Phonon anharmonicities in graphite and graphene

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We determine from first-principles the finite-temperature properties—linewidths, line shifts, and lifetimes—of the key vibrational modes that dominate inelastic losses in graphitic materials. In graphite, the phonon linewidth of the Raman-active $E_{2g}$ mode is found to decrease with temperature; such anomalous behavior is driven entirely by electron-phonon interactions, and does not appear in the nearly-degenerate infrared-active $E_{1u}$ mode. In graphene, the phonon anharmonic lifetimes and decay channels of the $A_1'$ mode at $K$ dominate over $E_{2g}$ at $\Gamma$ and couple strongly with acoustic phonons, highlighting how ballistic transport in carbon-based interconnects requires careful engineering of phonon decays and thermalization.

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Carbon nanotubes and graphene nanoribbons are intensely studied as candidates for future electronic and optoelectronic devices. In particular, metallic tubes have some of the highest current densities reported in any material and could lead to extremely promising applications as electrical interconnects. However, in carbon nanotubes or graphite, high currents or optical excitations can induce a non-thermal phonon distribution, with significant overpopulation of the optical phonons $E_{2g}$ at $\Gamma$ and $A_1'$ at $K$. These hot phonons develop because of a slower anharmonic decay rate with respect to the generation rate, and cause a significant reduction of the ballistic conductance of carbon nanotubes at bias potentials larger than ~0.2 V, severely limiting interconnect performance. A microscopic characterization of phonon decays is thus a key step in improving the transport properties of these materials, whereas engineering individual decay channels would allow to control energy relaxation and ultimately performance.

Information on the phonon scattering mechanisms can be obtained from Raman or infra-red (IR) measurements of the linewidths and line shifts of the phonon modes. Indeed, the intrinsic linewidth $\gamma^{in}$ in a defect-free sample is $\gamma^{in} = \gamma^{EP} + \gamma^{PP}$, where $\gamma^{EP}$ and $\gamma^{PP}$ represent the electron-phonon (EP) and anharmonic phonon-phonon (PP) interactions. The shift with temperature of the harmonic phonon frequencies is also due to PP interactions. While experimental measurements are now available on graphene, graphite and carbon nanotubes, their interpretation is not always straightforward. For example, graphene has a $E_{2g}$ at $\Gamma$ Raman-active mode (the $G$ band) with a linewidth of ~13 cm$^{-1}$ [13]. In graphite this phonon splits in nearly-degenerate modes: the Raman-active $E_{2g}$ and the IR-active $E_{1u}$ [14]. The linewidth of the Raman-active mode (11.5 cm$^{-1}$ [15]) remains similar to that of graphene, suggesting a negligible effect of the interactions among different graphitic planes. On the other hand, IR measurements show that the linewidth of the $E_{1u}$ mode is much smaller (~4 cm$^{-1}$ [14]). The finite-temperature line shift of $E_{2g}$ is also puzzling: recent experimental results have shown very little difference between graphite and graphene [16], while first-principles calculations find a room-temperature in-plane thermal expansion coefficient for graphene more than three times as large as that of graphite (both are negative) [17]. Prompted by these results, and by the central role played by phonon decays in controlling inelastic losses, we characterize here the EP and PP scattering parameters of the $E_{2g}$, $E_{1u}$ and $A_1'$ modes in graphite or graphene using state-of-the-art first-principles calculations. These parameters are then used to compute the linewidths and line shifts of the Raman and IR bands, and the PP decay lifetimes.

