Quantum Nature of Charge Transport in Inkjet Printed Graphene Revealed in High Magnetic Fields up to 60T

Oleg Makarovsky
University of Nottingham, UK

EMFL Nottingham 11 June 2024

The team

Nottingham Physics
Nathan Cottam, Oleg Makarovsky, Amalia Patane,
Mark Fromhold, Laurence Eaves

Nottingham Engineering, Centre for Additive Manufacturing
Lyudmila Turyanska, Feiran Wang, Jonathan S. Austin,
Christopher J. Tuck, Richard Hague

LNCMI Toulouse
Walter Escoffier, Michel Goiran, Mathieu Pierre

LNCMI

EMFL European Magnetic Field Laboratory

EPSRC Engineering and Physical Sciences Research Council

Centre for Additive Manufacturing

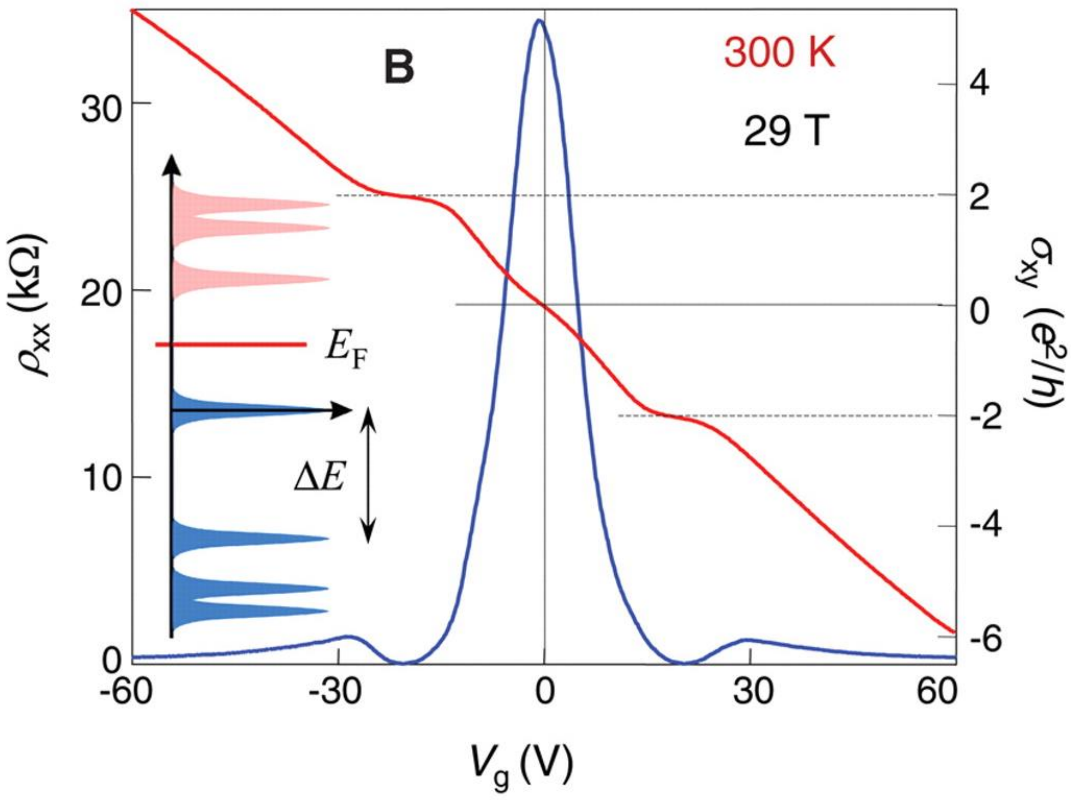
The University of Nottingham

OUTLINE

- Quantum Hall effect in different types of graphene.
- Ink-jet printed graphene (iGraphene).
- Droplets vs Stripes. How different iGraphene devices behave in high magnetic fields.
- Do we see quantum effects in iGraphene?

Quantum Hall effect in graphene. The best.

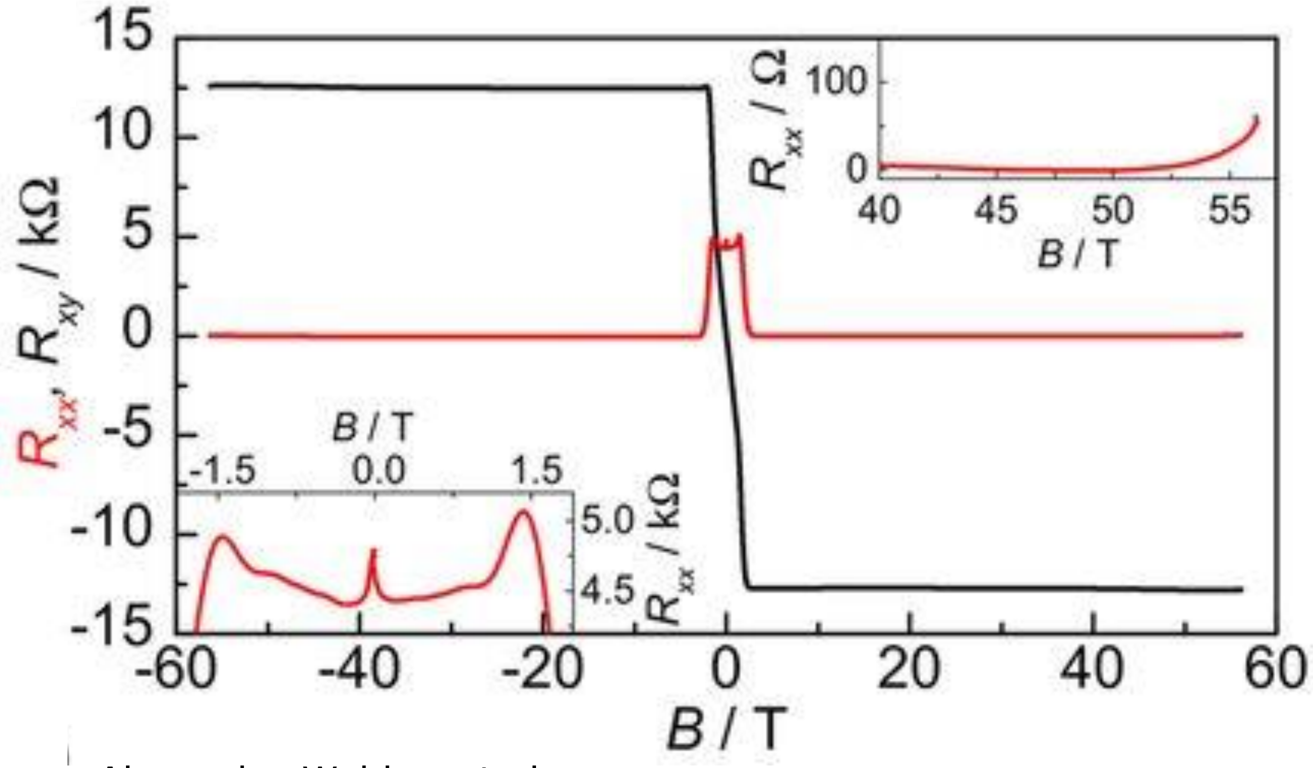
At 300 K in exfoliated graphene



Room Temperature Quantum Hall effect

Novoselov et al., Science 315, 1379 (2007)

