Carbon nanotubes: Ballistic transport or room-temperature superconductivity?

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We theoretically estimate the electron-phonon coupling constant \( \lambda \) for metallic single-walled carbon nanotubes with a diameter of 1.4 nm. The partial electron-phonon coupling constant for the hardest phonon mode is estimated to be about 0.0036, in good agreement with that deduced from Raman scattering data assuming superconductivity above room temperature. Assuming no superconductivity, we estimate the room-temperature inelastic mean free path \( l_{ep} \) due to electron-phonon scattering to be about 0.46 \( \mu \text{m} \), and the total room-temperature inelastic mean free path \( l_{in} \) to be about 0.16 \( \mu \text{m} \). We then argue that the electrical transport data of individual multi-walled nanotubes cannot be explained by ballistic transport at room temperature but provide strong evidence for quasi-one-dimensional superconductivity above room temperature.

Our recent articles have provided strong evidence for very high-temperature superconductivity in both single-walled and multi-walled carbon nanotubes [1,2,3,4]. The mean-field superconducting transition temperatures \( T_{c0} \)'s for both single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs) can be higher than 600 K. It has also been shown that the non-zero on-tube resistance state below \( T_{c0} \) in some individual nanotubes is caused by quantum phase slips (QPS) inherent in quasi-one-dimensional (quasi-1D) superconductors [5], as observed in ultrathin wires of conventional superconductors such as PbIn and MoGe [6]. The temperature dependence of the resistance in an individual SWNT or MWNT is very similar to that in the ultrathin wires of MoGe and can be naturally explained by the QPS theory [5].

Remarkably, negligible on-tube resistances have been observed in a multi-walled nanotube bundle consisting of two MWNTs with a diameter \( d = 16 \text{ nm} \) (Ref. [7]), in an individual MWNT with \( d = 40 \text{ nm} \) (Ref. [8]), in about 50 individual MWNTs [9], as well as in a single-walled nanotube bundle consisting of two SWNTs with \( d = 1.4 \text{ nm} \) (Ref. [10]). These electrical transport data have been tentatively explained in terms of ballistic transport at room temperature.

Here we theoretically estimate the electron-phonon coupling constant \( \lambda \) for metallic single-walled carbon nanotubes with a diameter of 1.4 nm. The partial electron-phonon coupling constant for the hardest phonon mode is estimated to be about 0.0036, in good agreement with that deduced from Raman scattering data assuming superconductivity above room temperature. We also estimate the room-temperature inelastic mean free path \( l_{ep} \) due to electron-phonon scattering to be about 0.46 \( \mu \text{m} \), and the total room-temperature inelastic mean free path \( l_{in} \) to be about 0.16 \( \mu \text{m} \) assuming no superconductivity. We then argue that the electrical transport data of individual multi-walled nanotubes cannot be explained by ballistic transport at room temperature but provide strong evidence for quasi-one-dimensional superconductivity above room temperature.

We first make a theoretical estimate of the electron-phonon coupling constant for carbon nanotubes. Because there are some common features in graphites, \( C_{60} \) and carbon nanotubes, one could estimate the electron-phonon coupling constant \( \lambda \) for the carbon nanotubes from the known \( \lambda \) values of graphites and \( C_{60} \). It was argued that curvature-induced hybridization in both \( C_{60} \) and carbon nanotubes opens additional electron-phonon scattering channels that are not available to flat graphite sheets. Neglecting second-order effects, the electron-phonon pairing potential can be decomposed into two components, one of which is present in flat sheet, and the other arising from new scattering channels due to non-zero curvature. The pairing potential in \( C_{60} \) is

\[
U_{\text{ball}} = U_{\text{flat}} + U_{\text{curve}} \left( \frac{R_0}{R} \right)^2, \tag{1}
\]

where \( U_{\text{curve}} \) is the curvature contribution to the pairing potential for a ball of radius of \( R_0 \). Since the contribution to the electron-phonon matrix element from new scattering channels in single-walled nanotubes is half the size of the contribution in \( C_{60} \), one readily shows that

\[
U_{\text{tube}} = U_{\text{flat}} + \frac{1}{4} U_{\text{curve}} \left( \frac{R_0}{R} \right)^2. \tag{2}
\]

