Phonon renormalisation in doped bilayer graphene

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We report phonon renormalisation in bilayer graphene as a function of doping. The Raman G peak stiffens and sharpens for both electron and hole doping, as a result of the non-adiabatic Kohn anomaly at the Γ point. The bilayer has two conduction and valence subbands, with splitting dependent on the interlayer coupling. This results in a change of slope in the variation of G peak position with doping, which allows a direct measurement of the interlayer coupling strength.

PACS numbers: 73.63.-b, 63.20.Kr, 81.05.Uw, 78.30.Na,

Graphene is the latest carbon allotrope to be discovered\textsuperscript{1, 2, 3, 4, 5}. Near-ballistic transport at room temperature and high carrier mobilities\textsuperscript{2, 3, 4, 5, 6, 7, 8}, make it a potential material for nanoelectronics\textsuperscript{9, 10, 11}, especially for high frequency applications. It is now possible to produce areas exceeding thousands of square microns by means of micro-mechanical cleavage of graphite. An ongoing effort is being devoted to large scale deposition and growth on different substrates of choice.

Unlike single layer graphene (SLG), where electrons disperse linearly as massless Dirac fermions\textsuperscript{1, 2, 3, 4, 5}, bilayer graphene (BLG) has two conduction and valence bands, separated by γ, the interlayer coupling\textsuperscript{12, 13}. This was measured to be ~0.39eV by angle resolved photoelectron spectroscopy\textsuperscript{14}. A gap between valence and conduction bands could be opened and tuned by an external electric field (~100meV for~10\textsuperscript{13} cm\textsuperscript{-2} doping)\textsuperscript{14}, making BLG a tunable-gap semiconductor.

Graphene can be identified in terms of number and orientation of layers by means of elastic and inelastic light scattering, such as Raman\textsuperscript{17} and Rayleigh spectroscopies\textsuperscript{18, 19}. Raman spectroscopy also allows monitoring of doping and defects\textsuperscript{4, 20, 21, 22, 23, 24, 25}. Indeed, Raman spectroscopy is a fast and non-destructive characterization method for carbons\textsuperscript{26}. They show common features in the 800-2000 cm\textsuperscript{-1} region: the G and D peaks, around 1580 and 1350 cm\textsuperscript{-1}, respectively. The G peak corresponds to the breathing modes of sp\textsuperscript{2} atoms and involves phonons around K+Δq\textsuperscript{17, 23}. Δq depends on the excitation energy, due to double-resonance, and the linear dispersion of the phonons around K\textsuperscript{17, 29, 30}. 2D is a single peak in SLG, whereas it splits in four in BLG, reflecting the evolution of the band structure\textsuperscript{17}. The 2D peak is always seen, even when no D peak is present, since no defects are required for overtone activation.

In SLG, the effects of back and top gating on G-peak position (Pos(G)) and Full Width at Half Maximum (FWHM(G)) were reported in Refs\textsuperscript{20, 21, 24}. Pos(G) increases and FWHM(G) decreases for both electron and hole doping. The G peak stiffening is due to the non-adiabatic removal of the Kohn-anomaly at Γ\textsuperscript{20, 24}. FWHM(G) sharpening is due to blockage of phonon decay into electron-hole pairs due to the Pauli exclusion principle, when the electron-hole gap is higher than the phonon energy\textsuperscript{20, 32}, and saturates for a Fermi shift bigger than half phonon energy\textsuperscript{20, 21, 32}. A similar behavior is observed for the LO-G\textsuperscript{−} peak in metallic nanotubes\textsuperscript{33}, for the same reasons. The conceptually different BLG band structure is expected to renormalize the phonon response to doping differently from SLG\textsuperscript{13, 34}. Here we prove this, by investigating the effect of doping on the BLG G and 2D peaks. The G peak of doped BLG was recently investigated\textsuperscript{35}, and reproduced that of SLG, due to the very low doping range(~ 5 × 10\textsuperscript{12} cm\textsuperscript{-2}), not enough to cross the second BLG subband. Here we reach much higher values (~5 × 10\textsuperscript{13} cm\textsuperscript{-2}), probing the further renormalisation resulting from crossing to the second BLG subband.