At 2 K in epitaxial graphene on SiC

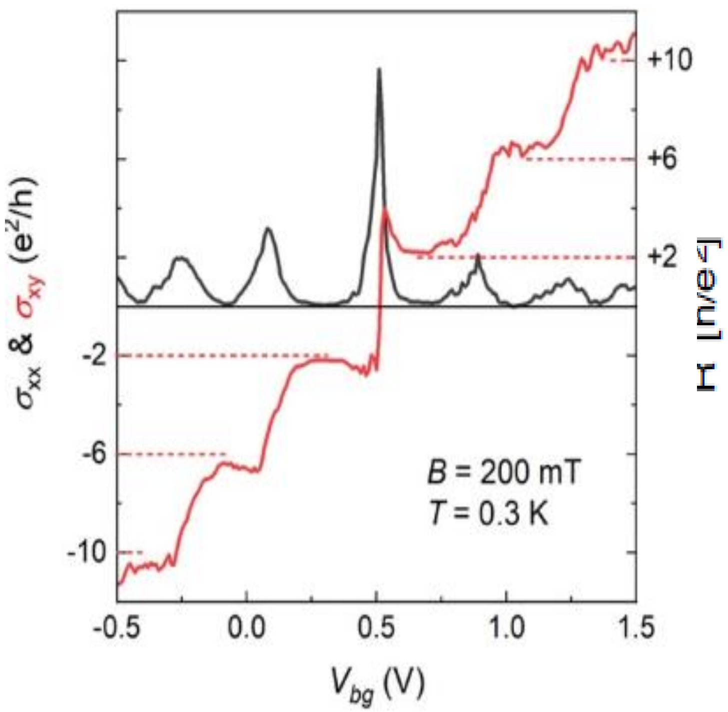


Alexander-Webber et al.,
"**Giant quantum Hall plateaus** generated by charge transfer in epitaxial graphene"
Scientific Reports 6, 30296 (2016)

Quantum Hall effect in graphene. The rest.

High mobility CVD

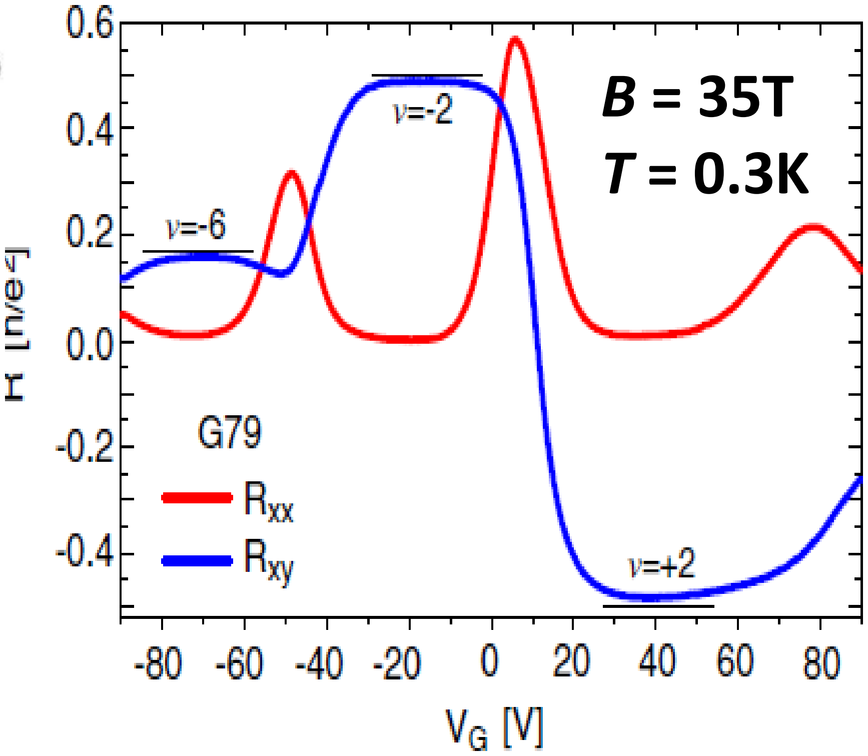
$\mu > 10{,}000\ cm^2/Vs$



Siyu Zhou et al., Nanomaterials. 12, 13777 (2022)

Low mobility CVD

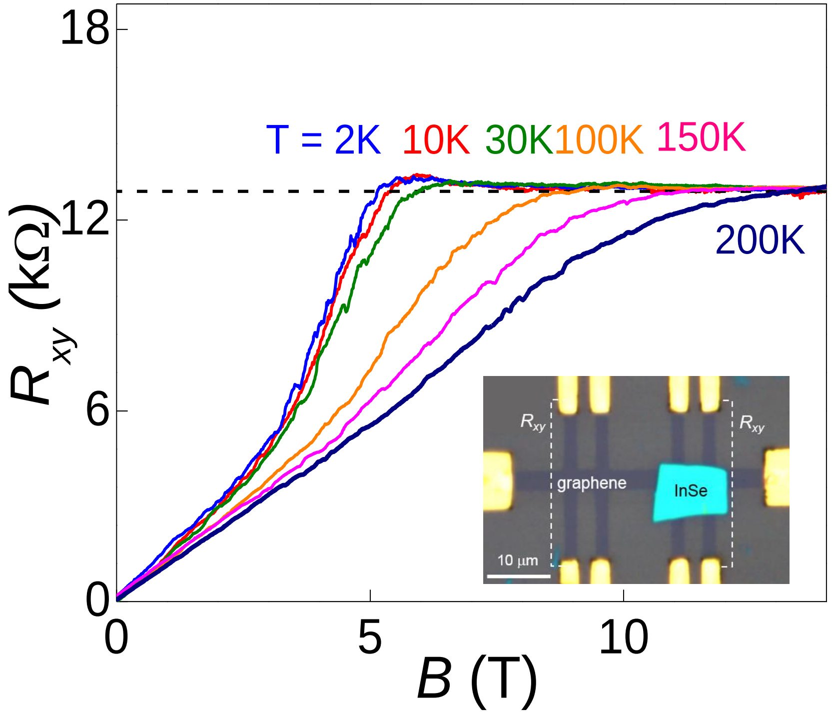
$\mu < 1000\ cm^2/Vs$



K. Bennaceur et al., PRB. 92, 125410 (2015)

Heterostructures

Graphene/InSe

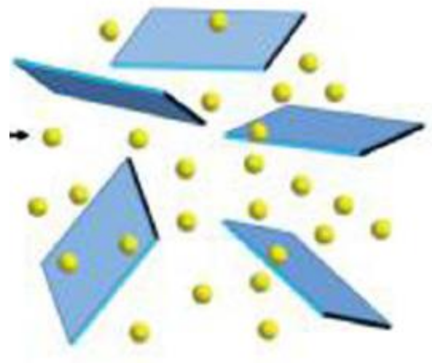


Kudrynskyi et al., Phys. Rev. Lett. 119, 157701, 2017

Is any graphene a good quantum material?

ink-jet-printed Graphene (iGraphene).

Flakes



Flake size ~ 50nm

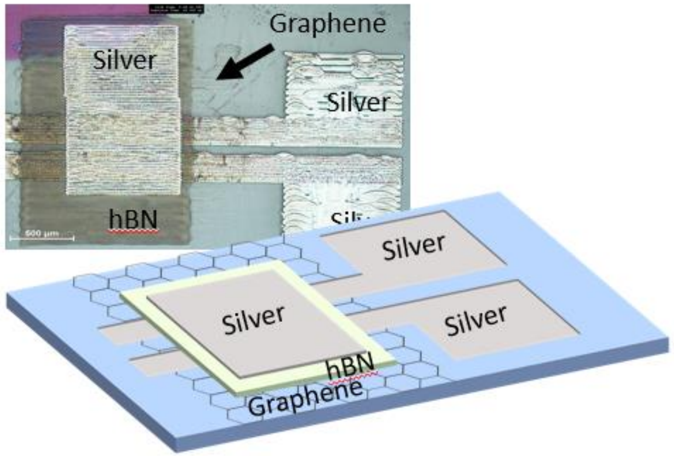
Ink

Sigma-Aldrich (793663)

Printer

Fujifilm Diamatix DMP-2800 and a 10 pL drop volume cartridge with nozzles of a = 21.5 μm

