Weak localization in electric-double-layer gated few-layer graphene

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Abstract

We induce surface carrier densities up to $\sim 7 \cdot 10^{14}$ cm$^{-2}$ in few-layer graphene devices by electric double layer gating with a polymeric electrolyte. In 3-, 4- and 5-layer graphene below 20–30 K we observe a logarithmic upturn of resistance that we attribute to weak localization in the diffusive regime. By studying this effect as a function of carrier density and with $ab initio$ calculations we derive the dependence of transport, intervalley and phase coherence scattering lifetimes on total carrier density. We find that electron–electron scattering in the Nyquist regime is the main source of dephasing at temperatures lower than 30 K in the $\sim 10^{13}$ cm$^{-2}$ to $\sim 7 \cdot 10^{14}$ cm$^{-2}$ range of carrier densities. With the increase of gate voltage, transport elastic scattering is dominated by the competing effects due to the increase in both carrier density and charged scattering centers at the surface. We also tune our devices into a crossover regime between weak and strong localization, indicating that simultaneous tunability of both carrier and defect density at the surface of electric double layer gated materials is possible.

1. Introduction

Electrolytic gating, initially developed for polymeric transistors (see ref. [1] and references therein), is now used to study the transport properties of a wide range of materials, from semiconductors [2], to insulators [3] and superconductors [4–6]. This technique induces an orders-of-magnitude enhancement in the electric field at the sample surface, when compared to conventional solid gate techniques [7–10]. When a potential is applied between the sample and a counter electrode, the ions inside the polymeric (or liquid) electrolyte migrate and accumulate at the two surfaces, building up the so-called electric double layer (EDL) [7, 8]. This acts as a nanoscale capacitor, and allows one to obtain surface variations of the carrier density, $n_{\text{edl}}$, up to $\sim 10^{14}$–$10^{15}$ cm$^{-2}$ [5], depending on the density of states of the sample and the electrochemical stability window of the electrolyte itself.

We firstly exploited an EDL to gate single layer graphene (SLG) in ref. [11] and bilayer graphene (BLG) in ref. [12]. Since then, this technique has been widely applied to study the transport properties of SLG [13–15] and few-layer graphene (FLG) [16–18]. Refs. [14, 15] studied the dominant scattering mechanisms in SLG for $n_{\text{edl}}$ up to 6 and $11 \cdot 10^{13}$ cm$^{-2}$, respectively. Ref. [15] reported a gate-tunable crossover of the resistivity from $\rho \propto T$ to $\rho \propto T^4$, in the range from 1.5 K up to room temperature (RT). This provides a clear example of Bloch–Grüneisen behavior in two dimensions (2d) due to a crossover from small-angle to large-angle electron–phonon (e–p) scattering [19]. Ref. [16] reported an electric field-induced, gate-tunable band gap in rhombohedral stacked three-layer graphene (3LG) for $n_{\text{edl}} \leq 1 \cdot 10^{13}$ cm$^{-2}$. Ref. [17] showed that the $n_{\text{edl}}$ achievable by electrolyte gating is large enough to populate the higher-energy bands in two layer (2LG) and three layer (3LG) graphene, away from the charge neutrality point. Ref. [18] demonstrated a gate-tunable crossover from weak localization (WL) to weak anti-localization (WAL) in the low-$T$ transport properties of 3LG on SiC.

We reported $n_{\text{edl}}$ up to $\sim 3.5–4.5 \cdot 10^{13}$ cm$^{-2}$ in thin films of Au and other noble metals with EDL gating by using a polymer electrolyte system (PES) of improved capacitance [21, 22] compared to previous experiments [7–10]. By using the same PES, we induced $n_{\text{edl}} > 6 \cdot 10^{14}$ cm$^{-2}$ in few-layer graphene (FLG)
2. Fabrication and characterization

FLG flakes are prepared by micromechanical exfoliation of graphite on Si/SiO₂ [32, 33]. The number of layers, N, is determined by a combination of Raman spectroscopy [34, 35] and optical microscopy [31, 36]. EDL field-effect devices are then prepared by electron beam lithography and deposition of Cr/Au contacts in the Hall bar configuration, as shown in figure 1(b). A coplanar gate contact is deposited on the side. A protective poly(methyl methacrylate) (PMMA) layer is spin-coated, patterned and hard-baked on the completed devices in order to avoid interactions between the electrolyte and the metallic leads. A reactive mixture precursor of the PES is then drop-cast onto the whole device and UV-cured, to get a cross-linked photopolymer electrolyte [21, 23], figure 1(a). The precursor viscous liquid reactive mixture is composed of methacrylic oligomers and lithium salt: bisphenol A ethoxylate dimethacrylate (BEMA; average Mn: 1700, Aldrich), poly(ethylene glycol)methyl ether methacrylate (PEGMA; average Mn: 475, Aldrich), and 10% of lithium bis(trifluoromethanesulfonyl)
imide (LiTFSI) along with the addition of 3 wt% 2-hydroxy-2-methyl-1-phenyl-1-propanon as the free radical photoinitiator (Darocur 1173, Ciba Specialty Chemicals). No annealing is performed in the time between contact deposition and PES casting, and the devices are stored in a desiccator under low vacuum (∼10−1–1 mbar) to prevent contamination. We do not perform any annealing step before double-step chronocoulometry and transport measurements, because we are not interested in probing the properties of our samples close to the Dirac point. Thus, \( n_{2d} \) near the charge neutrality point is larger compared to the typical values for exfoliated flakes (∼10^{11}–10^{12} cm\(^{-2}\)) [66, 67]. Four-wire resistance measurements are done under high vacuum (<10^{-5} mbar) in the chamber of a Cryomech pulse-tube cryocooler via a Keithley 6221/2182A current source/nanovoltmeter assembly. The gate potential is controlled through a Keithley 2410 sourcemeter, whose negative electrode is set at the current drain contact. Gate leakage is monitored to ensure that no electrochemical reactions occur at the graphene/EDL interface. Magnetoresistance measurements are performed in an Oxford Instruments helium cryostat equipped with a superconducting magnet.

