Coupled dynamics of electrons and phonons in metallic nanotubes: current saturation from hot phonons generation

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(Dated: September 8, 2018)

We show that the self-consistent dynamics of both phonons and electrons is the necessary ingredient for the reliable description of the hot phonons generation during electron transport in metallic single-wall carbon nanotubes (SWNTs). We solve the coupled Boltzmann transport equations to determine in a consistent way the current vs. voltage (IV) curve and the phonon occupation in metallic SWNTs which are lying on a substrate. We find a good agreement with measured IV curves and we determine an optical phonon occupation which corresponds to an effective temperature of several thousands K (hot phonons), for the voltages typically used in experiments. We show that the high-bias resistivity strongly depends on the optical phonon thermalization time. This implies that a drastic improvement of metallic nanotubes performances can be achieved by increasing the coupling of the optical phonons with a thermalization source.

PACS numbers: 61.46.Fg, 63.20.Kr, 65.80.+n, 72.15.Lh, 73.63.Fg

I. INTRODUCTION

Much interest is currently devoted to the study of electronic transport properties in carbon nanotubes (CNTs), both metallic and semiconducting. The main reason is the possibility to use CNTs in electronic integrated circuits thanks to catalizator-assisted on-site growth. Semiconducting CNTs are envisageable as new components for transistors and logic circuits. On the other hand, metallic CNTs are particularly suited as a new type of interconnects due to their small dimensions and the large electron current density (∼10^9 A/cm^2) they can support. The current vs. voltage (IV) curve of metallic single-wall carbon nanotube (SWNTs) has been recently measured by several groups. For voltages ≥ 0.2 V, they observe a sudden increase of the resistivity which is due to the scattering with optical phonons. In long tubes, this leads to a saturation current of ~ 25 μA for voltages ≥ 5 V. Such behavior limits the performances of metallic SWNTs as interconnects. The understanding of this phenomenon is, thus, a crucial step toward finding methods to boost SWNTs performances and has important technological consequences.

Two recent papers suggested the possibility that, at high bias, the electron transport induces an anomalously high optical-phonons occupation (hot phonons) which, in turn, induces an increase of the resistivity. In Ref. the hypothesis is formulated on the basis of the comparison between scattering lengths (obtained from IV measurements and electron-phonon coupling values (obtained from ab-initio calculations and inelastic X-ray scattering measurements). However, the extent of Ref. conclusions is limited, because Ref. does not provide neither a scheme to reproduce experimental IV curves, nor a reliable quantitative determination of the phonon occupation. The conclusions of Ref. apply to tubes which are lying on a substrate. This is the very typical situation encountered in experiments.

Ref. reports the comparison between IV curves measured on SWNTs in two different situations: when the tubes are lying on a substrate and when the tubes are suspended between the two electrodes. Ref. concludes that hot phonons are present in the tubes which are suspended but are absent in those which are lying on a substrate (for bias < 1 V). The presence of hot phonons is clearly demonstrated by the experimental observation of a negative differential resistance in suspended tubes. On the other hand, the absence of hot-phonons is inferred from a simplified theoretical model in which the electron scattering length (at zero temperature) is a fitting parameter. The claim of absence of hot phonons, for the tubes lying on a substrate, is contradicting the conclusions of Ref. where the scattering length is obtained from ab-initio calculations of the electron-phonon coupling.

Concluding, a quantitative model to describe the anomalous phonon heating is not available. Moreover, given the contradicting conclusions of Refs. it is not clear whether hot phonons generation is present for tubes lying on a substrate. This last point is particularly relevant. In fact, if the high-bias resistance measured for tubes lying on a substrate is due to hot phonons, one could conceive some methods to reduce the optical phonon temperature and thus diminish the high bias resistance. This would not be possible if hot phonons were not present in tubes lying on a substrate.