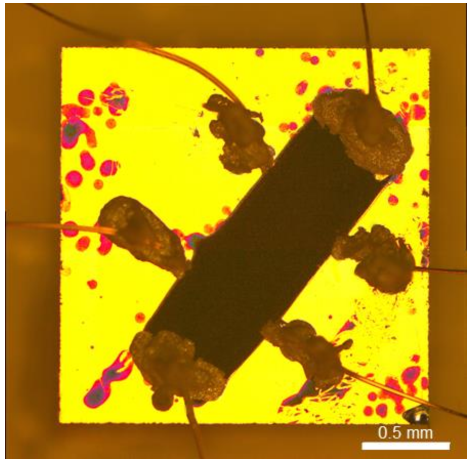
Devices



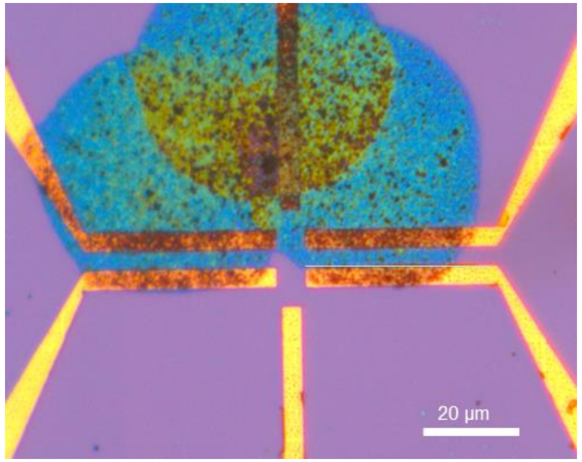
Fully ink-jet-printed transistor

F. Wang, et al., Adv.Func.Mater. 2021, 31, 2007478

Stripes

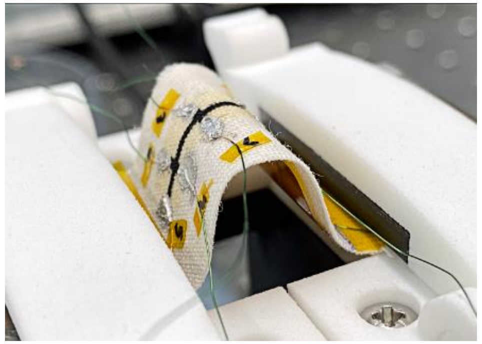


Droplets

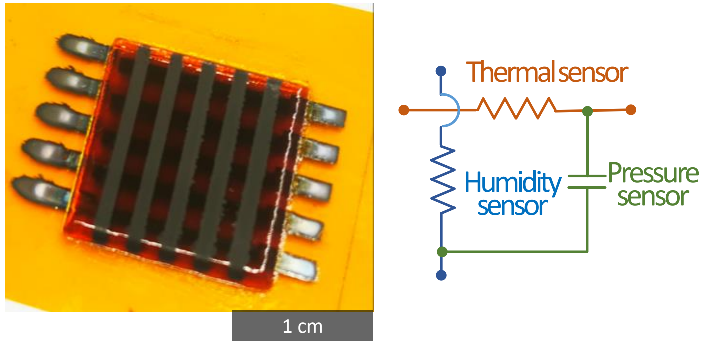


N. Cottam et al., Small 2311416 (2024)

Flexible detector

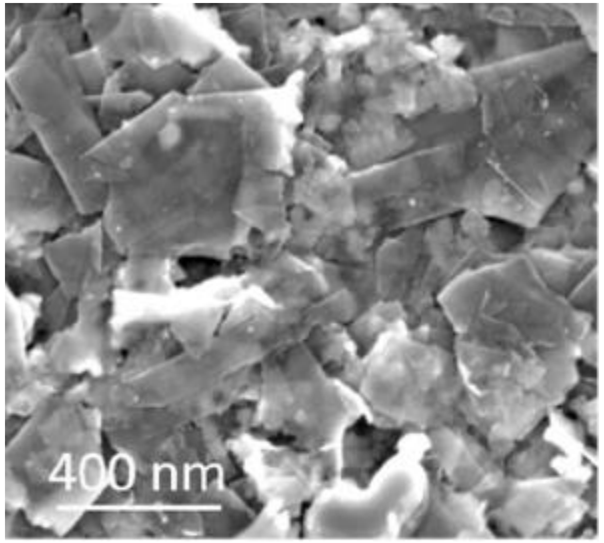


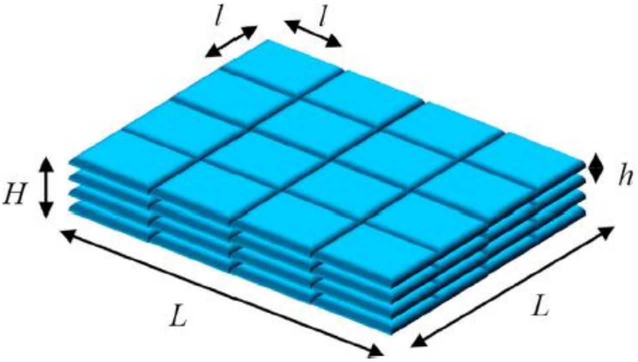
Multifunctional Sensor



F. Wang, et al., Multifunctional inkjet-printed graphene sensor, to be submitted in 2024

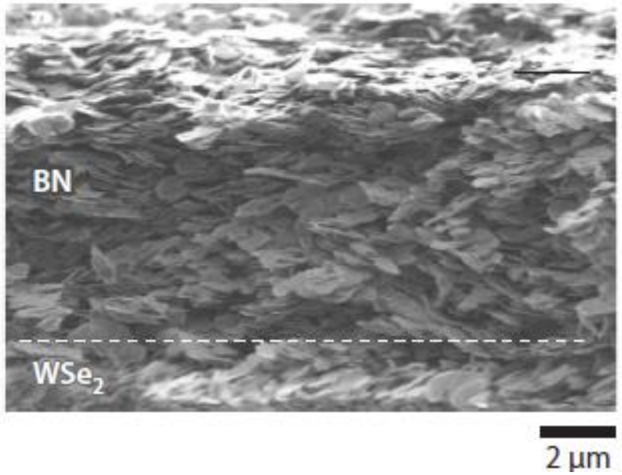
Electron transport in iGraphene. Network of 2D nanosheets.

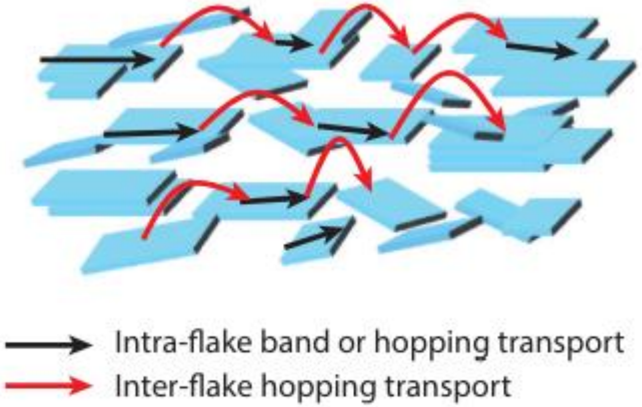




Percolation transport, strongly dependent on porosity, and inter-flake junction distance.