For doped \( C_{60} \), four independent calculations lead to a similar electron-phonon coupling constant [11]. The average electron-phonon coupling constant \( \lambda = N(0)U \) from the four independent calculations is \( \lambda = 0.40 \) assuming that the density of states at the Fermi level \( N(0) = 0.24 \) states per carbon atom per eV (Ref. [12]). The contribution from the hardest mode (\( \hbar \omega = 197 \text{ meV} \)) is \( \lambda^h = 0.09 \) (Ref. [12]). Further, the coupling constant for doped graphites with \( N(0) = 0.24 \) states per carbon atom per eV is 0.25 (Ref. [11]). Substituting the

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above values into Eq. 1 yields $U_{\text{curve}} = 0.6U_{\text{flat}}$. For SWNTs with $R = 0.7$ nm, $N(0) = 0.015$ states per carbon atom per eV (Ref. [13]). The low density of states in the SWNTs implies a low electron-phonon coupling constant. Using Eqs. 1-2 and the relation $R \approx 2R_c$, we can easily show that the electron-phonon coupling constant for the 1.4 nm diameter SWNTs is $\lambda = 0.016$, and the contribution to the electron-phonon coupling constant from the hardest phonon mode $\lambda^h = 0.0036$.

The electron-phonon coupling constant for a particular phonon mode could be estimated from the phonon self-energy effects due to superconducting pairing. The phonon self-energy effects due to superconductivity can lead to shifts in both the frequency and width of the phonon modes if the phonons are coupled to conduction electrons. Such phonon self-energy effects were clearly demonstrated in the high-$T_c$ cuprate superconductors [14] [15] [16]. The width shifts of the Raman active phonon modes in 90 K superconductors RBa$_2$Cu$_3$O$_{7-y}$ (R is a rare-earth element) are in quantitative agreement with the theoretical calculation [15].

![FIG. 1. The temperature dependence of the relative frequency shift for the hardest Raman active mode with $h\omega = 197$ meV. The data are from R. Walter et al. at the University of North Carolina [17]. The detailed procedure for obtaining $\Delta \omega$ has been described in Ref. [4].](image)

The phonon self-energy effects were also seen in the hardest Raman-active G-band ($h\omega = 197$ meV) of single-walled carbon nanotubes with superconductivity above 600 K (Ref. [4]). In Fig. 1, we plot the temperature dependence of the relative frequency shift for the hardest Raman active mode with $h\omega = 197$ meV. The data are from R. Walter et al. at the University of North Carolina [17]. The detailed procedure for obtaining $\Delta \omega$ has been described in Ref. [4]. It is apparent that the frequency starts to shift down at 632 K, reaching to a minimum at $T^* = 370$ K. Such a temperature dependence is similar to the calculated one where the frequency starts to decrease below 0.95$T_c$ and reaches a shallow minimum at about 0.6$T_c$ (see Fig. 8 of Ref. [18] in the case of $h\omega/2\Delta(0) = 0.88$, where $\Delta(0)$ is the gap at zero temperature). The shallow minimum in the frequency shift is related to a sharp minimum in the real part of the polarization $\Pi(\omega, T)$, which occurs at $h\omega/2\Delta(T^*) = 1.05$ for strong coupling and at $h\omega/2\Delta(T^*) = 1.0$ for weak coupling [18] [19]. The weaker the coupling, the sharper the minimum in the real part of the polarization [19], and thus the more pronounced the minimum in the frequency shift. If we assume weak coupling and take $T_c = 660$ K (because $0.95T_c = 630$ K), we obtain $T^* = 0.57T_c$, and thus $\Delta(T^*) = 0.93\Delta(0)$ from the BCS theory. Then $2\Delta(0) = 1.07\Delta(T^*) = 1.07h\omega = 210$ meV, in excellent agreement with that deduced from the independent tunneling spectrum [3].

We can evaluate the contribution to the electron-phonon coupling constant from the hardest phonon mode $\lambda^h$ using a relation [13]: $\Delta \omega/\omega = 0.5\lambda^h\Re \Pi /N(0)$. The theoretical calculations [18] [19] suggest that $\Re \Pi/N(0) \approx -2$ at $T^* = 0.57T_c$ for strong coupling, and that $\Re \Pi/N(0)$ becomes more negative when the coupling decreases. Therefore, we may expect that the value of $\Re \Pi/N(0)$ should be in the range between $-2$ and $-3$ at $T^* = 0.56T_c$ for weak coupling. Then we obtain $\lambda^h = 0.0037-0.0056$, which is consistent with the theoretical estimate above. This consistency suggests that the unusual temperature dependence of the frequency for the hardest phonon mode of the single-walled nanotubes is indeed related to superconductivity above 600 K, and that the theoretically estimated coupling constant $\lambda$ is reliable.