We recently demonstrated a SLG top-gated by poly-
**mer electrolyte**\(^{24}\), able to span a large doping range, up to \(\approx 5 \times 10^{13} \text{cm}^{-2}\)\(^{24}\). This is possible because the nanometer thick Debye layer\(^{24}\) \(36, 37\) gives a much higher gate capacitance compared to the usual 300nm SiO\(_2\) back gate\(^{5}\). We apply here this approach to BLG. Fig.\(^1\) shows the scheme of our experiment. A sample is produced by micromechanical cleavage of graphite. This consists of a SLG extending to a BLG, as proven by the characteristic SLG and BLG 2D peaks in the inset of Fig.\(^1\)\(^{17}\). An Au electrode is then deposited by photolithography covering both SLG and BLG, Fig.\(^1\). Top gating is achieved by using a solid polymer electrolyte consisting of LiClO\(_4\) and polyethelyne oxide (PEO) in the ratio 0.12:1\(^{24}\). The gate voltage is applied by placing a platinum electrode in the polymer layer. Note that due to screening effects, the gate would give a separate contribution, \(n_{\text{SLG}} = 2\left(\frac{n_{\text{TG}}}{n_{\text{SLG}}} - 1\right)^{24}\). The gate capacitance \(C_{\text{TG}}\) is given by the chemical (quantum) capacitance of graphene. For BLG\(^{13, 39, 40}\) and SLG\(^{1}\), these trends can be explained by considering the effects doping on the phonons:(i) a change of the equilibrium Fermi energy. For BLG\(\gamma_1=0.4\text{eV}\) (since its variation for \(n\) up to \(\approx 10^{13} \text{cm}^{-2}\) is <5%)\(^{14, 15}\). Eqs.\(^1\)\(^2\) then give \(E_{\text{TG}} = E_F + \nu E_F^2\) (1).

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rium lattice parameter with a consequent "static" stiffening/softening, \( \Delta \text{Pos}(G)^{\text{st}} \); (ii) the onset of "dynamic" effects beyond the adiabatic Born-Opennheimer approximation, that modify the phonon dispersion close to the Kohn anomalies, \( \Delta \text{Pos}(G)^{\text{dyn}} \) [20, 31]. Thus, the total phonon renormalization can be written as [20, 31]:

\[
\text{Pos}(G_E) - \text{Pos}(G_0) = \Delta \text{Pos}(G) = \Delta \text{Pos}(G)^{\text{st}} + \Delta \text{Pos}(G)^{\text{dyn}}
\]

(3)

For SLG, we compute \( \Delta \text{Pos}(G)^{\text{st}} \) by converting \( E_F \) into the corresponding electron density \( n^{\text{SLG}} \), then using Eq.3 of Ref. [31]. For BLG, we assume \( n^{\text{BLG}} \) equally distributed on the two layers, each behaving as a SLG with an electron concentration \( n^{\text{BLG}}/2 \). Eq.3 of Ref. [31] is then used to compute \( \Delta \text{Pos}(G)^{\text{st}} \) for BLG. \( \Delta \text{Pos}(G)^{\text{dyn}} \) is calculated from the phonon self-energy \( \Pi \) [11]:

\[
h\Delta \text{Pos}(G)^{\text{dyn}} = \Re \{ \Pi(E_F) - \Pi(E_F = 0) \}.
\]

(4)

The electron-phonon coupling (EPC) contribution to FWHM(G) is given by \([11, 42, 43]\):

\[
\text{FWHM}(G)^{\text{EPC}} = 2\Im \{ \Pi(E_F) \}
\]

(5)

The self-energy for the \( E_{2g} \) mode at \( \Gamma \) in SLG is [20, 31]:

\[
\Pi(E_F)^{\text{SLG}} = \alpha' \int_{-\infty}^{\infty} \frac{f(\epsilon) - f(-\epsilon)}{2\epsilon + \hbar \omega_0 + i\delta} |\epsilon| d\epsilon,
\]