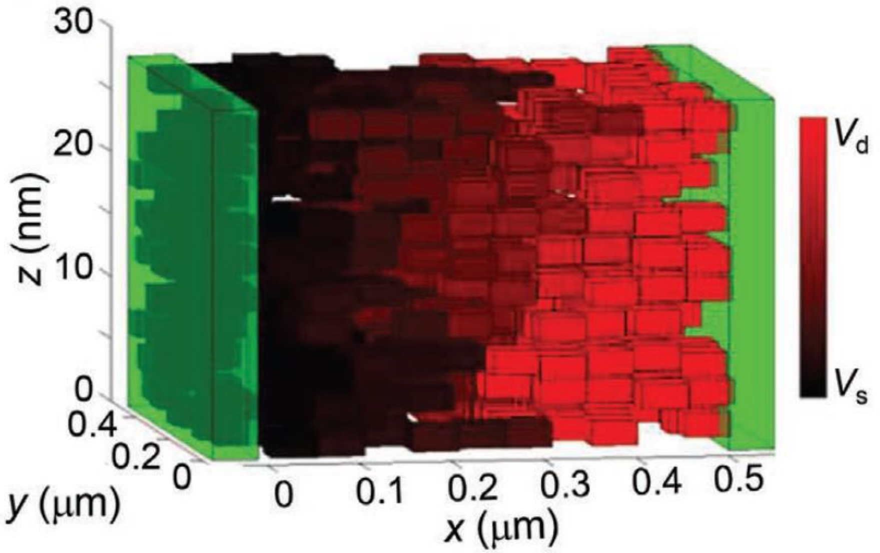
S. Barwichet al., Carbon 171, 306 (2021)

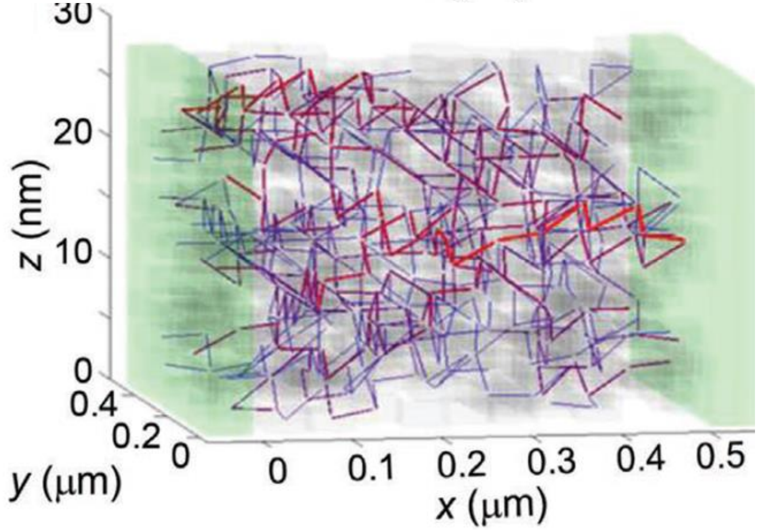




Charge transport within an individual flake can be diffusive or hopping-type, interflake transport is can be variable-range hopping,

V. K. Sangwan et al., Annu. Rev. Phys. Chem. 69, 299 (2018)

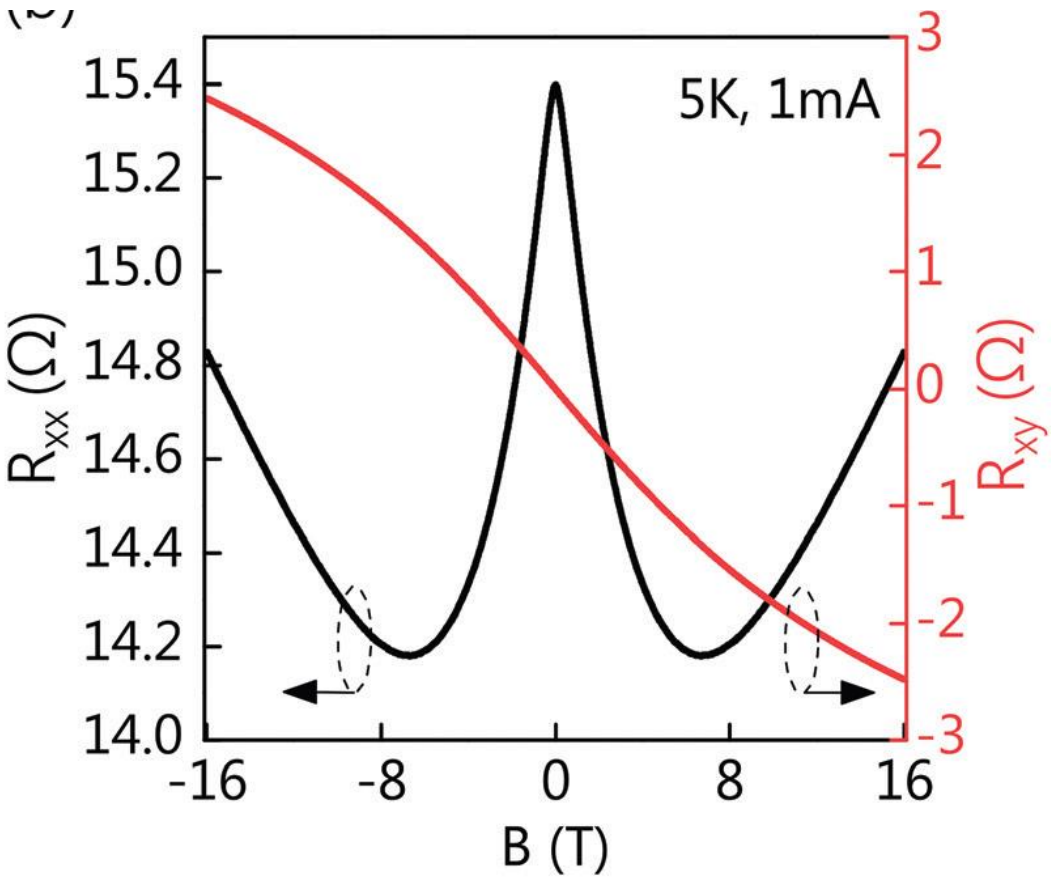




Monte Carlo simulation of the potential (top) and electron trajectories (bottom) in a very small iGraphene device

Feiran Wang et al., Adv. Funct. Mater 2007478 (2020)

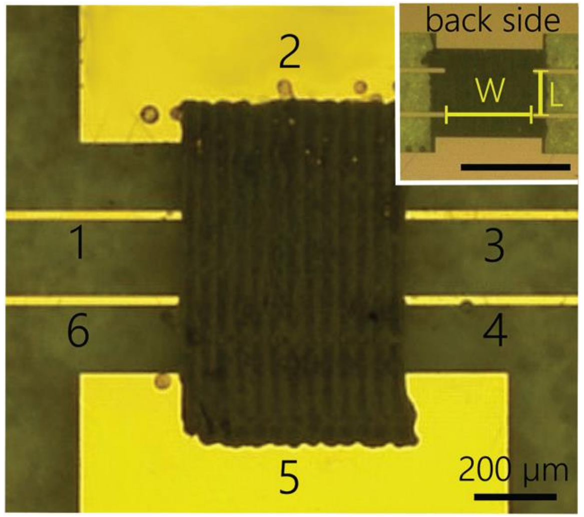
Typical iGraphene in magnetic field.

