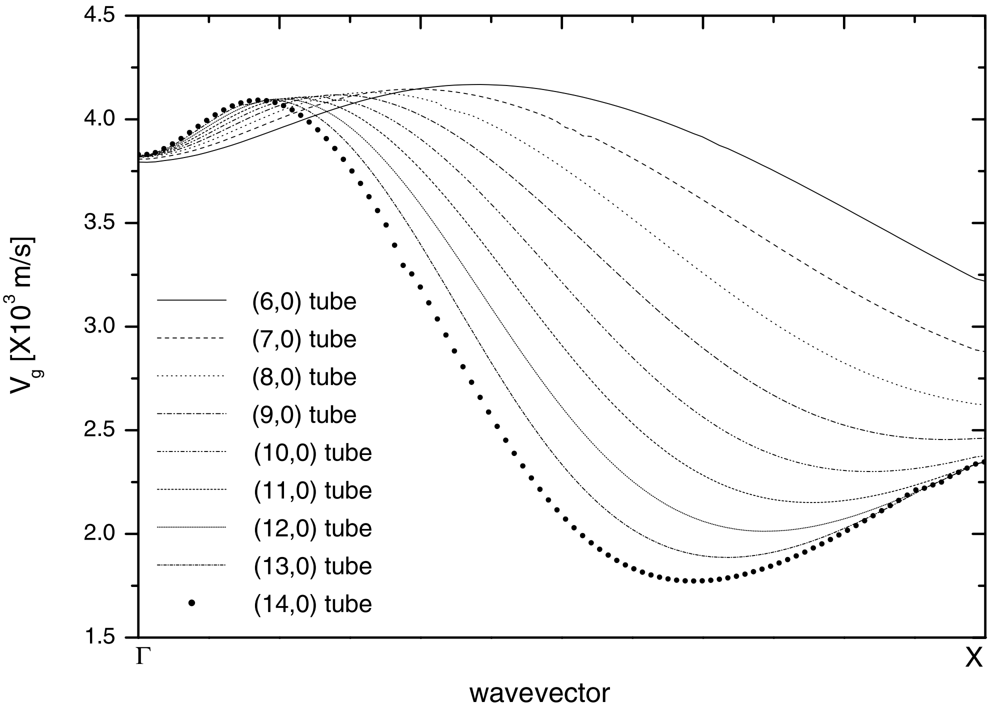

Figure 2. The group velocity for $(n, 0)$ SWCNs, $n = 6$–14.

of the curve for the L mode is bent to a position close to that for the T mode. In contrast to the case for the T and L modes, one linear relation for the W mode for all SWCNs holds for the whole frequency range. By virtue of the acoustic phonon modes, it can be seen that there is an opening of an energy gap ω_g between phonon modes. This may be attributed to the quantization of the radial phonon wavevector of the SWCNs. The energy gap ω_g^{TL} between the T and L modes would decrease with increasing diameter, while the energy gap ω_g^{WL} between the W and L modes would increase. The energy gap ω_g would have an important influence on the occurrence of the Umklapp process.

Figure 2 shows the phonon group velocity of the T mode for $(n, 0)$ $(n = 6$–14) SWCNs. The solid curve represents the phonon group velocity of the (6, 0) SWCN. It increases slowly from the Γ point, goes through a maximum, and then rapidly decreases to the X point. An analogous situation is found for $(n, 0)$ $(n = 6$–9) SWCNs. With increasing diameter, the maximum becomes more obvious and a minimum appears near the X point (see the curves for the (10, 0) to (14, 0) SWCNs in figure 2). In addition, the maximum moves leftward while the minimum moves rightward with increasing diameter. The latter might be attributed to the deviation of the T mode at high frequency.

From the first-order perturbation theory, the single-mode relaxation rate of the Umklapp process for a phonon mode can be written as

$$\frac{1}{\tau_U} = \sum_{q'} 2|C_3|^2 \frac{\hbar}{M^3 \omega\omega'\omega''} \pi\delta(\omega + \omega' - \omega'')(N_0(\omega') - N_0(\omega'')), \tag{1}$$

where $|C_3|^2 = (4\gamma^2/3n_a)(M^2/v_g^2)\omega^2\omega'^2\omega''^2$, τ_U is the relaxation time of the Umklapp process, γ is the Grüneisen parameter, n_a is the number of atoms per unit volume, M is the atom mass. $N_0(\omega)$, the equilibrium occupancy of phonon mode q, is given by the usual Planck distribution