In this paper, we solve the coupled Boltzmann transport equations for both phonons and electrons to determine in a consistent way the IV curve and the phonon occupation in metallic SWNTs. The quantitative determination of the anomalous phonon heating during electron transport allows us to settle the debate on the presence/absence of hot phonons in nanotubes lying on a substrate. We are interested in the high bias (> 0.2 V) region, where the transport properties are determined by the scattering with optical phonons. We use the zero-temperature electron scattering lengths obtained from ab-initio calculations based on the density functional the-
In a metallic SWNT, there are only two phonons which can be generated by transport electrons via a back-scattering process. Using the graphene notation, they correspond to the \( E_{2g} \) LO (here \( E \) stands for longitudinal along the tube axis) mode at \( \Gamma \) and to the \( \Delta' \) mode at \( K \) (equivalent of the \( \Delta' \) at \( K' \)). For simplicity, we label them \( \Gamma \) and \( K \). \( \tau_{bs}^\Gamma \) and \( \tau_{bs}^K \) are the corresponding electron scattering times, i.e. the average time an electron can travel before emitting a phonon. \( \tau_{bs} = l_{bs}/v_F \), where \( l_{bs} \) is the scattering length and \( v_F = 8.39 \times 10^7 \) cm/s is the Fermi velocity. According to precise ab-initio calculations, at zero temperature \( \tau_{bs}^\Gamma = 538 \) fs and \( \tau_{bs}^K = 219 \) fs (for tubes with a diameter of 2.0 nm, which is the diameter typically used in experiments). Electrotransport induces not-thermal high-occupation of phonons if the generation time of the phonons (\( \tau_{bs}^\Gamma \) and \( \tau_{bs}^K \)) is shorter than their thermalization time. For metallic SWNTs, the optical-phonons thermalization time \( \tau_{th} \) is due to anharmonic scattering into acoustic phonons. Time-resolved terahertz spectroscopy measurements, on graphite, reported an optical-phonon thermalization time of 7 ps. This value is comparable with the optical-phonon linewidth of diamond (the other carbon polymorph) \( \sim 1 \) cm\(^{-1} \), which corresponds to a relaxation time of 5 ps, and is due to phonon-phonon scattering. A \( \tau_{th} \) value of the same order is obtained by preliminary calculations of phonon-phonon scattering on graphite and nanotubes done with the ab-initio methods of Refs. \[17,19\]. Concluding, we expect \( \tau_{th} \) to be of the order of 5 ps. Since \( \tau_{bs}^\Gamma \) and \( \tau_{bs}^K \) are much smaller than \( \tau_{th} \), hot-phonon generation is \textit{a priori} expected to occur during electron transport in metallic SWNTs.

In the following, we consider the model schematized in Fig. 1. Transport electrons can scatter with the optical phonons \( \Gamma \), \( K \) and \( K' \) (\( K' \) is equivalent of \( K \) and is not shown). \( \tau_{bs}^\Gamma \) and \( \tau_{bs}^K \) are the electron scattering times. \( \tau_{ep}^\Gamma \) and \( \tau_{ep}^K \) are phonon scattering times, i.e. the average time a phonon lives before emitting an electron-hole pair. For metallic SWNTs, it can be shown that \( \tau_{ep}^\Gamma = \tau_{bs}^\Gamma / 4 \) and \( \tau_{ep}^K = \tau_{bs}^K / 2 \). The optical phonons can, also, scatter into acoustic phonons with a characteristic thermalization time \( \tau_{th} \sim 5 \) ps. Both the acoustic phonons and the substrate are thermalized at room temperature, and are acting as a thermal bath. The present model is not valid if the tube is suspended between the two electrodes, as in some of the experiments of Ref. \[3\]. In this case, the acoustic phonons are not thermalized with the environment and their occupation should be determined self-consistently. We are not considering this case.

\[ \begin{align*} \tau_{bs}^\Gamma &= 538 \text{ fs} \\
\tau_{ep}^\Gamma &= \tau_{bs}^\Gamma / 4 \\
\tau_{bs}^K &= 219 \text{ fs} \\
\tau_{ep}^K &= \tau_{bs}^K / 2 \end{align*} \]

FIG. 1: Scheme of the model used in this paper (see the text).
that, given the small phonon velocity (with respect to $v_F$) the optical phonons do not have the time to diffuse along tubes longer than 100 nm (the thermalization scattering lengths are $\tau_{th}^R = v_{ph}^R \tau_{th} \sim 15$ nm and $\tau_{th}^K = v_{ph}^K \tau_{th} \sim 36$ nm). This was already pointed out in Ref. [8]. Thus, the resulting IV curve is only slightly affected by the exact value of $|v_{ph}|$. For given $x$ and $t$,

$$\partial_t f_L|_{bs} = \sum_{\nu} \frac{1}{\tau_{bs}^{\nu}} \left\{ [1 - f_L] f_R(-k^+) - [1 - f_R(-k^-)] f_L \right\}$$