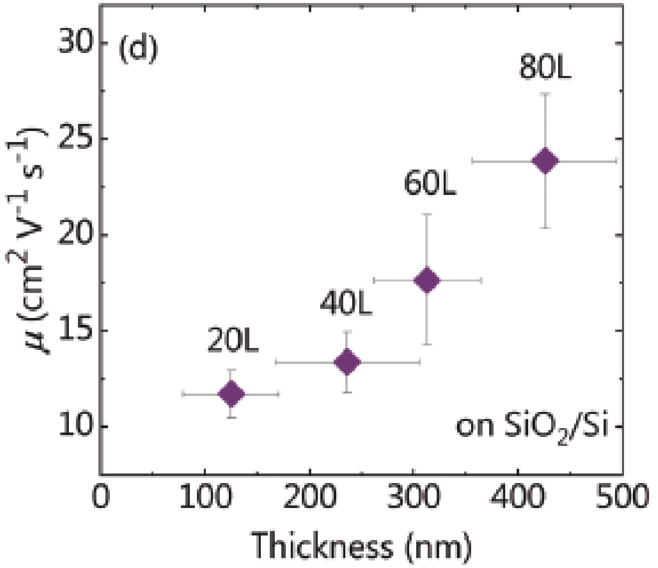


Nanoscale
ROYAL SOCIETY OF CHEMISTRY
PAPER
View Article Online
View Journal | View Issue
Check for updates
Cite this: *Nanoscale*, 2020, **12**, 6708

Inkjet-printed graphene Hall mobility measurements and low-frequency noise characterization

Gabriele Calabrese, *†[a] Lorenzo Pimpolari,†[a] Silvia Conti, [a] Fabrice Mavier,[a] Subimal Majee, [b] Robyn Worsley,[b] Zihao Wang,[c] Francesco Pieri, [a] Giovanni Basso,[a] Giovanni Pennelli,[a] Khaled Parvez, [b] David Brooks,[b] Massimo Macucci,[a] Giuseppe Iannaccone,[a] Kostya S. Novoselov,‡[c,d] Cinzia Casiraghi [b] and Gianluca Fiori[a]

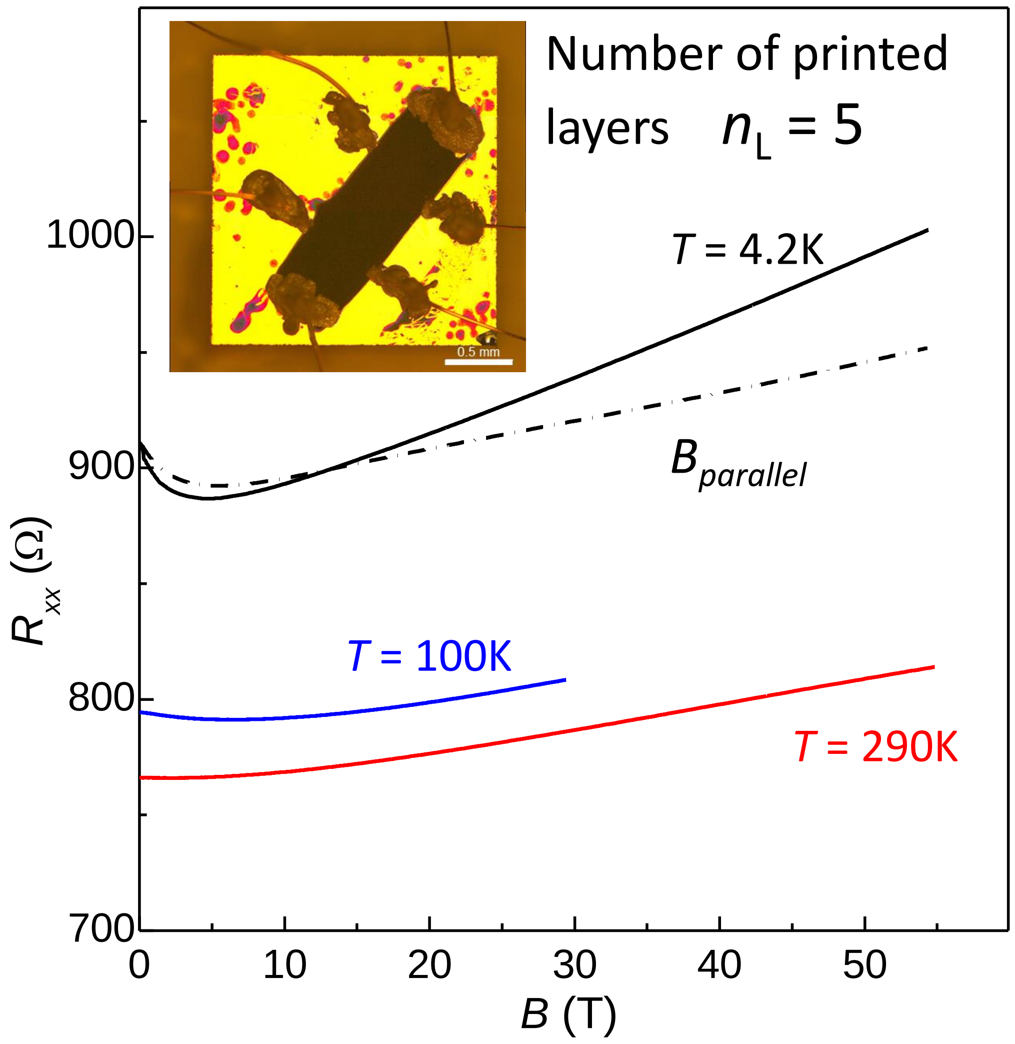


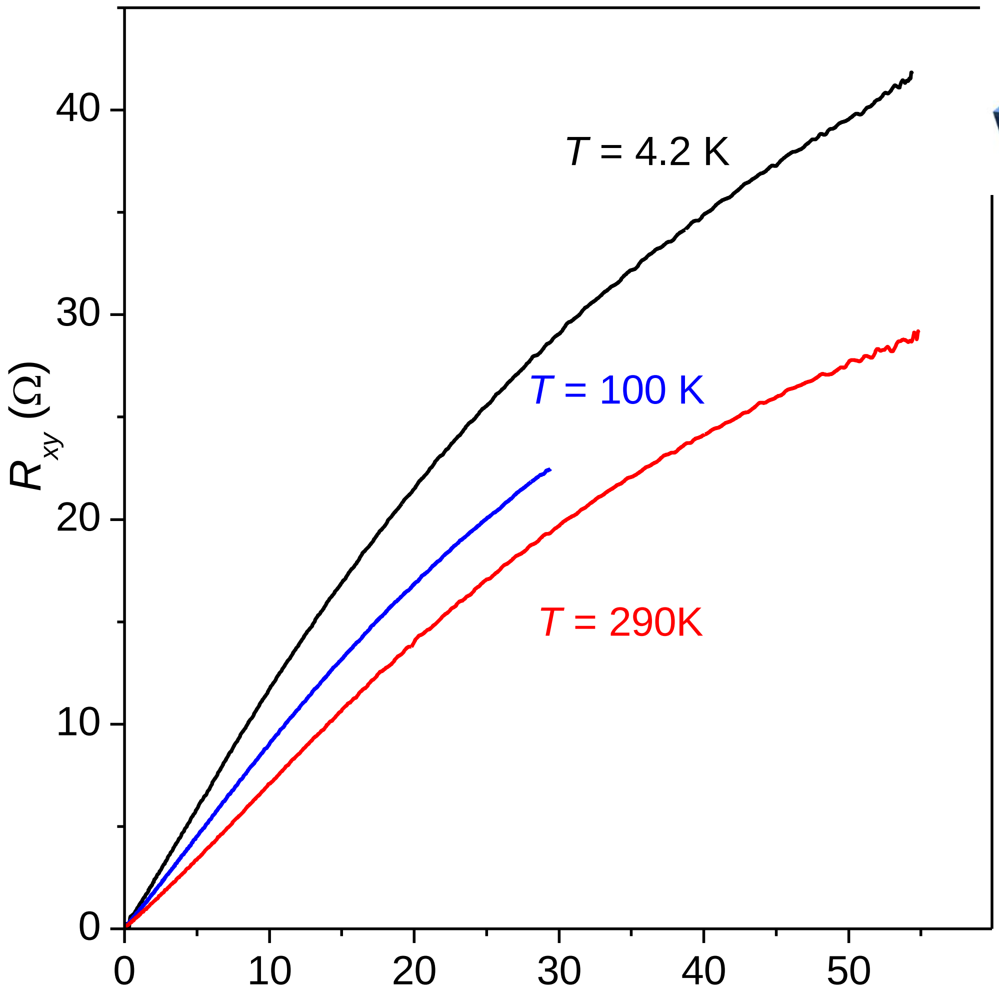


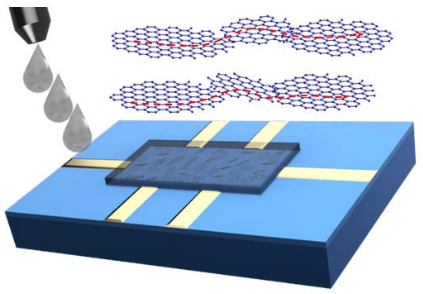
Strong fluctuations of R_{xy},
Hall effect measurable at >20 layers only
Sublinear Hall

Weak localisation at $B < 7$ T

iGraphene Stripes in high magnetic field.