From the values of the total coupling constant $\lambda$ and the Debye temperature $\theta_D$, we can now calculate the inelastic electron-phonon scattering time $\tau_{ep}$ using an equation [20]

$$\frac{1}{\tau_{ep}} = 24\pi\xi(3)\frac{\lambda}{1 + \lambda}\frac{k_B T^3}{\theta_D^3},$$  

(3)

where $\xi(3) = 1.2$ and $T_e$ is the temperature of electrons. Usually, the value of $\theta_D$ is about 1.2$h\omega_{\text{in}}/k_B$ (Ref. [21]). With $h\omega_{\text{in}}/k_B = 1400$ K (Ref. [14]), we have $\theta_D = 1680$ K. Substituting $T_e = 300$ K, $\lambda = 0.016$, and $\theta_D = 1680$ K into Eq. 3, we obtain $\tau_{ep} = 0.56$ ps at room temperature.

On the other hand, the room-temperature electron-phonon scattering time $\tau_{ep} = 18$ ps was estimated from the measured time dependence of electron temperature $T_e(t)$ (Ref. [22]). This value is larger than the above theoretical estimate by a factor of about 30. The recent work by the same group [23] appears to indicate that $\tau_{ep}$ is much smaller than their previous estimate and that the value of $\tau_{ep}$ depends strongly on the data sets. In fact, the
ways to determine $\tau_{ep}$ in Ref. \[22\] and Ref. \[28\] are not robust. In Ref. \[22\], the authors fit their high-temperature data ($> 400$ K) with a formula that is only valid at low temperatures ($T_c << \theta_D$). Accordingly, the value of $\tau_{ep}$ deduced from the fit to the high-temperature data is obviously unreliable. On the other hand, the data analysis in Ref. \[22\] may be justified if there were no superconductivity in those nanotubes. The basic idea in the data analysis of Ref. \[22\] is that, if there is no superconductivity in those nanotubes, the normal-state electronic specific heat and $\gamma$ is about three times smaller than the calculated one ($\gamma_0 \approx 0.2$) in the normal state, and goes to zero at zero temperature. This is because for $0.5T_c < T < 0.9T_c$, $N_s$ is much smaller than $N(0)$ and $C_{es} > C_e$, while for $T < 0.2T_c$ both $N_s(0)$ and $C_{es}$ tend to zero so that $N_s^2/C_{es}$ tends to zero. Just slightly below $T_c$, $N_s \approx N(0)$ and $C_{es} = 2.43C_e$ such that $N_s^2/C_{es} \approx (1/2.43)|N(0)|^2/C_e$. This scenario can naturally explain why $dT_c/dt$ tends to zero even when $T_c$ is higher than the lattice temperature by more than 100 K (see Fig. 3 of Ref. \[22\]). In fact, the initial slope $dT_c/dt$ at $T_c \approx 730$ K (see Fig. 3 of Ref. \[22\]) is consistent with $T_c \approx 730$ K and $q_0 \approx 2$ Å$^{-1}$. If we use $T_c \approx 730$ K and $q_0 \approx 2$ Å$^{-1}$, we find that the data in the whole temperature range can be well fitted by $N_s(T) = 2N(0)/(\exp[\Delta(T)/k_B T] + 1)$.

By taking $q_0 = 2.5$ Å$^{-1}$, $\gamma_0 = 2.5$ eV, and using Eq. 28 of Ref. \[22\], we find that the room-temperature electron-phonon scattering time due to the longitudinal acoustic phonon is 1.05 ps. Considering the contributions of the electron-phonon scattering from other phonon modes, one expects that the total $\tau_{ep} < 1.05$ ps, in agreement with the independent theoretical estimate above.