$$+ [f_R(-k^-) - f_L] n^\nu(-k - k^+) + [f_R(-k^-) - f_L] n^\nu(k + k^-)$$

$$[\partial_t n^\nu]|_c = \frac{1}{2 \tau_{ep}^{\nu}} \left\{ [1 - f_L \left( -\frac{k^+}{2} \right)] f_R \left( \frac{k^-}{2} \right) + \left[ 1 - f_R \left( -\frac{k^-}{2} \right) \right] f_L \left( \frac{k^+}{2} \right) +$$

$$\left[ -f_L \left( -\frac{k^+}{2} \right) + f_R \left( \frac{k^-}{2} \right) - f_R \left( -\frac{k^-}{2} \right) + f_L \left( \frac{k^+}{2} \right) \right] n^\nu(k) \right\} - \frac{1}{\tau_{th}} n^\nu(k),$$

where $k^\pm = k \pm (\omega^\nu/v_F)$, $f_L$ stands for $f_L(k)$, the variables $x$ and $t$ are omitted, and $\nu = F, K$. $\omega^\nu$ is the phonon pulsation, $\hbar \omega^F = 196.0$ meV, $\hbar \omega^K = 161.2$ meV and the $\omega^\nu$ dependence on $k$ can be neglected. Notice that Eq. (4) can be obtained from Eqs. (12) and (3) imposing the conservation of energy and momentum in the back-scattering processes. We recall that, to be consistent with the Boltzmann treatment, the scattering times $\tau_{bs}^{\nu}$ and $\tau_{ep}^{\nu}$ of Eqs. (3) and (4) are computed with zero phonon occupation. 

We impose the equilibrium distributions as boundary conditions:

$$f_L(k, 0) = f_R(-k, L) = \{ \exp[\hbar \omega_F k/(k_B T)] + 1 \}^{-1}$$

$$n^\nu(k > 0, 0) = n^\nu(k < 0, L) = 0,$$

where $T = 300$ K and $k_B$ is the Boltzmann constant. The current is given by:

$$I = \frac{4e}{h} \int (f_L - f_R) \hbar v_F dk.$$

The stationary solution of Eqs. (1) and (2) is found by numerical integration in time. 

The present approach is similar to that of Refs. [5,6] but has two important differences. First, in Refs. [5,6] the phonon occupation is considered to be thermalized at room temperature ($n \approx 0$). Thus, in Refs. [5,6] Eq. (4) is not taken into account and, in Eq. (3) the terms depending on $n$ are not considered. Second, in Refs. [5,6] the scattering time $\tau_{bs}$ is considered as a parameter and its value is fitted to reproduce the experimental IV curves, supposing that hot phonons are absent. In the present work, we do not make any assumption on the phonon occupation $n$ and we determine $n$ by solving the transport equation. Moreover, the zero-temperature scattering times $\tau_{bs}^{\nu}$ are not fitted to recover a better agreement with measurements, but are fixed to the values obtained from ab-initio calculations [4,10,12].

![FIG. 2: (Color online) Lower panel: current vs. voltage characteristic of a 300 nm long carbon nanotube (CNT). Calculations are done fixing the phonon occupation to zero (cold phonons) or allowing phonons to heat up (hot phonons, $\tau_{th} = 5.31$ ps). Measurements are from Refs. [6,7]. Upper panel: phonon effective temperature of the Raman $G$ peak (see the text) as a function of the voltage.](image)

**III. RESULTS**

### A. CURRENT VS. VOLTAGE

In Fig. 2 we show the comparison between the measured IV curves and our calculations done imposing the phonon occupation $n = 0$ (cold phonons) or allowing the $n$ to vary according to Eqs. (2) and (3) using $\tau_{th} = 5.31$ ps (hot phonons). This value corresponds to an anharmonic contribution to the phonon linewidth (full width) $\gamma =1$ cm$^{-1}$, which is expected from independent calculations and measurements [16,17,18] (see discussion above). Imposing $n = 0$ the resulting IV curve dramatically underestimates the experimental resistivity.
On the contrary, if the phonon occupation $n$ is determined self-consistently the IV curve nicely reproduces the experimental data. Already at 0.2 V the hot-phonon and the cold-phonon curves significatively differ. This implies that the hot phonon generation dominates the resistivity behavior already at $V>0.2$ V, also for tubes lying on a substrate.

In Fig. 4 we show our calculations for tubes with different lengths $L$. The dependence of the IV-curve on $L$ is similar to that observed experimentally in Refs. 6, 7. Despite the presence of the hot phonons, for bias $>0.5$ V the differential resistance $dV/dI$ is almost independent from the voltage.