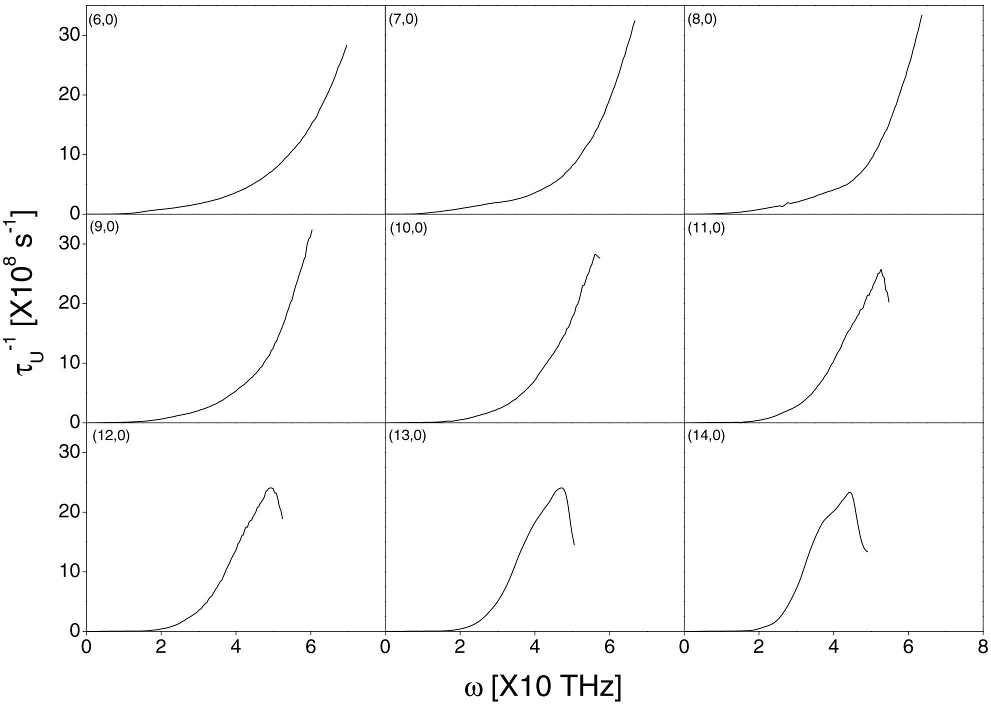

Figure 3. The relaxation rate for $(n, 0)$ SWCNs at 300 K, $n = 6$–14.

$N_0(\omega) = 1/[\exp(\hbar\omega/k_B T) - 1]$. The evaluation of the relaxation rate of the mode q requires the summation of all allowed channels.

In the case of the three-phonon Umklapp process, phonon collisions should obey the laws of the energy conservation and momentum quasiconservation:

$$\omega + \omega' = \omega'', \tag{2}$$

$$q + q' = q'' + G, \tag{3}$$

where ω, ω', and ω'' represent the frequencies of phonons with wavevectors q, q', q''; G is the reciprocal-lattice vector. According to the selection rules, it is required that (I) all three interacting modes cannot belong to the same polarization branch, and (II) the resultant mode should be above the two initial (interacting) modes [19]. Thus, the possible three-phonon Umklapp channels are as follows:

$$\begin{array}{lll} \mathrm{T} + \mathrm{T} \Leftrightarrow \mathrm{L}, & \mathrm{T} + \mathrm{T} \Leftrightarrow \mathrm{W}, & \mathrm{T} + \mathrm{L} \Leftrightarrow \mathrm{L}, \\ \mathrm{T} + \mathrm{L} \Leftrightarrow \mathrm{W}, & \mathrm{T} + \mathrm{W} \Leftrightarrow \mathrm{L}, & \mathrm{T} + \mathrm{W} \Leftrightarrow \mathrm{W}. \end{array} \tag{4}$$

In figure 3, we present the Umklapp relaxation rate as a function of phonon frequency for zigzag $(n, 0)$ ($n = 6$–14) SWCNs at 300 K. The rate of relaxation of the (6, 0) SWCN increases exponentially with a cut-off frequency at low frequency. A similar increasing rule for $1/\tau_U$ can be seen for the zigzag (7, 0) to (9, 0) SWCNs. Comparing with these small-diameter tubes, the rates of relaxation of the $(n, 0)$ SWCNs ($n = 10$–14) have maxima at high frequency. This may be seen from equation (1), i.e., $1/\tau_U \propto 1/v_g$. In addition, the semiempirical expression for the relaxation rate,