All the calculations are performed using density-functional theory (DFT) and density-functional perturbation theory (DFPT) as implemented in the PWSCF package of the QUANTUM-ESPRESSO distribution. We use the local-density approximation, norm-conserving pseudopotentials and a plane-wave expansion up to a 55 Ry cut-off. Brillouin-zone sampling is performed on $32 \times 32 \times 8$ and $32 \times 32 \times 1$ Monkhorst-Pack meshes for graphite and graphene, with a Fermi-Dirac smearing in the electronic occupations of 0.02 Ry. For graphite, the equilibrium lattice parameters $a = 2.43$ Å and $c/a = 2.725$ are used [17], for graphene, an interlayer spacing of 7 Å is adopted. The DFT accuracy in calculating vibrational properties in graphite even in the presence of van der Waals interactions is discussed in Ref. [17]. The phonon frequencies, dynamical matrices, and EP matrix elements are obtained using DFPT. The phonon anharmonic self-energy is given, at the lowest order in the perturbative expansion with respect to the atomic mass, by the tadpole, loop and bubble diagrams corresponding to three- and four-phonon scattering terms. Thus, we calculate the third-
and fourth-order derivatives of the total energy with respect to atomic displacements; the former are obtained from DFPT [18, 23], while the latter from finite differences over the relevant phonon eigenvectors. The dynamical matrices are computed on a 16\times16\times1 or a 8\times8\times4 mesh (for graphene and graphite, respectively), higher-order derivatives on 4\times4\times1 or 4\times4\times2 meshes. Fourier interpolation [18] then provides all these quantities on finer grids (200\times200\times50 and 200\times200\times1 for graphene and graphite), over which we perform all numerical integrations.

At the lowest order, a phonon acquires a finite linewidth by decaying into two lower-energy phonons (\(\gamma^{pp}\)) or by creating an electron-hole pair (\(\gamma^{pp}\)). The PP contribution \(\gamma^{pp}\) is given by the imaginary part of \(\Pi\) [8, 22], which is determined by 3-phonon scattering processes. In the electron-hole creation process, a phonon with wavevector \(q\) excites an electronic state |\(k\rangle\) with wavevector \(k\) into the state |\(k+q\rangle\). The scattering probability is thus given by the EP coupling matrix element \(g_{(k+q)j\mid k}\) [24]. According to the Fermi golden rule [25],

\[
\gamma^{ep}_{j}(T) = \frac{4\pi}{N_{k}} \sum_{k,i,j} |g_{(k+q)j\mid k}|^{2} |f_{ki}(T) - f_{(k+q)i}(T)| \times \delta[\epsilon_{ki} - \epsilon_{(k+q)i} + \hbar\omega_{q}],
\]

where \(\omega_{q}\) is the phonon frequency, the sum is on \(N_{k}\) \(k\) vectors, \(f_{ki}(T)\) is the Fermi-Dirac occupation at temperature \(T\) for an electron with energy \(\epsilon_{ki}\), and \(\delta\) is the Dirac delta [26] (throughout the paper we will consider full-width at half-maximum (FWHM) linewidths).

We report in Fig. 1 the linewidths for the \(E_{2g}\) and \(E_{1u}\) modes in graphite and graphene, computed according to the aforementioned procedure. Very good agreement is found with respect to measurements [13, 14, 15]. More importantly, our calculations show that the phonon linewidth for the \(E_{2g}\) mode, and its dependence on temperature, is completely dominated by the EP coupling, with a decreasing linewidth as a function of temperature. This effect is due to the strong \(T\) dependence of \(\gamma^{ep}\), which is only partially compensated by \(\gamma^{pp}\).

In order to rationalize this result, we consider a simplified model for the temperature dependence of \(\gamma^{ep}\) for the \(E_{2g}\) modes: we assume a linearized band dispersion around the Fermi energy (\(\epsilon_{F}\)) and a model EP coupling [24]. It can be easily shown (e.g. following Eq. 3 in Ref. [13]) that at finite \(T\)

\[
\gamma^{ep}(T) = \gamma^{ep}(0) \left[ f \left( \frac{-\hbar\omega_{0}}{2k_{B}T} \right) - f \left( \frac{-\hbar\omega_{0}}{2k_{B}T} \right) \right],
\]

where, from DFT, \(\gamma^{ep}(0) = 11.01 \text{ cm}^{-1}\) [15], \(\hbar\omega_{0} = 196 \text{ meV}\) is the \(E_{2g}\) phonon energy, \(k_{B}\) is the Boltzmann constant and \(f(x) = 1/[\exp(x) + 1]\). Eq. 2 reproduces very well the full calculation of Eq. 1 (see Fig. 1) and can be used to understand the temperature dependence of \(\gamma^{ep}(T)\), since this is now proportional to the difference between the occupations of states below and above \(\epsilon_{F}\). As \(T\) increases, the occupation of filled states below \(\epsilon_{F}\) decreases, while the empty states are occupied more, resulting in the observed decrease of \(\gamma^{ep}(T)\) with temperature.