We estimate \( n_{2d} \) as a function of the gate voltage, \( V_G \), from the measured gate current through double-step chronocoulometry [39] (DSCC), as shown in figure 1(c) for 3LG, 4LG and 5LG (green triangles, violet diamonds and orange pentagons, respectively) and described in detail in ref. [23]. This technique is based on the fact that, in absence of chemical reactions at the electrodes, the current flowing through the electrolyte can be split into two contributions [39]. The first, due to the EDL build-up, decays exponentially over time [39]. The second, due to ion diffusion through the bulk of the electrolyte [39], decays as the square root of time [39]. By fitting the gate current response to a step-like application and removal of \( V_G \) with a function that separately accounts for both effects, the two contributions can be distinguished and, thus, the EDL charge estimated. Further details on the technique can be found in refs. [21, 23, 39]. These results are checked with independent Hall-effect measurements performed on a 4LG device (red squares in figure 1(c)). We conservatively use the DSCC values in the full \( V_G \) range.

We also compare the RT resistance as a function of \( V_G \) in a 3LG with the earlier measurements of ref. [17]. Figure 1(d) shows how, in both cases, regions of sharp non-monotonic behavior are present in the resistance curves away from the Dirac point. The position of these upturns is associated with a specific charge density, such that the Fermi level, \( E_F \), is crossing the bottom of the split-off bands [17], which can be used for voltage-\( n_{2d} \) calibration. This comparison indicates that our PES allows us to reach the split-off bands at lower potential than the ionic liquid of ref. [17], thus supporting a higher charge induction capability.

3. Results and discussion

We first measure the four-contact resistance in the 4–290 K range as a function of \( N \) and \( n_{2d} \). In each measurement, \( V_G \) is applied at RT and the system...
is then cooled to a base $T \sim 4\text{–}10\text{ K}$, depending on sample. Any further modification of $n_{2d}$ below the PES glass transition at $\sim 230\text{ K}$ [23] is prevented by the quenched ion motion [4, 6]. The samples are then allowed to spontaneously warm up, taking advantage of the absence of $T$ fluctuations associated with the cryocooler’s thermal cycles. We reported a detailed analysis of the $T$ dependence of $R$ for these device in the 30–290 K range in ref. [23]. Here we focus on the anomalous behavior that emerges in the 4–30 K range.

For all the three $N$, a logarithmic upturn is observed for $T < 100\text{ K}$ in the resistance curves for samples in the metallic regime, as shown in figure 2. Figures 2(a)–(d) plot the low-$T$ ($\lesssim 100\text{ K}$) variations of $R$ with respect to its minimum value $R_{\text{Min}}$ for 3LG, 4LG and 5LG as function of $T$ in a semi-logarithmic scale. $R_{\text{Min}}$ decreases with increasing $n_{2d}$ for all $N$, and saturates for 4LG (see top panel of figure 2(e)). Both the amplitude of the logarithmic upturn ($R_0(5\text{K}) - R_{\text{Min}}$) and the $T_{\text{Min}}$ at which $R_{\text{Min}}$ is reached strongly depend on $n_{2d}$ and $N$, as shown in the central and bottom panels of figure 2(e). Similar logarithmic upturns in the resistance of conductors in the diffusive regime, such as Si MOSFETs [41], GaAs heterostructures [42, 43], and transition metal alloys [44] are usually attributed to Kondo effect [45], WL [46, 47], and e–e interactions [50–52], or to a superposition of any of the previous sources [49].

We first consider the Kondo effect, which is caused by carrier scattering from diluted magnetic impurities [44, 45]. Unlike in ref. [48], we do not intentionally introduce any defects in our samples. We thus employ Raman spectroscopy to monitor the amount of Raman active defects in our devices, before and after PES drop-casting. Raman measurements are carried out at RT in a Renishaw InVia microspectrometer equipped with a 100X objective. The spot size is $\sim 1\mu \text{m}$, the excitation wavelength is 514 nm and the incident power is kept well below 1 mW in order to avoid heating. Figure 3(a) plots the Raman spectrum of a 3LG device. The PES shows several peaks between $\sim 1000$ and $1500\text{ cm}^{-1}$. The broad peak between $\sim 1400$ and $1500\text{ cm}^{-1}$ can be assigned to the methylene bending mode [102], the peak at $\sim 1280\text{ cm}^{-1}$ to methylene twisting [103], and that at $\sim 1243\text{ cm}^{-1}$ to either trifluoromethyl stretching [102] or methylene twisting [103].