(6)

while for BLG it is given by [13]:

\[
\Pi(E_F)^{\text{BLG}} = \alpha' \int_{-\infty}^{\infty} \gamma^2 k dk \sum_{s,s',j,j'} \phi_{s,j}^{+} \phi_{s',j'}^{-} \times \left[ \frac{f(\epsilon_{s,j,k}) - f(\epsilon_{s',j',k})}{\epsilon_{s,j,k} - \epsilon_{s',j',k}} - \frac{\epsilon_{s,j,k}}{(\hbar \omega_0 + i\delta)^2} \right]
\]

(7)

where \( \alpha' = \frac{\hbar A_{\text{uc}} \text{EPC(}\Gamma^2)}{2\hbar \omega_0 (\text{FWHM(F)})^2} \), \( A_{\text{uc}} = 5.24 \text{Å}^2 \) is the graphene sheet unit-cell area, \( M \) is the carbon atom mass, \( f(\epsilon) = 1/\exp(-\epsilon/k_B T) + 1 \) is the Fermi-Dirac distribution, \( \delta \) is a broadening factor accounting for charge inhomogeneity, EPC(\( \Gamma \)) is the electron phonon coupling [20], \( s = \pm 1 \) and \( s' = \pm 1 \) label the conduction (+1) and valence (-1) bands, while \( j = 1, 2 \) and \( j' = 1, 2 \) label the two parabolic subbands. \( \epsilon_{s,j,k} \) is computed from Eq.2.8 of Ref. [13], and \( \phi_{s,j}^{+} \) is given by Eq.3.1 of Ref. [13]. By using Eqs. [6, 7] in Eqs. [4, 5], we get \( \Delta \text{Pos}(G)^{\text{dyn}} \), FWHM(G)^{\text{EPC}} for SLG and BLG.

To compare Eqs. [6, 7] with the experimental data, we use \( \alpha' = 4.4 \times 10^{-3} \) obtained from the DFT values of EPC(\( \Gamma \)) and \( v_F \) [20, 30], the experimental \( \hbar \omega_0 \) for SLG and BLG, and \( T = 300 \text{K} \). \( \delta \) is fitted from the experimental FWHM(G) to FWHM(G)=FWHM(G)^{\text{EPC}}+FWHM(G)^{\text{0}}, with FWHM(G)^{\text{0}} a constant accounting for non-EPC effects (e.g. resolution and anharmonicity). For SLG (BLG) we get \( \delta = 0.13 \text{eV} (0.03 \text{eV}) \) and FWHM(G)^{\text{0}}=4.3 \text{cm}^{-1} (5.1 \text{cm}^{-1}) . These \( \delta \) values are then used to compute Pos(G). Note that the relation between \( n \) and \( E_F \) implies that charge inhomogeneity causes different \( E_F \) broadening in SLG and BLG (e.g. \( \delta n \sim 10^2 \text{cm}^{-2} \) would give \( 0.13 \text{eV} \) and \( 0.03 \text{eV} \) in SLG and BLG, respectively).