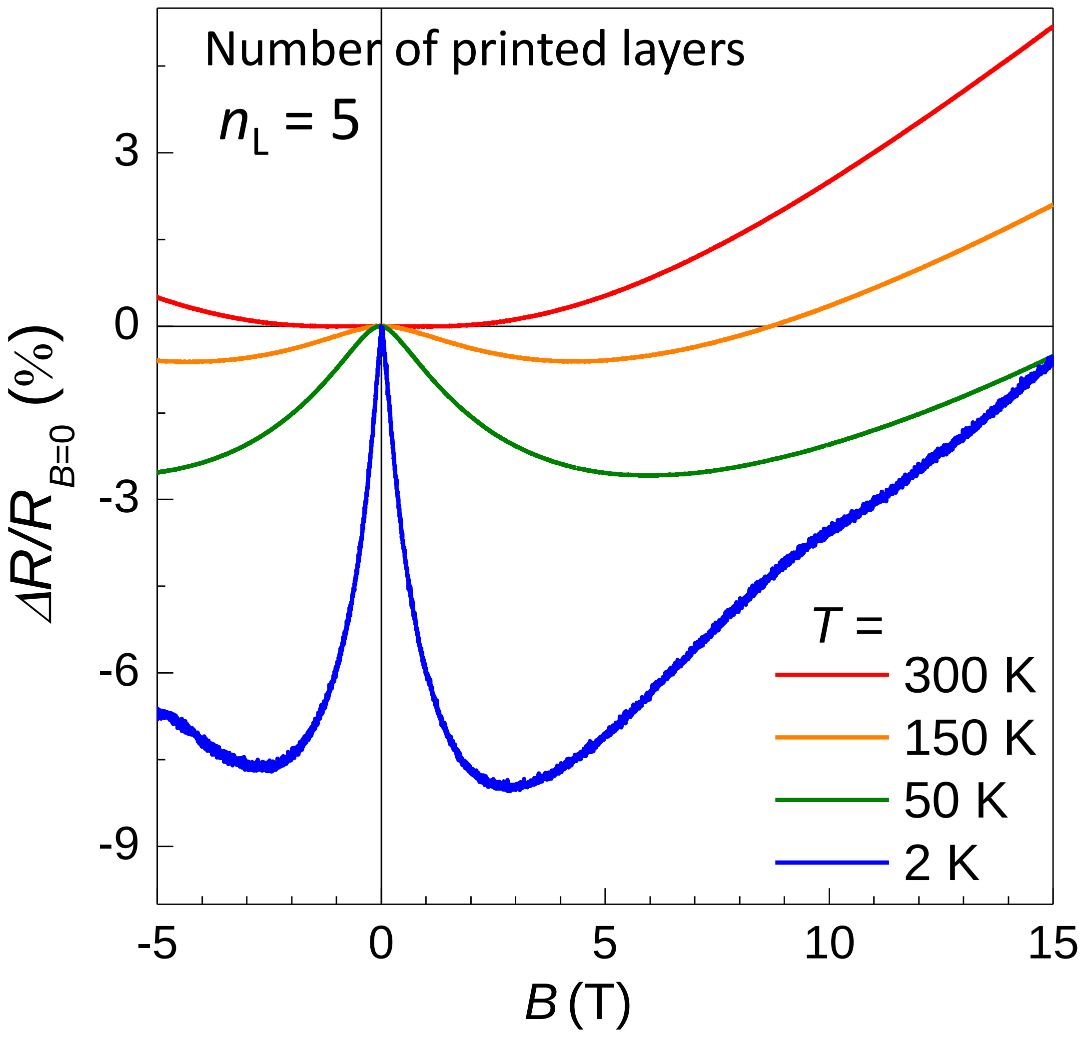
No Shubnikov – de Haas oscillations or Quantum Hall effect

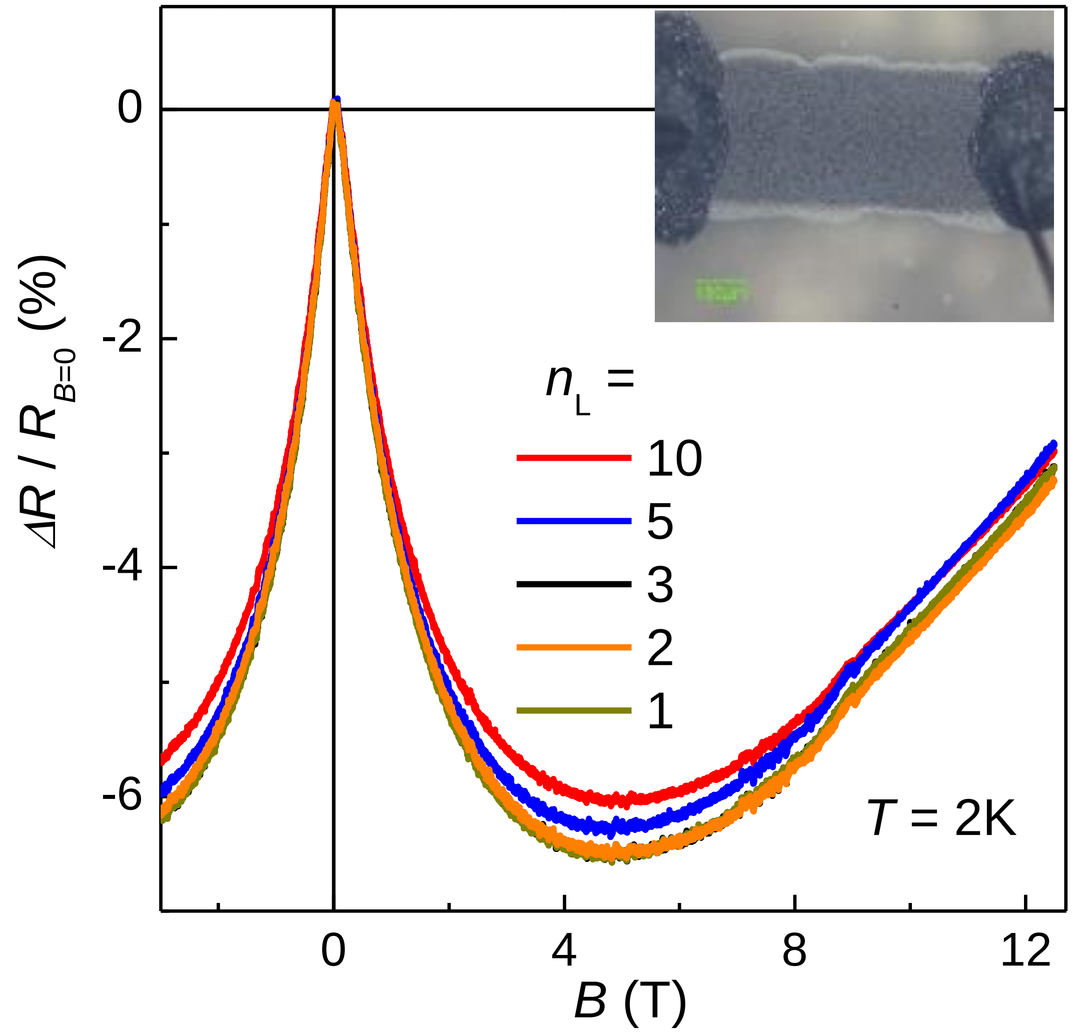
In high fields linear $R_{xx}(B)$ and sublinear $R_{xy}(B)$

Hall mobility $\mu_H \approx 10$ cm^2/Vs

N. Cottam et al., Small 2311416 (2024)

iGraphene Stripes and in "low" magnetic field.