We computed the $dV/dI$ at high bias (in between 1.0 and 1.4 V) for tubes with different lengths $L$ (Fig. 4). Beside $\tau_{th}=5.31$ (γ = 1 cm$^{-1}$), we also considered $\tau_{th}=2.65$, 0.885, and 0 ps (corresponding to $\gamma=2.6, +\infty$ cm$^{-1}$), to investigate whether a significant reduction of the resistance can be achieved by a reduction of $\tau_{th}$. $dV/dI$ is clearly linear with respect to $L$ and is, thus, possible to define a linear resistivity $\rho$. For a one-dimensional channel with 4 sub-bands, in the incoherent limit:

$$\rho = \frac{1}{L} \frac{dV}{dI} = \frac{1}{l_{sc}} \frac{h}{4e^2},$$  (5)

where $h/(2e^2) = 12.9$ kΩ is the quantum of resistance and $l_{sc}$ is the effective scattering length. Eqs. 5 can be used to obtain $l_{sc}$ from the measured resistivity $\rho$. Using this approach, several independent experimental works found a scattering length $l_{sc}$ of the order of 10 nm, at high bias, for tubes lying on a substrate. We remark that $l_{sc}$ is not to be confused with the $l_{bs}$ of the present paper.

While $l_{bs}$ is calculated for zero phonon occupation, $l_{sc}$ is an effective scattering length that includes the effects of the finite phonon occupation. To compare our calculations with the measured $l_{sc}$, we make a linear fit of the data in Fig. 4, we obtain $\rho$ and, thus, $l_{sc}$ through Eq. 5. This is done for the different $\tau_{th}$ values. For $\tau_{th}=5.31$ ps (which is our best $\tau_{th}$ estimate) we obtain $l_{sc}=12$ nm. Again, this compare very well with $l_{sc}=8.5$ nm which we extracted from the experimental values reported in Fig. 4.

Given the fact that the IV curves strongly depend on the optical phonon occupation (Fig. 2), we expect that the thermalization time $\tau_{th}$ might play a crucial role. In fact, a smaller $\tau_{th}$ induces a lower optical phonons occupation (Fig. 4). In turn, this results in lower resistivity or a higher scattering length $l_{sc}$. Indeed, for $\tau_{th}=2.65$, 0.885, and 0 ps, we obtain $l_{sc}=22$, 42, and 108 nm, respectively (inset of Fig. 4). This strong dependence of $l_{sc}$ on $\tau_{th}$ implies that even a small decrease of $\tau_{th}$ induces an important amelioration of the nanotube performances. A higher optical phonon thermalization can be obtained, e.g., by using a substrate characterized by vibrational frequencies similar to those of a CNT.

Finally, the calculations done with $\tau_{th}=0$ are equivalent of imposing $n^\nu=0$ (cold phonons) in Eqs. 4.

For $n=0$, it is usually assumed that $l_{sc}$ is a measure of the optical phonon back-scattering length, i.e. $(l_{sc})^{-1} = (l_{bs})^{-1} + (l_{K})^{-1}$. Indeed, from our calculations for $n=0$ ($\tau_{th}=0$) $l_{sc}=108$ nm, which is 20% smaller than $[l_{bs})^{-1} + (l_{K})^{-1}]^{-1}=131$ nm.

**B. PHONON OCCUPATION**

In Fig. 4 we show an example of the computed phonon occupation $n(k,x)$ at voltage 1.4 V, $L=300$ nm. The phonon occupation is clearly distributed in a not uniform way. Two important peaks with $n \sim 20$ are present near the electrodes. For a given phonon occupation $n(k,x)$, we define an effective temperature $T^{eff}(k,x)$ as the corresponding temperature within the Bose-Einstein statistics: $n = 1/[exp[h\omega/(k_B T^{eff})]-1]$. $n \sim 20$ is extremely high and corresponds to $T^{eff} \sim 40000$ K. Using simple arguments, it can be shown that $n(k,x) \neq 0$ only for
indeed concentrated around $\Gamma$, the same as in Fig. 2, with voltage 1.4 V.

\[ E_{\alpha}^{at} = \sum_{\nu} \frac{m^{\nu} h \nu}{2 \pi N_{\alpha}^{at}} \int n^{\nu}(k, x) \, dk \, dx, \]

where $N_{\alpha}^{at}$ is the number of atoms in the tube, $m^{\Gamma} = 1$ and $m^{K} = 2$ (to take into account both $K$ and $K'$). $E_{\alpha}^{at}/k_B = 50.6$ K, at bias 1.4 V and $L = 300$ nm. Thus, the actual average kinetic energy per atom, associated to the hot phonons, is not particularly high despite the high values reached by the hot phonons distribution, $n^{\nu}(k, x)$. Indeed, only a small subset of optical phonons is heated in a limited region of the $k$-space. Concluding, the presence of hot phonons having temperatures of several thousands $K$ is compatible with the fact that the tubes are not melting during electron transport.