$$\frac{1}{\tau_U} = A\omega^{\alpha} T^{\beta} \mathrm{e}^{-(B/T)}, \tag{5}$$

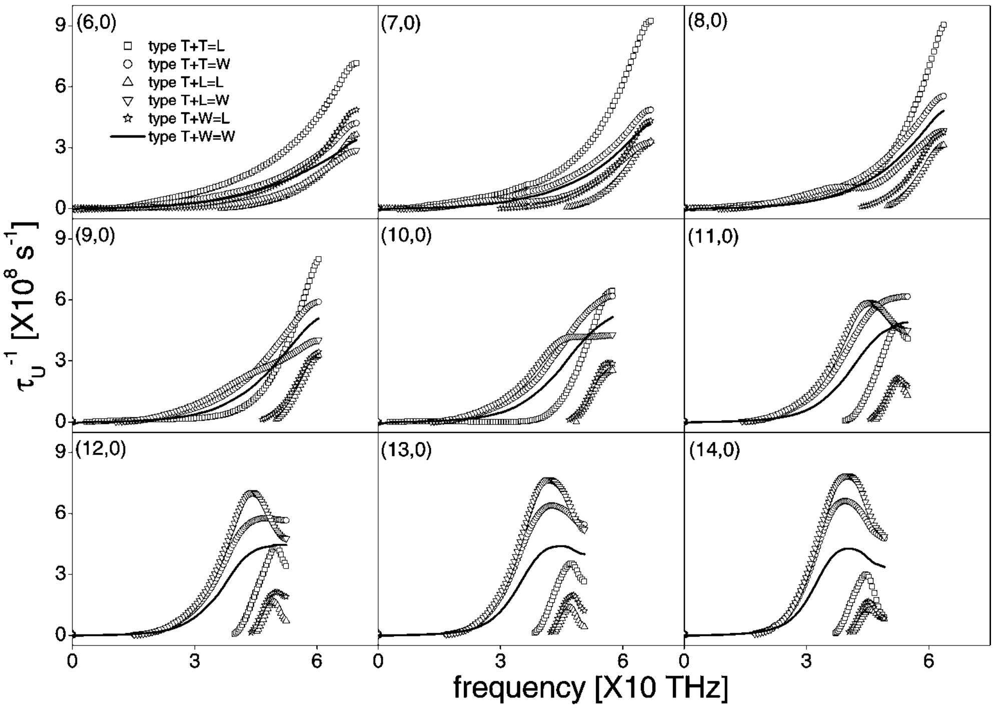

Figure 4. The relaxation rate of each channel for $(n, 0)$ SWCNs at 300 K, $n = 6$–14.

has been widely used to analyse the experimental results [20, 21], where A, B, α, and β are adjustable parameters. By analogy to the relaxation rate described in equation (5), our results provide a precise and direct estimate of the relative strengths of the Umklapp phonon scattering mechanism and the thermal resistance. It is shown that the maximal relaxation rate is about 30×10^8 s^{-1} for all these zigzag SWCNs, which suggests that the phonon mean free path $l = v\tau$ would be above 1 μm. The result is nearly consistent with the estimate based on a measurement for SWCN ropes [11]. So large a phonon mean free path of zigzag SWCNs would lead to a higher thermal conductivity, comparing with that of nanowires [17].

To make clear the contribution of each possible channel to the relaxation rate, we calculate the relaxation rate of each channel as shown in figure 4. One can see that there exists a cut-off frequency for each channel at low frequency. The cut-off frequency would shift to high frequency with the increase in tube diameter. Because the ratio of the equilibrium occupancies of two nearest phonon modes $N_{n+1}/N_n = \exp[-\hbar\omega_g/k_B T]$ decreases with increasing gap ω_g^{LW}, the result is that the low-frequency thermal mode becomes more and more difficult to link with the modes near the zone boundary as the tube's diameter increases. In addition, the curves in figure 4 can be divided to two groups based on the possible three-phonon Umklapp process, i.e., T + A = L and T + A = W (A is an interacting mode including T, L, W modes). For $(n, 0)$ $(n = 6$–10) SWCNs with small diameter, the values of the relaxation rate for the two groups have the same order of magnitude. However, with increasing diameter, the relaxation rate of the T + A = W group becomes larger while the relaxation rate of the T + A = L group becomes smaller. Hence, the T + A = W group would dominate the three-phonon Umklapp process in large-diameter SWCNs.

In figure 5(a), we present the relaxation rates of (6, 0) SWCNs at 100, 200, 300, 400, 500, 600 K. The relaxation rates at different temperatures are zero at low frequency, while they