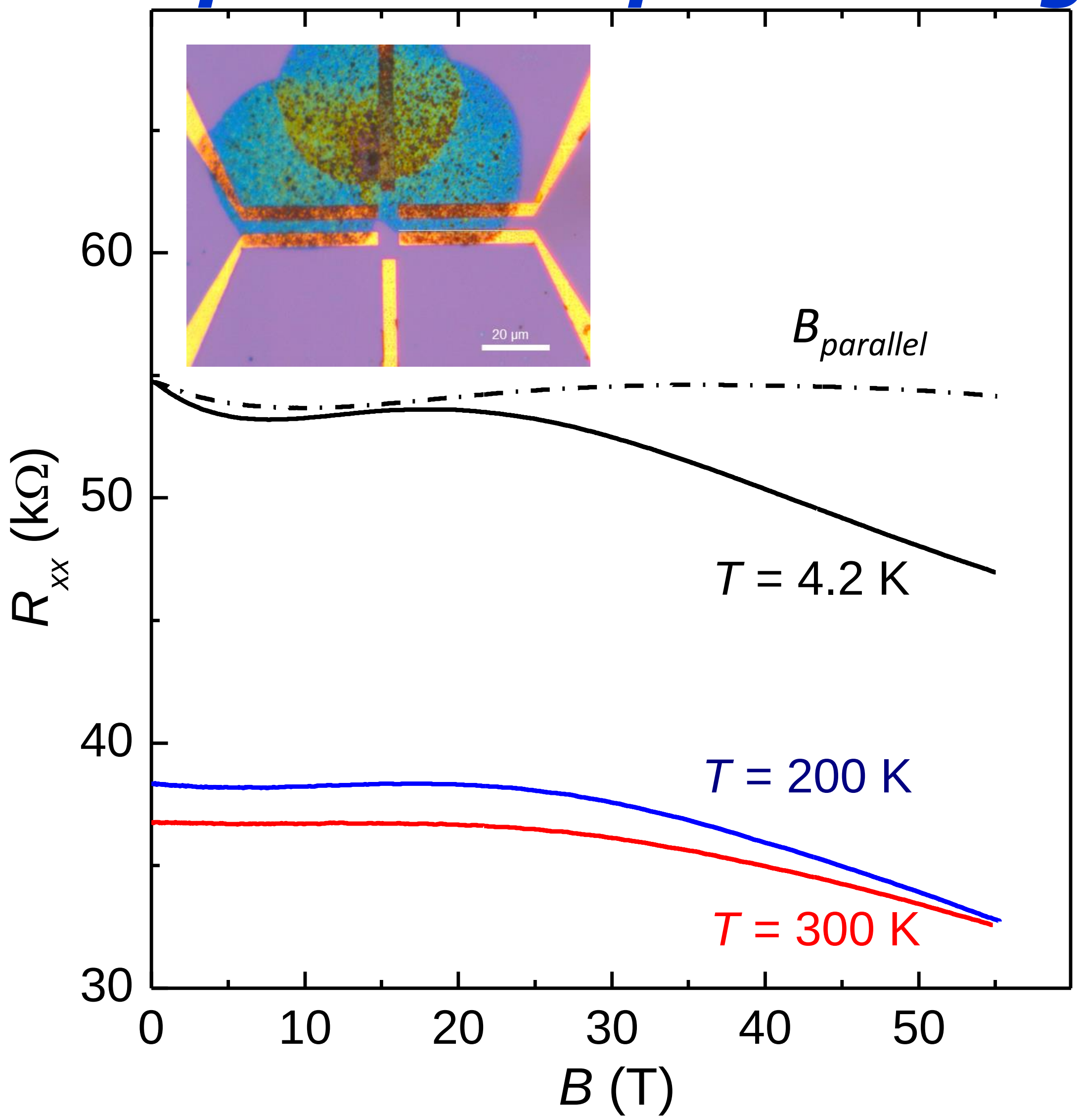




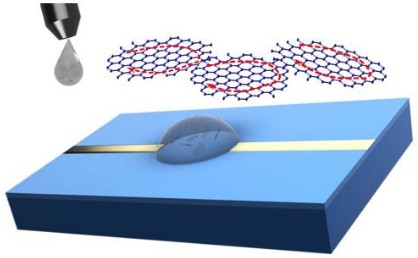
Strong temperature dependence.

No dependence on the film thickness.

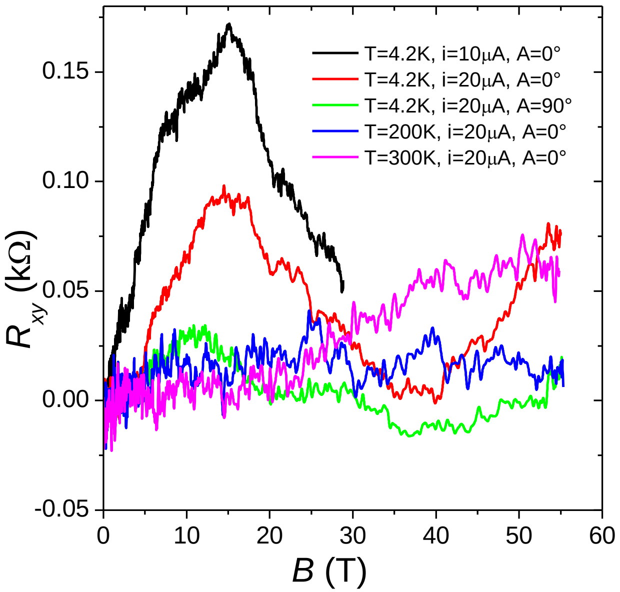
iGraphene Droplets in high magnetic field.