We perform a background subtraction by normalizing to the low-frequency PES peaks near the D peak. This gives an upper limit for the ratio between the intensity of the D peak and the intensity of the G peak, $I(\text{D})/I(\text{G})$, $\sim 0.015$, which leads to an estimated defect density $\sim 3 \times 10^{10}\text{ cm}^{-2}$ [37, 38]. For comparison, in order to obtain a sizeable Kondo effect ($\delta \rho/\rho \approx 6\%$ at $T = 0.3\text{ K}$), in ref. [48] it was necessary to induce a defect density $\sim 3 \times 10^{11}\text{ cm}^{-2}$, which produced a corresponding $I(\text{D})/I(\text{G}) \sim 2.8$, for an excitation wavelength of 633 nm [48]. Our values indicate that our devices are at least two orders of magnitude less defective. Thus, we discard contributions from the Kondo effect to the resistance upturn.

3.1. Weak localization in few-layer Graphene

WL arises from the constructive interference between pairs of time-reversed trajectories of electrons

![Figure 3. (a) Raman spectrum measured at 514 nm for a 3LG device, before (black) and after (blue) PES drop-casting, together with the Raman response from the PES (red) and the spectrum with the subtracted background (green). (b) Raman 2D region for 3LG (green), 4LG (violet) and 5LG (orange).](image-url)
This means that in SLG the T, as shown. Figure 4(b) shows 0.021F\v \text{v}

classical coherence is maintained is called phase coherence probability of inelastic scattering associated with the

electrons \[49\] in the electrostatic potential generated by the other

of the diffraction of an electron wave by the oscillations

[49], and it is typically of the order of few tens K \[49\]. A widely exploited approach to dis-

criminate between these two contributions is the meas-

urement of the sample magnetoconductance \[49, 50,

which dominates for lower

T \[49\]. The

important for higher

T \[49\]. A phase dif-

fERENCE arises between any two time-reversed electron

trajectories, whose constructive interference, in prin-

CIPLE able to localize electrons \[49\], is therefore broken

elastically scattering in a closed loop \[49\]. This increases

the probability of charge-carrier backscattering in a

conductor in the diffusive regime \[46, 47\], thus reducing

the conductance \[49\]. In order for WL to appear, phase

coherence must be maintained throughout the entire

closed loop, followed by the electrons undergoing

elastic scattering, as described by a characteristic

lifetime \[46\]. WL is thus suppressed by an increased

probability of inelastic scattering associated with the T

increase \[46\]. The average time interval in which phase

coherence is maintained is called phase coherence lifetime \(\tau_c\) \[49\]. Typically, two inelastic processes determine \(\tau_c\) \[49\]. E–ph scattering \[53\], which is

important for higher \(T\) \[49\], and e–e scattering \[54, 55\],

which dominates for lower \(T\) \[49\]. The \(T\) that marks a
crossover between these two scattering processes

depends on the transport properties of each material

\[49\], and it is typically of the order of few tens K \[49\].

In a diffusive system a conductivity suppression at low \(T\) may also be caused by e–e interactions, as a result

of the diffraction of an electron wave by the oscillations

in the electrostatic potential generated by the other

electrons \[49–52\]. A widely exploited approach to dis-

criminate between these two contributions is the measure-

urement of the sample magnetoconductance \[49, 50,

56\]. In the presence of a perpendicular magnetic field

B, time-reversal symmetry is broken \[49\]. A phase dif-

fERENCE arises between any two time-reversed electron

trajectories, whose constructive interference, in prin-

CIPLE able to localize electrons \[49\], is therefore broken

[56]. As a consequence \[49\]: (i) a negative magnetocon-

ductance is associated with WAL \[57\]; (ii) a vanishing

magnetoconductance is associated with e–e interaction (insensitive to B) \[56\]; (iii) a positive magnetocon-

ductance is associated with WL \[56, 57\].

In order to determine the origin of the resistance

upturn we thus measure the magnetoconductance of a

3LG device at 2 K. We find it positive, and reaching a

maximum at \(B_e = 2h/4\epsilon_0^2\tau_e\), \(\tau_e = 0.021\text{ T}\), as shown

in figure 4(a), where the magnetoconductance relative
to the value at zero field is plotted as a function of \(B\). In

order to rule out even a partial contribution from e–e

interactions, we also measure the device resistance while

heating the sample under \(B = B_e\). Figure 4(b) shows

that the logarithmic upturn is suppressed within the

noise level. This behavior is reversible upon removal of

\(B\). The logarithmic upturn saturates for \(T \lesssim 4\text{ K}\), a

feature usually assigned to the effect of finite channel size

\[66\]. These data support the conclusion that, in our

devices, WL is the source of the measured resistance

upturn and that the logarithmic correction to the con-

ductivity due to e–e interaction can be disregarded.

This is in contrast with earlier reports on SLG, where both

contributions were shown to be relevant \[69\]. We also

note that the magnetoconductance behavior of our 3LG

is qualitatively different from that in ref. \[18\], where

spin–orbit coupling was found to affect the magneto-

conductance behavior of EDL-gated 3LG. We do not

observe any significant influence of spin–orbit coupling.

We note, however, that the devices reported in ref. \[18\]

were obtained from FLG grown on silicon carbide. The

enhanced spin–orbit coupling reported in ref. \[18\] may

thus be associated both with the different fabrication

process and substrate.

The carrier lifetimes determine the WL behavior

\[49, 57\], and can thus be obtained from figure 4(a) \[58, 59\].