As suggested in Ref. 8, the occupation of the $E_{2g}$ phonon at $k = 0$, $n^{\Gamma}(0, x)$, is accessible experimentally using Raman spectroscopy. Indeed, this mode is responsible for the $G$ peak observed in Raman spectroscopy.\textsuperscript{24,25} The Stokes and anti-Stokes $G$ peak intensities are proportional to $n^{\Gamma}(0, x) + 1$ and $n^{\Gamma}(0, x)$, respectively. From the measured Stokes and anti-Stokes ratio one can extract $n^{\Gamma}(0, x)$ of a SWNT during electron transport. In the upper panel of Fig. 2 we show, as a function of the applied bias, the effective temperature $T_{\text{eff}}$ of the Raman active $E_{2g}$ phonon, obtained from the average over the tube length of $n^{\Gamma}(0, x)$. Already at 1.0 V, we find a $T_{\text{eff}} = 2500$ K (Fig. 2), corresponding to $n = 0.7$.

Finally, Refs. 8,24 built two oversimplified models to describe the hot-phonon generation. Both models are based on the assumption that there is a simple relation between the effective scattering length $l_{sc}$, the zero-temperature back-scattering length $l_{bs}$, and the average phonon occupation $n$:

\[ l_{sc} = \frac{l_{bs}}{2n + 1} \] (6)

(see Eq.10 of Ref. 8 and lines 4-12, page 2 of Ref. 9). Although a priori reasonable, Eq. 6 is in contradiction with the observation that the differential resistance (and hence $l_{sc}$) is constant with the voltage at high-bias (Fig. 3), while the phonon occupation $n$ is increasing with the voltage (upper panel of Fig. 3). Therefore Eq. 6 can not be used to construct quantitative models for the description of hot phonons in metallic SWCNs. The high-bias linearity of the IV curve, that is observed experimentally in tubes with $L < 500$ nm, might have led Refs. 5,6,7,9 into neglecting hot-phonons effects for tubes lying on a substrate.

\section*{IV. CONCLUSIONS}

In conclusion, the explicit and self-consistent dynamics of both of phonons and electrons is the necessary ingredient for the reliable description of the hot phonons generation during electron transport in metallic SWNTs. We find a remarkable agreement with the experimental IV curves. We have shown that the hot phonon generation can not be properly described using the simplified models reported in Refs. 8,24. We demonstrate the presence of hot phonons for voltages > 0.2 V also for tubes which are lying on a substrate. We have shown that the high-bias resistance strongly depends on the thermalization time of the optical phonons. As a direct consequence, an important improvement of metallic nanotubes performances is, in principle, possible by increasing the optical-phonons thermalization time.

\section*{ACKNOWLEDGMENTS}

We thank N. Bonini, N. Marzari and G. Galli for useful discussions. Calculations were performed at IDRIS (Orsay, France); project 051202.
Following Ref. 8, the scattering lengths are proportional to the tube diameter $d$, in particular $b_\Gamma = 225.5 \times d$ for the $\Gamma$-E$_{2g}$ LO mode and $b_K = 91.9 \times d$ and for the $\mathbf{K}$-A$_1'$. These values are computed using the Fermi golden rule, with zero phonon occupation. $\tau_{\text{bs}}^\theta = \frac{\Gamma_{\text{bs}}}{v_F}$ and $\tau_{\text{bs}}^K = \frac{\Gamma_{\text{bs}}}{v_F}$.

In general, $\tau_{\text{bs}}$ is also determined by the direct coupling of the SWNT optical phonons with the substrate. Such coupling is relevant when the optical phonon frequencies are similar to those of the substrate. In the typical experimental situation, we expect this coupling to be negligible because the nanotube is lying on a SiO$_2$ substrate. SiO$_2$ phonon frequency are smaller than the SWNTs optical phonon frequencies.

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13. Because of the momentum conservation, only the phonons near $\mathbf{K}$ or $\mathbf{\Gamma}$ can be involved in a scattering process with electrons near the Fermi level. Moreover, the $\mathbf{\Gamma}$-E$_{2g}$ LO mode and the $\mathbf{K}$-A$_1'$ are the only phonons with a not negligible electron-phonon coupling for back-scattering events.
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