With $v_F = 8 \times 10^3$ m/s (Ref. \[13\]), the room-temperature inelastic mean free path due to electron-phonon scattering is $l_{ep} = 0.46$ µm. Since $l_{ep}$ is inversely proportional to the density of states per carbon which in turn is itself inversely proportional to the tube diameter, $l_{ep}$ is proportional to $d$,

$$l_{ep} = 0.46 \frac{d}{d_0} \, \mu\text{m}. \quad (4)$$

where $d_0 = 1.4$ nm.

We now discuss the electrical transport of carbon nanotubes. The scattering properties of the metallic subbands (the central two subbands of metallic tubes) and the semiconducting subbands (the bands that do not cross the Fermi level of undoped metallic tubes) are very different. It was shown that the electron backscattering from a single impurity with long range potential is nearly absent in metallic subbands while this backscattering becomes significant for semiconducting subbands \[27\]. When the Fermi level crosses the semiconducting subbands in doped metallic SWNTs, one should expect that the two metallic subbands provide the main contribution to the electrical transport. Indeed, the elastic mean free path $l_{el}$ for individual metallic SWNTs with $d = 1.4$ nm was theoretically estimated to be about $3$ µm, implying a possibility of ballistic transport \[23\].

On the other hand, the situation in multi-walled nanotubes becomes much more complicated. The chiralities of different shells constituting a MWNT play an important role in electrical transport. If several shells have the same chiral angle, their periodicities along the nanotube axis are commensurate. If chiral angles of different shells are varied, their periodicities are incommensurate, which should be case in real systems \[21\]. In the absence of defects, the intershell coupling allows the electron to spread over several shells, and when their periodicities are incommensurate, the electrical transport is theoretically shown to be non-ballistic \[29\]. Only if all the shells are commensurate, which is very unlikely in real materials, can ballistic transport be a possibility \[29\]. However, defects and disorders are inevitable in real materials. The electron backscattering is shown to be much more pronounced in a MWNT which consists of commensurate metallic chirality shells than in a MWNT with alternating metallic and semiconducting chirality shells \[27\]. Therefore, electrical transport in MWNTs should not be ballistic unless there are no defects and at least two adjacent shells have the same metallic chiral angle.

Although the probability of producing a defect free MWNT which has more than two adjacent shells with the same metallic chiral angle is low, we could calculate the resistance per unit length at room temperature for a model MWNT where the number of outermost adjacent layers with the same metallic chiral angle is $N_m$. At most, $N_m$ outermost shells have an infinitely long elastic mean-free path so that the total mean free path in each
of these shells is equal to the inelastic mean free path. Considering that \( N_m \) shells mainly contribute to electrical transport due to the fact that the transport in other incommensurate shells is non-ballistic, the resistance per unit length of the model MWNT at room temperature is then given by

\[
R_L = \frac{R_Q^2 N_m L_{in}}{2}, \tag{5}
\]

where \( R_Q = \frac{h}{2e^2} = 12.9 \text{ kΩ} \). Since there are inelastic electron-electron, electron-plasmon, and electron-phonon scattering, we expect that \( l_{in} < l_{ep} \). Using Eq. 4 and the above inequality, we find

\[
R_L > \frac{14000d}{N_md} \text{ (Ω/μm).} \tag{6}
\]

In Fig. 2, we plot the calculated lower limits of the room-temperature \( R/L \) as a function of \( d \) for \( N_m = 1, 3, \) and 10 in the case of nonsuperconducting transport. The upper limits of the measured \( R/L \) are also included in Fig. 2 for comparison. These two data are taken from Refs. [8]. In Ref. [8], extensive transport investigations have been carried out on MWNTs with diameters ranging from 5 to 25 nm. These MWNTs which protrude from unprocessed arc produced nanotube fibers and are contacted with liquid metals show small per unit length resistances \( R/L < 100 \text{ Ω/μm} \) at room temperature. For example, \( R/L = 14 \text{ Ω/μm} \) for a MWNT with \( d \approx 20 \text{ nm} \). In Ref. [8], a reliable technique of making ideal Ohmic contacts on MWNTs was developed to study electrical transport in individual MWNTs. It was found that the on-tube room temperature resistance per unit length \( R/L < 0.5 \text{ Ω/μm} \) for a MWNT with \( d = 40 \text{ nm} \).