In SLG it was predicted that, due
to lattice symmetries, an additional \(\pi\) Berry phase is

accumulated by charge carriers scattering in closed

loops \[62–64\]. In 2LG such additional Berry phase is

instead \(2\pi\) \[59, 65\]. This means that in SLG the quantum

interference due to localization is always

destructive \[60, 61\], leading to an anti-localization

\[57\], while in 2LG the effect of the additional

cancel out, and the material should retain the

standard WL behavior \[59\]. In addition, WAL,

where the underlying elastic scattering mechanism

is due to charged impurities, is strongly suppressed

by intervalley scattering and trigonal warping \[58\].

Furthermore, refs. \[58, 59\] showed that SLG and

2LG have another quantum correction to the Drude

resistivity, always localized, due to elastic intervalley

scattering, and not affected by trigonal warping. As

a consequence, various localization behaviors were

reported \[57, 66, 67, 81–85\], depending on the sample

preparation and on the explored regime.

To the best of our knowledge, a WL model for \(N > 2\)

has not yet been developed. Earlier WL reports in FLG

made use of models developed for SLG and 2LG \[89–91\].
The simultaneous presence of both Dirac-like and parabolic bands in odd-N flakes makes an a priori determination of the total Berry phase difficult. The correction to the conductance due to the Berry phase is suppressed in all our experiments. This allows us to conclude that only elastic intervalley scattering is relevant for quantum interference.

Following the theoretical approach of ref. [59], the T dependence of the quantum correction to the 2d conductance is determined by the T behavior of the phase coherence lifetime $\tau_\phi$, as:

$$\delta\sigma_{WL}(T) = -\frac{e^2}{\pi h} \ln \left( 1 + 2^{1/2} \frac{\tau_\phi(T)}{\tau_\phi} \right) - \ln(\tau_\phi, \tau_\phi, \tau_\phi)$$

where $\tau_\phi$ is the interintervalley scattering lifetime, $\tau_\phi = 2\tau_\phi$ is the transport lifetime (associated with scattering from charged impurities [66, 67]) and $\tau_\phi$ is an effective lifetime associated with intravalley scattering and trigonal warping. On the right hand side of equation (1), the first term arises from interintervalley scattering, and resembles the conventional WL correction [49], apart from the factor two and the different elastic lifetime involved. Since the argument of the logarithm is always greater than one, this term is always negative.

The second term, arising from intravalley scattering, is positive or negative depending on the Berry phase, and is strongly suppressed the larger the value of $\tau_\phi^{-1}$ [58, 59]. The B dependence of the quantum correction to the conductance can be written as [58, 59]:

$$\delta\sigma_{WL}(B) = -\frac{e^2}{\pi h} \left[ F\left( \frac{B}{B_0} \right) - F\left( \frac{B}{B_0 + 2B_t} \right) \right] + \delta(B, B_0, B_t)$$

where:

$$F(x) = \ln(x) + \psi(1/2 + 1/x)$$

and

$$B_{\phi,\psi,\lambda} = (\hbar/4D_{\lambda,\psi}) \tau_{\phi,\psi,\lambda}^{-1}$$

with $\psi$ denoting the digamma function [59], $D_{\lambda,\psi} = \nu_\lambda^2/\rho_{\lambda,\psi}$ the diffusion coefficient [59], and $\nu_\lambda$ the Fermi velocity. We obtain $\tau_\phi$ by combining the measurement of $R_0$ from ab initio DFT calculations (see equation (7)), which gives $\tau_\phi = 5.48$ fs and $D_{\lambda,\psi} = 469$ cm$^{-2}$ s$^{-1}$ used henceforth.

For the data in figure 4(a) (3LG), the Berry phase is $\pi$ and $\delta(B, B_0, B_t) = -(-4e^2/\pi \hbar) F(B/(B_0 + B_t))$. We therefore use equation (2) to fit $\sigma_{2d}$ as a function of B in the 0–0.5 T range (red solid curve in figure 4(a)). This gives $\tau_\phi = 31.95$ ps, $\tau_\phi = 33.2$ ps and $\tau_\phi = 0.29$ ps. Thus, we are in the condition $\tau_\phi \ll \tau_{\phi,\psi,\lambda}$, where the zero-field antilocalization term $\delta_0$ is suppressed to the point of being negligible [58, 59].

We can compare these results with the existing literature at $T = 4$ K, immediately before the signal saturation for $T \lesssim 4$ K, shown in figure 4(b). Ref. [67] presented a WL study in SLG for different carrier densities, expressed in terms of the characteristic length-scales $L_{\phi,\psi,\lambda} = (D_{\lambda,\psi} \tau_{\phi,\psi,\lambda})^{1/2}$. For $n_2d \approx 1.5 \cdot 10^{12}$ cm$^{-2}$ and $T = 4$ K, they report $L_{x} = 1.5$ $\mu$m, $L_{y} = 0.8$ $\mu$m and $L_{z} = 75$ nm. This is the value of $n_2d$ closest to that in our devices, even if still at least one order of magnitude smaller. The characteristic lifetimes in our device give $L_{x} = 0.93$ $\mu$m, $L_{y} = 0.95$ $\mu$m and $L_{z} = 88$ nm, in agreement with the existing data [67].