It is important to note that \(\gamma^{ep}(0)\) for the \(E_{1u}\) mode in graphite is almost five times smaller than for the case of \(E_{2g}\). This difference can be understood by decomposing Eq. 1 in parallel and perpendicular contributions, where \(k_{\parallel}\) is the component perpendicular to the graphene planes and \(k_{\perp}\) is the in-plane projection. We define \(\gamma_{\parallel}(k_{\perp})\) as the contribution to the EP linewidth obtained from Eq. 1 when restricting the k-point integration on those vectors \(k\) that satisfy \(\hat{c} \cdot k = k_{\perp}\), where \(\hat{c}\) is the unit vector perpendicular to the graphene planes. With such definition \(\gamma^{ep} = \int_{0}^{1} \gamma_{\parallel}(k_{\perp}) dk_{\perp}\), where \(k_{\perp}\) is in units of \(\pi/c\). The electronic states with a non-zero contribution to Eq. 1 are those allowed by energy conservation and by a non-zero EP coupling. Energy conservation alone selects the four \(\pi\) bands near the Fermi level (labeled 1 to 4, from the lowest to the highest, in Fig. 2). For the \(E_{1u}\) mode the computed EP coupling allows mainly transitions from band 1 to 3 and from band 2 to 4. Since the minimum gap between bands 1 and 3 (and 2 and 4) varies considerably as a function of \(k_{\perp}\), and the IR transition satisfies energy conservation only for \(k_{\perp} \gtrsim 0.8\) (Fig. 3), we have a small \(\gamma^{ep}\) for this mode. On the contrary, for the \(E_{2g}\) mode the EP coupling allows mainly transitions from band 1 to 4 and from band 2
The PP contribution to line shifts is given by and that provides powerful information on the anharmonicity that is easily accessible by e.g. Raman spectroscopy, and that the temperature-dependent line shift is another quantity that is easily accessible by e.g. Raman spectroscopy, and that provides powerful information on the anharmonicity. The PP contribution to line shifts is given by

to 3; energy-conservation means that only the transition between 2 and 3 is essentially active. Since the minimum gap between bands 2 and 3 is always zero, the transition is active for any $k_{\perp}$. It turns out that $\gamma_{E_{2g}}(k_{\perp})$ is almost a constant and its value is similar to that of graphene (Fig. 2) and much larger than that for the IR-active mode $\gamma_{E_{1u}}(k_{\perp}) \sim 5 \times 10^{12}$ cm$^{-1}$. Interestingly, the IR-active mode of a graphene bilayer should have a vanishing $\gamma_{\perp}$, since the bilayer bands are very similar to those of graphene with $k_{\perp} = 0$.

The temperature-dependent line shift is another quantity that is easily accessible by e.g. Raman spectroscopy, and that provides powerful information on the anharmonicity. The PP contribution to line shifts is given by the real part of the self-energy $\Pi$ [22]; as mentioned before, at the lowest order this includes both 3-phonon and 4-phonon scattering terms. A further contribution descends straightforwardly from the lattice thermal expansion, that is especially large and negative in graphene [17]. This contribution is obtained by computing the harmonic frequency at the lattice parameter appropriate to the given temperature, obtained within the quasi-harmonic approximation [17]. Within the present approach the EP contribution to the frequency shift is taken into account exactly (within DFT) in the harmonic frequencies [18].

Fig. 3 shows our computed line shifts for the $E_{2g}$ mode [27]. The results are in good agreement with available experiments [28, 29], and in excellent agreement with recent measurements for graphite and graphene [10]. In both cases the frequencies shift down with temperature—an unusual result for an optical mode where the bond-bond distances are predicted to become shorter with temperature. In reality, lattice contraction does provide the expected upward shift—and a much larger one for graphene than for graphite. Still, the overall behavior is dominated by a downshift driven by the 4-phonon scattering term, almost two times stronger in graphene than in graphite (Fig. 3). Thus, while the individual anharmonic contributions in graphite and graphene are quite different, the $E_{2g}$ line shifts are always downwards (driven by the 4-phonon contributions) and very similar in the two systems thanks to the compensation between different but opposite contributions.