From Fig. 2, one can clearly see that the measured resistance per unit length at room temperature is even far below the calculated lower limit for \( N_m = 10 \). Since the probability of producing a defect free MWNT which has 10 outermost shells with the same metallic chiral angle is nearly zero, the electrical transport data reported in Refs. [8] cannot be explained if MWNTs were not room temperature superconductors. Since the periodicities for the majority of MWNTs should be incommensurate and non-ballistic in real world [29], it is very difficult to understand how such small per unit length resistances \( R/L < 100 \text{ Ω/μm} \) at room temperature in the majority of the MWNTs studied [8] could arise if the MWNTs were not room temperature superconductors.

The calculated curves in Fig. 2 are the lower limits of \( R/L \) since we have only considered the contribution from electron-phonon scattering, which is very weak and cannot lead to high-temperature superconductivity. In fact, electron-plasmon coupling in quasi-1D systems is strong and could result in superconductivity as high as 500 K [30]. We can estimate the total room-temperature inelastic mean free path from electrical transport data assuming no superconductivity. Fig. 3 shows the temperature dependence of the resistance for a single-walled nanotube with \( d = 1.5 \text{ nm} \). The data are extracted from Ref. [31] at zero gate voltage.

The distance between the two contacts is about 200 nm and the contacts are nearly ideal with the transmission probability of about 1 [31]. From Fig. 3, we can see that the resistance increases with increasing temperature. The temperature dependent part of the resistance should arise from the inelastic scattering if there were no superconductivity. Then we find that the room-temperature resistance per unit length due to inelastic scattering is about 40 kΩ/μm (the difference between the resistance at room-temperature and the one at zero temperature).

![Figure 2](image2.png)

**FIG. 2.** The calculated lower limits of the room-temperature \( R/L \) as a function of \( d \) for \( N_m = 1, 3, \) and 10, in the case of nonsuperconducting transport. The upper limits of the measured \( R/L \) are also included for comparison. These two data are taken from Refs. [8].
Substituting this value into Eq. 5 yields $l_n = 0.16\ \mu m$ at room temperature. With such a short inelastic mean free path at room temperature and using Eq. 5, one finds that the on-tube resistance at room temperature across a length of 1 \( \mu m \) would be larger than 20 k\( \Omega \) for a SWNT bundle that consists of two coupled SWNTs \[10\]. This is in sharp contrast with a negligible on-tube resistance (<3 k\( \Omega \)) observed in this bundle \[11\]. The more plausible explanation is that the metal-like temperature dependence of the resistance shown in Fig. 3 is not caused by inelastic scattering but is associated with the quantum-phase slips, as discussed in Ref. \[3\]. The Josephson coupling between two SWNTs suppresses quantum phase slips and reduces the resistance of the bundle to a value that is remarkably smaller than the sum of the individual resistances.

Quantum-phase slip theory \[3\] can also naturally explain the semiconductor-like behavior below room temperature in individual MWNTs that are lithographically contacted \[3\]. The lithographically contacted MWNTs may contain high density of defects or imperfections which are introduced through purification and other processing steps \[3]. Defects and disorders enhance quantum-phase slips and the localization of Cooper pairs, which would lead to a semiconductor-like temperature dependence of the resistance below $T_{c0}$ (Ref. \[3\]).

In summary, we theoretically estimate the electron-phonon coupling constant $\lambda$ for metallic single-walled carbon nanotubes with a diameter of 1.4 nm. The partial electron-phonon coupling constant for the hardest phonon mode is estimated to be about 0.0036, in good agreement with that deduced from Raman scattering data assuming superconductivity of about 700 K. Assuming no superconductivity, we estimate the room-temperature inelastic mean free path $l_{ep}$ due to electron-phonon scattering to be about 0.46 \( \mu m \), and the total room-temperature inelastic mean free path $l_{in}$ to be about 0.16 \( \mu m \). We further demonstrate that the electrical transport data of individual MWNTs cannot be explained by ballistic transport at room temperature but instead provide strong evidence for quasi-1D superconductivity above room temperature.

Acknowledgment: I am grateful to Dr. R. Walter et al. for sending me their unpublished data, and to Prof. W. A. de Heer for sending me their preprint \[9\]. I thank Dr. Pieder Beeli for bringing my attention to Ref. \[3\] and for his critical reading and comments on the manuscript. The author acknowledges financial support from the State of Texas through the Texas Center for Superconductivity and Advanced Materials at the University of Houston where some of the work was completed.

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