Since the T dependence of $\tau_\phi$ contains information on the most relevant inelastic scattering mechanisms [49, 57] and following the previous results, we can use equation (1) with $\delta_0 = 0$ to describe the low-$T$ $(\lesssim 20–30$ K $)$ part of the $R_0$ as a function of T curves in figure 2. This approach is sound, since the smallest doping in our measurements is $\sim 1 \cdot 10^{13}$ cm$^{-2}$, a large value for solid-dielectric gating experiments [7, 8], and we do not find anti-localized behavior at these doping levels. Refs. [66, 68, 80] also reported that doping strongly enhances $\tau_\phi^{-1}$ (thus reducing $\delta_0$), since trigonal warping becomes more relevant the higher the energy separation from the Dirac point. This makes our approximation $\delta_0 = 0$ valid also for higher doping.

We can thus write the complete expression for the conductance of our FLG devices, valid for $T \lesssim 90$ K:

$$\sigma_{2d} = \sigma_{\text{Drude}} + \delta\sigma_{WL}$$

where $\sigma_{\text{Drude}}$ is [71]:

$$\sigma_{\text{Drude}} = \frac{e^2}{4} \tau \sum_i (\nu_i \nu_i^* \nu_i^* N_i) = e^2 \tau P(n_{2d})$$

Here $\nu_i$ and $\nu_i^*$ are the valley and spin degeneracies, respectively, $\nu_i^*$ is the Fermi velocity and $N_i$ the DOS at the $E_F$ of the $i$th band. Taking into account the Matthiessen rule [101] on the carrier lifetime at finite $T$ we have:

$$\tau^{-1} = \tau_{\text{tr}}^{-1} + \tau_{\text{inl}}^{-1}$$

where $\tau_{\text{inl}}$ is the T-dependent inelastic scattering lifetime. Substituting in equation (3) we get:

$$\sigma_{2d} = e^2 P(n_{2d}) \cdot \left( \tau_{\text{tr}}^{-1} + \tau_{\text{inl}}^{-1} \right)^{-1} = \frac{e^2}{\pi h} \ln \left( 1 + 2^{1/2} \frac{\tau_\phi}{\tau_\phi} \right) \tau_{\text{tr}},$$

In order to proceed further, we need to determine the prefactor $P(n_{2d})$, the transport lifetime $\tau_{\text{tr}}$ and the $T$ dependence of $\tau_\phi$.

We estimate $P(n_{2d})$ by computing the FLG band-structure through ab initio Density Functional Theory (DFT) for all our doping levels. We also perform a consistency check of the DFT estimations by running independent self-consistent tight-binding calculations for the doped 4LG. Here we present the results for Ber- nal stacked 4LG and 5LG. As a first approximation, we assume these systems to be isolated, i.e. we consider the effects of the substrate to be negligible.

We first investigate the band-structures of FLG within the all-electron, full-potential, linear augmented plane wave (FP-LAPW) method as implemented in the ELK code [72]. The local density approximation (LDA)
is used to describe the exchange and correlation. We fix the in-plane lattice constant to \( a = 2.46 \, \text{Å} \), i.e. the experimental in-plane lattice constant of graphite [74]. To model FLG we consider a three-dimensional supercell with a very high value of the \( c \) lattice constant so that the periodic images of the structures are at least 10 Å apart, in order to avoid interactions (e.g. for 4LG we take \( c = 40 \, \text{Å} \)) while the layer-layer distance is taken to be 3.35 Å independent of \( N \). Doping is simulated by adding electrons to the systems, together with a compensating positive background, as in refs. [28, 75] (Jellium model). The Brillouin zone is sampled with a \( 28 \times 28 \times 1 \) k-point mesh. The radius of the muffin-tin spheres for the carbon atoms is taken as 1.34\( \text{Å}_0 \), where \( \text{Å}_0 \) is the Bohr radius. We set \( R_{\text{MT}} K_{\text{max}} = 8 \), where \( R_{\text{MT}} \) is the smallest muffin-tin radius, \( K_{\text{max}} \) is a cutoff wave vector and the charge density is Fourier expanded up to a total energy tolerance of \( 10^{-4} \) Hartree.

Figure 5 plots the results for both 4LG (panel a) and 5LG (panel b) for different doping. The extra induced charge shifts \( E_F \) away from the Dirac point, eventually crossing multiple bands at \( K \) and \( K' \). In all cases, the crossing occurs well within regions where the energy dispersion is nearly linear. For the highest \( V_0 \) (+3 and +4\, eV), an additional important feature appears in the bandstructure. The large induced charge density brings down a further band at \( \Gamma \), which becomes populated and can thus contribute to transport. The dispersion of this new band is parabolic, and its appearance is reminiscent of that of the interlayer band induced by alkali metal intercalation in graphite intercalated compounds (GICs) [24].

Our approach neglects the intense electric field at the EDL/graphene interface, that in transition-metal dichalcogenides increases with doping and affects the effective mass value [40]. The simplified Jellium model was shown to capture the fundamental physics of doped SLG [28] and single-layer MoS\(_2\) [75]. We thus perform a consistency check for 4LG by comparing DFT with tight-binding calculations where the screening of the electric field by the charge carriers is accounted for. We compare the same terms \( \sum \nu_i N_i \). The \( \nu_i \) and \( N_i \) values obtained by tight-binding and DFT are within 30%. This suggests that our DFT approach is correct at least to a first-order approximation.