The solid lines in Fig. 4 are the theoretical Pos(G) and FWHM(G) trends. The experimental and theoretical FWHM(G) are in excellent agreement, as expected since the latter was fitted to the former. The theoretical Pos(G) captures the main experimental features. In particular, the flat dependence for \( |E_F| < 0.1 \text{ eV} \) in both SLG and BLG, and the kink at \( 0.4 \text{ eV} \) in BLG. This kink is the most striking difference between SLG and BLG. It is the signature of the second subband filling in BLG. Indeed, a shift of \( E_F \), by acting on \( f(\epsilon) \) in Eq.7 modifies the type and number of transitions contributing to \( \Pi \). The only transitions giving a positive contribution to \( \Pi \) are those for which \( |\epsilon_{s,j,k} - \epsilon_{s',j',k}| < \hbar \omega_0 \), i.e. a subset of those between \( (s = -1; j = 1) \) and \( (s = 1; j = 1) \) (interband transitions, solid blue lines in Fig. 4). Intercb band transitions with \( |\epsilon_{s,j,k} - \epsilon_{s',j',k}| > \hbar \omega_0 \) (solid red lines in Fig. 4) and all intraband (between \( (s = \pm 1; j = 1) \) and \( (s = \pm 1; j = 2) \), dashed red lines in Fig. 4) contribute to \( \Pi \) as negative terms. It is convenient to distinguish three different cases: (I), \( |E_F| < \hbar \omega_0 \), (II) \( \hbar \omega_0 < |E_F| < \gamma_1 \), and (III) \( |E_F| > \gamma_1 \). For simplicity let us assume \( E_F > 0 \) (the same applies for \( E_F < 0 \)). In case (I), positive contributions from interband transitions are suppressed, and new negative intraband transitions are created. This results in strong phonon softening at low temperatures [35]. At \( T = 300 \text{K} \), these effects are blurred by the fractionary occupation of the electronic states, resulting in an almost doping independent phonon energy (see Fig. 3). In case (II), a shift of \( E_F \) suppresses negative interband contributions and creates new negative intraband transitions. By counting their number and relative weight (given by \( \Phi_{j,j'}/(|\epsilon_{s,j,k} - \epsilon_{s',j',k}|) \), one can show that interband transitions outweight intraband ones, resulting in phonon hardening. Case (III) is similar to (II), with the difference that the second subband filling suppresses negative intraband transitions at \( k \sim K \).
further enhancing the phonon hardening. It is also possible to demonstrate that, for $T$ and $\delta \rightarrow 0$, the slope of $\Delta\text{Pos}(G)^{dyn}$ just above $E_F = \gamma_1$ is double than that just below. Thus, the kink in Fig.3 is a direct measurement of the interlayer coupling strength from Raman spectroscopy.

In SLG the intensity ratio of 2D and G, $I(2D)/I(G)$, has a strong dependence on doping\cite{24}. Fig.5a plots $I(2D)/I(G)$ as a function of doping. For BLG we take the highest amongst $2D_{1A}$ and $2D_{2A}$. The SLG dependence reproduces our previous results\cite{24}. However, we find an almost constant ratio in BLG. Fig.5b plots the doping dependence of $\text{Pos}(2D)$ in SLG, and $\text{Pos}(2D_{1A}), \text{Pos}(2D_{2A})$ in BLG. To a first approximation, this is governed by lattice relaxation, which explains the overall stiffening for hole doping and softening for electron doping\cite{24}. A quantitative understanding is yet to emerge, and beyond DFT many body effects need be considered.

To conclude, we have simultaneously measured the behavior of optical phonons in single and bilayer graphene as a function of doping. In the latter, the G peak renormalizes as the Fermi energy moves from the 1st to the 2nd subband, allowing a direct measurement of $\gamma_1 \sim 0.4\text{eV}$.

We thank D. Basko for useful and stimulating discussions. AKS acknowledges funding from the Department of Science and Technology, India, SP from Pembroke College and the Maudsley society, ACF from The Royal Society and The Leverhulme Trust.

**FIG. 5:** (a) Ratio of 2D and G peaks intensities for SLG (solid circles) and BLG (open circles) as a function of $n$. (b) Position of 2D for SLG (solid circles) and 2D main components for BLG (open circles) as a function of $n$.  

\[ \Delta \gamma = \frac{\text{Pos}(2D)}{\text{Pos}(G)} \text{ for SLG} \text{, and Pos}(2D_{1A}), \text{Pos}(2D_{2A}) \text{ in BLG.} \]

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peak of metallic SWNTs with the theoretical HWHM.

[44] K. Ishikawa, T. Ando, J. Phys. Soc. Jap. 75, 084713 (2006).

[45] Note that the prefactor of Eq. 7 of Ref. [20] should be $\frac{2\alpha}{4c}$.

[46] EPC(Γ) is equivalent to $\langle G_Γ^2 \rangle_F$ as defined in Ref. [32].