Finally, we focus on the analysis of the anharmonic phonon decay processes. We show in Fig. 4 the anharmonic phonon lifetimes ($\tau = 1/\gamma_{PP}$) and the decay channels for the modes $E_{2g}$ at $\Gamma$ and $A_{1u}$ at $K$ in graphene; these are the two modes with the strongest EP coupling, and the ones that will be overpopulated during steady-state operation in an interconnect [4] (the results for graphite are very similar, see Fig. 1). The values obtained are of the same order of the optical-phonon thermalization time (7 ps) estimated in graphite from time-resolved terahertz spectroscopy [3]. This result is also in agreement with the empirical choice of Ref. [4] where the experimental I-V characteristic of metallic-tube interconnects was modeled by a coupled Boltzmann transport equation for phonons and electrons, assuming $\tau_{\Gamma} = \tau_{K} \sim 5$ ps. The values of $\tau_{\Gamma}$ and $\tau_{K}$ that we obtain from first-principles confirm this assumption, but provide much needed novel insight on the relative relevance of the different decay processes. In particular, it is found that $\tau_{K} > \tau_{\Gamma}$ (Fig. 4); in addition, since the EP coupling for the $K$ mode is stronger than for $\Gamma$ [4], we find that the phonon population at $K$ will be dominant in determining inelastic losses, with the high-bias resistivity due to scattering with $K$ phonons. Moreover, $\tau_{K}$ has a large decay channel towards low-energy acoustic phonon modes (Fig. 4 bottom right panel) that is not available
FIG. 4: (Color online) Upper left panel: computed PP lifetime of the \( E_{2g} \) and \( A'_1 \) modes of graphene. We also report the computed lifetimes (300 K) of the other modes at \( \Gamma \) and \( K \). Upper right panel: probability per unit time (300 K) that the \( E_{2g} \) mode at \( \Gamma \) decays into two phonons of wavevectors \( \mathbf{q} \) and \(-\mathbf{q}\). Upper part of the lower panel: schematic representation of the different PP decay channels for the modes \( E_{2g} \) at \( \Gamma \) (left) and \( A'_1 \) at \( K \) (right). Below, probability per unit time \( \gamma \) that the \( E_{2g} \) or the \( A'_1 \) modes (of frequency \( \omega_0 \)) decay into two modes of frequencies \( \omega \) and \( \omega_\mathbf{q} - \omega \). The relative weight of the decay channels is also reported.

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In conclusion, we have presented a detailed analysis of anharmonic effects in graphene and graphite, based on the explicit calculation of the PP and EP interactions within DFPT. Excellent agreement with experimental results—where available—is found. We have explained the large differences in the linewidths for the closely related Raman and IR G-bands in graphite, and the closely similar line shifts for the G-band in graphene and graphite, notwithstanding very different thermal-expansion parameters. Moreover, the anomalous decrease of the Raman G-band linewidth with temperature, predicted for both graphene and graphite, is rationalized through its dominant EP contribution; the negative dependence on temperature is accurately captured by a simple phenomenological expression. The PP decay channels for the critical vibrational excitations that limit ballistic transport have been identified, with fundamental consequences in understanding and engineering electronic transport in metallic nanotubes and graphene ribbons interconnects.
2430×2430×144 grid for graphite (and 2430×2430×1 for graphene), using for $\delta$ a Lorentzian with a 0.13 mRy (20 K) width. To reduce the computational costs, this sum can be restricted to a small region around the K-H line where the addends are different from zero.

[27] The EP contribution changes by less than 1 cm$^{-1}$ in the 0-800 K temperature range.

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[31] A polynomial of the form $aT^2 + bT^3 + cT^4 + dT^5$ fits well (especially between 150-900K) the ab initio results, with $a = 2.2679 \times 10^{-5}$, $b = -1.4836 \times 10^{-7}$, $c = 1.7869 \times 10^{-10}$ and $d = -7.1998 \times 10^{-14}$ for graphite and $a = -2.6595 \times 10^{-5}$, $b = -1.3568 \times 10^{-9}$, $c = 1.3633 \times 10^{-11}$ and $d = -4.0258 \times 10^{-15}$ for graphene.