These calculations allow us to obtain both the DOS and the electron velocity of the populated bands at \( E_F \) which, in turn, according to equation (4), determine \( P(n_{2d}) \). Once \( P(n_{2d}) \) is known, \( \tau_{\psi} \) can be evaluated. Figure 4(b) shows that, in the absence of WL, the resistance saturates to a constant value for \( T < 8 \, \text{K} \). Thus, the saturation Boltzmann conductance \( e^2 \tau_{\psi} P(n_{2d}) \) can be estimated from the minimum \( R_{\text{SMin}} \), before the onset of the logarithmic upturn. This underestimates the saturation conductance (thus the scattering time) by less than 1%, which is negligible compared to the other sources of uncertainty in the evaluation of \( \tau_{\psi} \). This approach allows us to compute \( \tau_{\psi} = 2\tau_{\phi} \) as a function of \( n_{2d} \) in all our devices as:

\[
\tau_{\psi}(n_{2d}) = \frac{R_{\text{SMin}}^{-1}(n_{2d})}{e^2 P(n_{2d})} \tag{7}
\]

3.2. Scattering lifetimes versus temperature

We now consider the \( T \) dependence of \( \tau_{\psi} \). This can be done by using equation (1) without the \( \delta_0 \) contribution (since \( \tau_{\psi} \ll \tau_{\phi} \)) in the analysis of the low-\( T \) part (\( 4 < T < 20 \, \text{K} \)) of the curves of figure 2. By inverting this simplified expression, we obtain the \( T \) dependence of \( \tau_{\psi}(T)/\tau_{\phi} \) as shown in figures 6(a) (4LG) and (b) (5LG). Since \( \tau_{\psi} \) for \( T \lesssim 30 \, \text{K} \), can be assumed almost independent of \( T \) [67], the \( T \) dependence of \( \tau_{\psi}/\tau_{\phi} \) is the same as that of \( \tau_{\psi} \). By expressing \( \tau_{\psi} \propto T^{-p} \), we associate the \( p \) value to specific scattering processes. For \( T \) lower than the Bloch–Grüneisen\( T \) [19], e–ph scattering gives \( p = 3 \) for a standard 2-dimensional electron gas (2DEG) [53] and \( p = 4 \) for SLG [19]. The e–e scattering gives \( p = 1 \) for the Nyquist (small momentum exchange) process [55] and \( p = 2 \) for the Coulomb (large momentum exchange) process [54]. As shown in figure 6, the \( \tau_{\psi}/\tau_{\phi} \) curves show almost no superlinear behavior in the WL region. Nyquist e–e scattering is thus the dominant mechanism in this \( T \) range. This is consistent with the existing literature on SLG [66] and 2LG [68, 70]. In ref. [23] we reported that the \( T \) dependence below 100\, K has a linear plus a quadratic contribution, the linear being dominant for \( T_{\text{SMin}} \lesssim T \lesssim 30 \, \text{K} \) (see figures 4(a) and 5(c) of ref. [23]) and assigned this to competing Coulomb and Nyquist e–e scattering processes. This is consistent with the present observation of a dominant Nyquist contribution for \( T < 20 \, \text{K} \).

As any energy exchange with the surrounding environment breaks phase coherence [49], WL is suppressed by an increased probability of inelastic scattering associated with the \( T \) increase [46]. Thus, since the most relevant contribution to the phase-breaking time \( \tau_{\phi} \) arises from the inelastic scattering due to e–e interaction \( \tau_{\text{inel}} \) [49], we can write the \( T \) dependence of \( \tau_{\psi} \) in the entire 4–90\, K range as:

\[
\tau_{\psi}(T) \approx \tau_{\text{inel}}^{-1} = A \cdot T + B \cdot T^2 \tag{8}
\]

By inserting equation (8) in the first terms of the Drude conductance of equation (6), we can fit the curves at different doping in the intermediate \( T \) region (30–90\, K) where the WL contribution can be neglected. With the previously determined values of \( P(n_{2d}) \) and \( \tau_{\phi}(n_{2d}) \), this fit provides us the parameters \( A(n_{2d}) \) and \( B(n_{2d}) \). Finally, combining \( \tau_{\psi}(T) \) determined here with \( \tau_{\text{inel}} \) obtained from the low \( T \) (4–20\, K) region, we can extract \( \tau_{\text{inel}} \). Figure 6(b) shows the agreement between a fit based on equation (8) (black dashed lines) and the experimental data in the WL region (solid lines).

We first apply this procedure to the \( R_S \) as a function of \( T \) curves of the device on which the magnetoresistance was measured, obtaining \( \tau_{\psi} = 39.7 \, \text{ps} \).
$\tau_i = 49.7$ ps at 4 K, in agreement with the values coming from the magnetoresistance fit at 2 K. Once again, the comparison is carried out at 4 instead of 2 K due to the signal saturation for $T \leq 4$ K in figure 4(b). This comparison indicates that the analysis of the magnetocconductance and of the $T$-dependence of $R_S$ leads to equivalent estimates for $\tau_{\phi}$ and $\tau_i$. Thus, since we can perform the $R_S$ versus $T$ characterization of our devices more easily and more extensively than the magnetotransport measurements, due to the thermal expansion coefficient mismatch between the devices and the frozen electrolyte, we repeat the $R_S$ versus $T$ analysis on the 4LG and 5LG devices for different $V_G$.