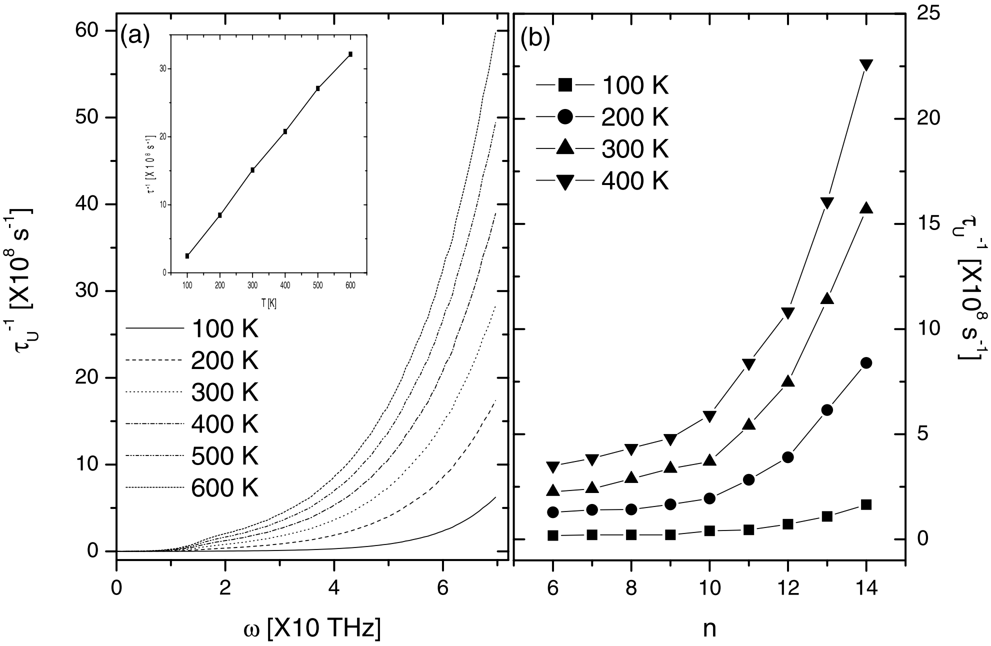

Figure 5. (a) Relaxation rates of (6, 0) SWCNs at different temperatures. The inset shows that the relaxation rate for 60 THz is proportional to the temperature. (b) Relaxation rates of $(n, 0)$ SWCNs at 35 THz at different temperatures.

increase rapidly with increasing temperature and phonon frequency. Numerical fitting shows that the relaxation rate at each temperature satisfies $1/\tau_U = Ae^{\omega/\omega_0}$, with $\omega_0 = 9.8$, 13.3, 14.4, 14.8, 15.1, 15.2 THz for $T = 100$, 200, 300, 400, 500, 600 K respectively. It is obvious that the value of ω_0 is constant for high temperature. This condition is believed to hold in our case, judging from the fact that all phonons are excited to participate in Umklapp processes at high temperature. Moreover, the relaxation rate is proportional to the temperature with a positive slope, as shown in the inset in figure 5(a). The linear dependence of the relaxation rate on the temperature can be understood from the equilibrium occupancies $N_0 = 1/[\exp(\hbar\omega/k_B T) - 1]$. In the high-temperature limit, $N_0 \propto T$, so $1/\tau_U \propto T$ according to equation (1). Since the specific heat does not change with temperature in the high-temperature region, we can predict the thermal conductivity of SWCNs to be proportional to temperature. This prediction is consistent with the result obtained by molecular dynamical simulation [14]. Figure 5(b) shows the dependence of the relaxation rate on the temperature for zigzag $(n, 0)$ SWCNs ($n = 6$–14) at 35 THz for 100, 200, 300, 400 K. At 100 K, the relaxation rate increases very slowly with increase in tube diameter. With increasing temperature, the relaxation rate rises at different rates at 200, 300, 400 K. Two features may be responsible for such phenomena: firstly, the number of phonons excited at low temperature is smaller than the number excited at high temperature, which leads to there being fewer phonon scattering events; secondly, the phonon scattering process within small-diameter SWCNs is restrained due to strong one-dimensional confinement, while that in SWCNs with large diameter is promoted and ultimately becomes similar to that of two-dimensional graphite. Recently, a measurement [16] on MWCNs showed that as a tube's diameter increases, its thermal conductivity decreases and becomes similar to the bulk measurement for a matlike sample [11]. Moreover, the value of the relaxation rate at 100 K is very small, which suggests that fewer phonons are excited to participate in the three-phonon Umklapp process. However, with increasing temperature, more and more phonons are excited, resulting in the rapid increase of the relaxation rate. This may lead to a drastic change of the thermal conductivity, which is in agreement with the experimental results [15, 16].

In conclusion, we have presented a study of the three-phonon Umklapp relaxation rate of zigzag SWCNs based on the first-order perturbation theory. The relaxation rate increases exponentially as a function of ω at low frequency. However, for large-diameter zigzag SWCNs, the relaxation rate would drop down rapidly at high frequency. Moreover, it is found that the relaxation rate increases linearly with temperature. The results also show that the dominating phonon scattering channel would change from $\mathrm{T} + \mathrm{A} = \mathrm{L}$ to $\mathrm{T} + \mathrm{A} = \mathrm{W}$ with increasing diameter of the SWCNs. The predicted phonon mean free path would reach a few micrometres, which is consistent with the estimate based on experimental results.

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