### 3.3. Transport scattering lifetime versus carrier density

We now discuss the measured trends of $\tau_i$ as a function of $n_{2d}$. In standard 2DEGs, such as GaAs heterostructures [43], $\tau_i$ is equivalent to the elastic scattering lifetime ($\tau_i = \tau^e$) and follows a $n_{2d}$ dependence, $1 < \gamma < 2$ [43, 94, 95]. This implies that $\tau_i$ increases for increasing $n_{2d}$ due to the increased

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**Figure 5.** Band structure evolution with increase of doping in 4LG (a) and 5LG (b), for selected values of $n_{2d}$. For $n_{2d} < 2 \cdot 10^{14}$ cm$^{-2}$, the effect of the extra carriers is comparable to a rigid-band shift. Larger doping induces new structures.
screening of elastic scatterers by the increased density of charge carriers [86, 87]. In our devices, however, \( \tau_2 \) does not follow this behavior, suggesting a significant increase of the number of elastic scatterers with increasing gate voltage.

If we consider the 4LG device first, we observe that \( \tau_2 \) shows a monotonically decreasing behavior (figure 7(a), blue dots). One possible explanation was suggested in ref. [88], where the authors reported a decreasing mobility at high \( n_{2d} \) for 2DEGs. In contrast to Coulomb disorder, short-range disorder would become stronger with increasing \( n_{2d} \), thus increasing the scattering rate [88]. However, we think that this is not the main source of the increase of \( \tau_2 \) in our case. A degradation of the mobility of EDL-gated devices was reported in strontium titanate [76] and rhenium disulfide [77], where it was suggested that ions in the electrolyte act as charged impurities. Thus, we attribute this effect to the microscopic dynamics of how EDL gating induces extra carriers. EDL gating is able to induce modulations in excess of 10^14 cm^-2 to \( n_{2d} \) by accumulating a packed layer of ions in close proximity (~1 nm [7, 8]) to its surface. Refs. [78, 79] reported that charge-donating impurities at the SLG surface act as scattering centers.

We thus propose that the \( \text{Li}^+ \) ions in the EDL have a similar role. Their increased density with \( V_G \) competes with the increased screening induced by the extra carriers and this determines \( \tau_2 \). In 4LG, the former effect would be stronger in the entire \( n_{2d} \) range, resulting in the monotonic reduction of \( \tau_2 \). If this is the case, we expect 5LG to be less sensitive to the extra scattering centers. These are localized at the surface of the first layer, and ref. [76] showed that introducing a thin spacer between the ions and the conductive channel greatly improves carrier mobility. With respect to 4LG, 5LG features one further conductive channel due to the fifth layer, which is thus further separated from the scattering centers. Indeed, this is what we observe: the 5LG device shows an initial decrease for \( n_{2d} \lesssim 2 \cdot 10^{14} \text{ cm}^{-2} \) followed by an increase for \( n_{2d} \gtrsim 4 \cdot 10^{14} \text{ cm}^{-2} \) (figure 7(b)), blue dots). Overall, the \( \tau_2 \) in 5LG is nearly constant with \( n_{2d} \), as if the two competing effects on mobility were almost canceling out. As for 3LG, we estimate \( \tau_2 \sim 2.5 \) fs at \( n_{2d} \sim 5.2 \cdot 10^{14} \text{ cm}^{-2} \), which is smaller than in 4LG. This corresponds to a suppression by a factor ~18 of the low-\( n_{2d} \) value in 3LG, higher than the ~15 times one in 4LG. Thus, 3LG appears even more sensitive to the accumulation of scattering centers at its surface than 4LG, in accordance with the previous results.

3.4. Dephasing and intervalley scattering lifetimes versus carrier density

Let us now consider the doping dependence of \( \tau_2 \) and \( \tau_i \) in 4LG and 5LG, in order to allow for a direct comparison with the corresponding values for 3LG estimated from magnetoresistance. Figure 7 shows that the doping dependence of \( \tau_i \) is weakly decreasing or nearly constant within the uncertainty range: from 6.6 ± 0.7 ps to 1.7 ± 0.9 ps for 4LG, from 9.8 ± 4.1 ps to 7.6 ± 5.0 ps for
5LG. This dependence was already observed [66, 80], albeit for $n_{2d} \lesssim 1.5 \times 10^{13} \text{ cm}^{-2}$, much lower than the $n_{2d}$ considered here ($n_{2d} \gtrsim 1 \times 10^{14} \text{ cm}^{-2}$). In contrast, the doping dependence of $\tau_\varphi$ is more significant, as it is monotonically decreasing in the entire range in 4LG, while it shows a small inversion in slope on the final point for 5LG. These results are in contrast with earlier findings on FLG for $n_{2d} < 2 \times 10^{13} \text{ cm}^{-2}$ [80]. As already pointed out, e–e Nyquist scattering is the dominant dephasing mechanism in the low $T$ range. Therefore, we can write [43]:

$$\tau_{\varphi}^{-1}(x) = \frac{k_B T \text{ ln}(x)}{2\hbar}, \quad x = \frac{E_F \tau_\varphi}{\hbar}. \quad (9)$$

The condition $x \sim 1$ (Ioffe–Regel criterion [96]) characterizes the Anderson metal-to-insulator transition [97]. The metallic regime corresponds to $x \gg 1$, leading to a $\tau_\varphi$ increasing with $n_{2d}$ (i.e. with increasing $E_F$). Under strong localization conditions, $x < 1$ and the Boltzmann model no longer holds [98]. Intermediate $x$ values mark a crossover from strong to weak localization [99] and correspond to a region where $\tau_\varphi$ can exhibit a decreasing behavior with $n_{2d}$. The exact form of the $\tau_{\varphi}(n_{2d})$ curves is determined by the dependence of $E_F$ on $n_{2d}$ (which, in the linear regions of the bands, is a square root [100]) and on $\tau_\varphi$. If we compute the value of $x$ corresponding to our data by using the $\tau_\varphi$ values determined at 4 K, we find that, for 4LG, $x = 2.7 \pm 0.2$ in the entire range of negative charge induction, while, for 5LG, $x < 2.7$ for $V_G = 1$ and 2 V, $x > 5$ for $V_G = 3$ and 4 V. Thus, the 4LG device is always in the ‘crossover’ condition, while in 5LG the typical 2DEG behavior is restored for $n_{2d} \gtrsim 2 \times 10^{14} \text{ cm}^{-2}$. Due to the dependence of $x$ on $\tau_\varphi$, these results are consistent with the fact that the ion dynamics in the EDL gating provides a competition between an increase in the number of elastic scattering centers and of $n_{2d}$ with increasing $V_G$. In 4LG the concurrent increase of $E_F$ and decrease of $\tau_\varphi$ (see figure 7(a)) could maintain $x$ almost constant. In 5LG at $n_{2d} \gtrsim 2 \times 10^{14} \text{ cm}^{-2}$ the increase of both $E_F$ and $\tau_\varphi$ (see figure 7(b)) would eventually lead to the increase of $x$. This behavior could be due to the differences in both surface-to-volume ratio and bandstructure of 4LG and 5LG, and is in agreement with the behavior of $\tau_\varphi$ in the two samples.

3.5. Comparison with the single-band scattering model

In order to further analyze these results, we evaluate the theoretical values of the e–e scattering lifetimes by using the definition of $x$ given in equation (9) with $E_F(n_{2d})$ determined by DFT and $\tau_\varphi$ taken from the determined $\tau_\varphi$ values. The results are shown in figure 7 as orange circles and shaded bands (that represent the uncertainty regions). Our $\tau_\varphi$ (black dots) are in agreement with the theoretical predictions within an order-of-magnitude. However, the latter are nearly doping-independent in contrast with experiments. This different behavior is particularly evident in 4LG. As expected, the addition of the Coulomb scattering term [66] does not affect appreciably the predicted values at this low $T$. Since the theoretical $\tau_\varphi$ are dependent on the details of the $ab$ initio calculations, the inconsistency might be related to the approximations in the DFT calculations of the effects of the high electric field. However, a more important reason for the mismatch lies in the limitation of the hypotheses underlying the theoretical derivation of the Nyquist scattering. Both the single-band and the parabolic-dispersion assumptions do not hold in FLG, particularly when the $E_F$ is so far from the Dirac point [92, 93].

3.6. Comparison with the scattering lifetimes as determined by pump-probe spectroscopy

A comparison with the other experimental technique able to probe the e–e scattering lifetime, i.e. pump-probe spectroscopy, is not immediate, due to the different conditions in the probed electron system between transport and spectroscopic measurements. Low-bias ($<0.2 \text{ V}$ [105]) transport measurements, such as the ones in this work, involve only scattering processes between carriers very close to the $E_F$. Pump-probe measurements, on the other hand, generate a strongly out-of-equilibrium carrier population by optical excitation. This population first thermalizes to a quasi-equilibrium distribution of ‘hot’ carriers via e–e [106, 108, 111] and e–ph [105–110] scattering processes. The ‘hot’ carriers then cool down to the rest of the Fermi sea over a much longer time scale by scattering with optical phonons [105–111]. This makes the two types of measurements hardly comparable, as the e–e scattering lifetime is heavily dependent on the difference in energy between the scattering electrons and the $E_F$ [104, 112]. Moreover, pump-probe experiments are typically performed at room $T$ [106–108, 110, 111], where the Coulomb term dominates e–e scattering, while our experiments are at low $T$, where the Nyquist term dominates. With all these caveats, if we extrapolate to room $T$ the e–e scattering lifetimes using equation (9) and imposing $T = 300 \text{ K}$. This gives $\tau_{\varphi}$ between $\sim 1$ and 7 fs, in agreement with existing literature [106, 108, 111].

4. Conclusions

We explored the electronic transport properties of 3-, 4- and 5-layer graphene in the doping regime in excess of $\sim 10^{13}$–$10^{14} \text{ cm}^{-2}$ and in the 4–30 K temperature range. We used electric double layer gating to dope the samples up to $\sim 7 \times 10^{14} \text{ cm}^{-2}$. We found evidence of quantum coherent transport in the entire carrier density range. Magnetoresistance measurements showed that, in the 4–30 K range, transport is dominated by weak localization in the diffusive regime, and that the behavior of 3LG, 4LG and 5LG is described by the theoretical models developed for SLG and 2LG. We combined the experimental results with DFT calculations to determine the carrier scattering lifetimes as a function of the carrier density for different number of layers, and determined
that electron–electron scattering with small momentum transfer (Nyquist process) is the main source of dephasing at low temperatures. Both the transport scattering lifetime and the phase coherence lifetime show a non-trivial dependence on |qdg|. We explained the behavior of τϕ in terms of a competing modulation of doping and density of charged scattering centers induced by EDL gating. The doping dependence of τϕ points to a gate-tunable crossover from weak to strong localization, highlighting the limits of applying single-band models to multi-band systems, such as heavily doped few-layer graphene.

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