iGr$_{drop}$



No measurable R_{xy}

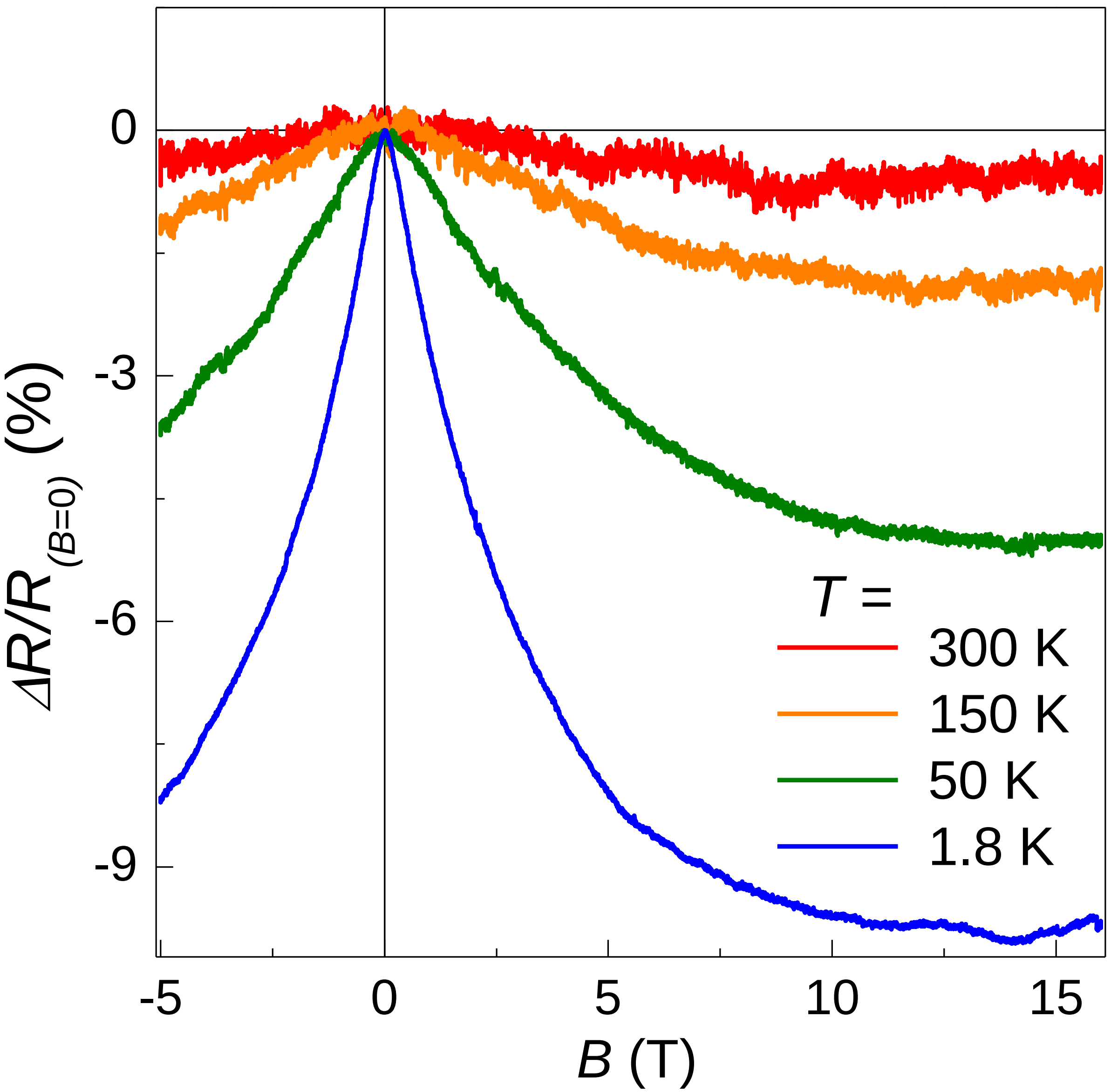


No Shubnikov – de Haas oscillations or Quantum Hall effect

In high fields negative, linear magnetoresistance absent in parallel field.

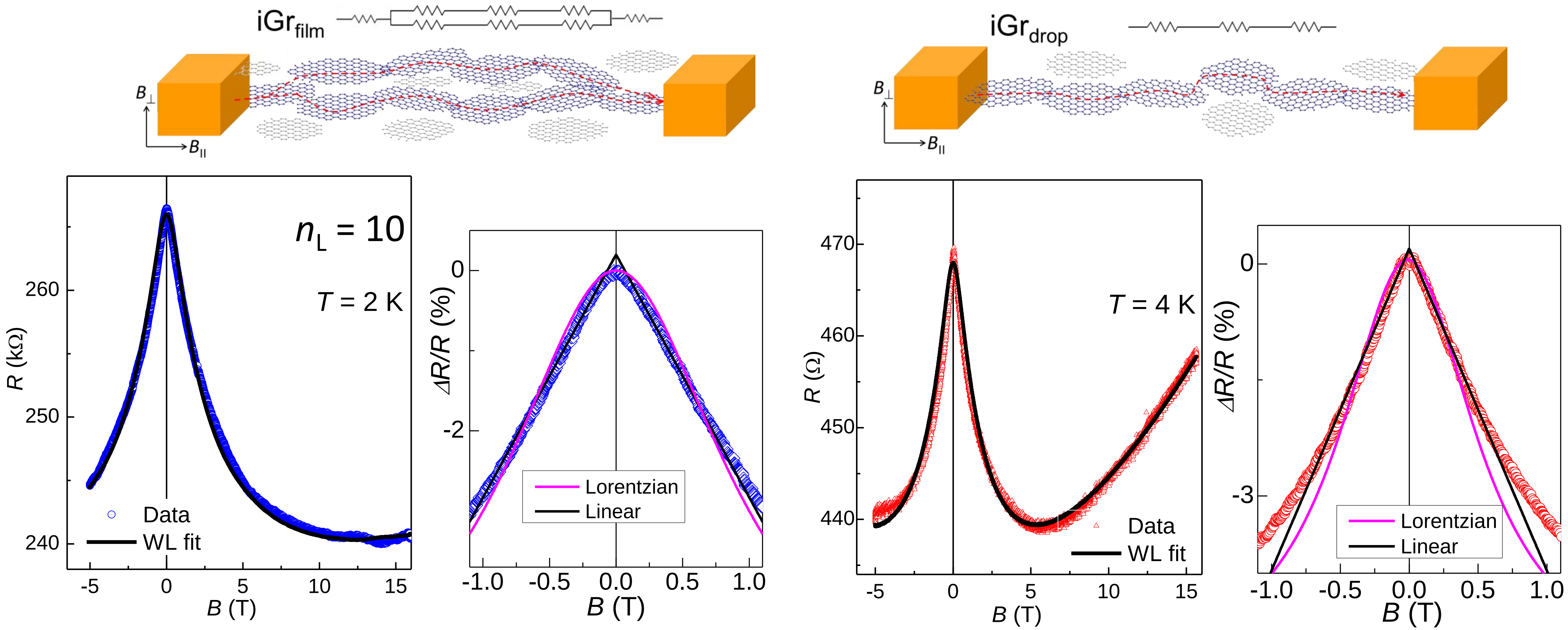
N. Cottam et al., Small 2311416 (2024)

iGraphene Droplet in "low" magnetic field.



N. Cottam et al., Small 2311416 (2024)

Droplets vs Stripes in low magnetic fileds



Very high WL critical magnetic field, $B > 5$T. Typical field for WL in single layer graphene <0.1T [*PRL 103, 226801 (2009)*].

Unusual (linear) shape of $R(B)$ at $B < 0.5$T for droplet devices

Modelling WL effect.

$$\Delta\rho_{iGr}(B) = N_{Gr}\frac{e^2\rho^2}{\pi h}\left[F\left(\frac{\tau_B^{-1}}{\tau_\varphi^{-1}}\right) - F\left(\frac{\tau_B^{-1}}{\tau_\varphi^{-1}+\tau_i^{-1}}\right) - 2F\left(\frac{\tau_B^{-1}}{\tau_\varphi^{-1}+\tau_*^{-1}}\right)\right] \qquad L_\varphi = \sqrt{D\tau_\varphi}$$

F.V. Tikhonenko et al., PRL 103, 226801 (2009)

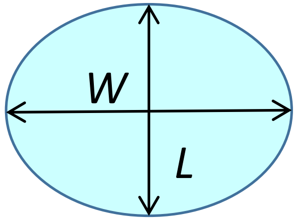
where N_{Gr} is effective number of layers, $F(x) = ln(x) + \psi\left(\frac{1}{2}+\frac{1}{x}\right)$, ψ is the digamma function, L_φ and τ_φ are the dephasing length and time due to inelastic scattering, τ_i is the elastic intervalley scattering time also associated with the edge scattering; τ^* is a scattering time relevant to a combination of different elastic intravalley scattering processes; $\tau_B^{-1}=4eDB/\hbar$ where diffusion coefficient $D=v_F L_0/2$ Fermi velocity is $v_F = 10^6$ m/s; $L_0=v_F\tau_{tr}$ is the mean free path where $\tau_{tr}=\mu m^*/e$ is the transport scattering time and graphene effective mass $m^* \approx 0.08 me$ ($V_a = 0$ and $p \approx 10^{13}$ cm^{-2}).

Sample	Number of layers, n_L	ρ_{max} [Ω]	N_{gr}	τ_φ [ps]	τ_i [ps]	τ_* [ps]	L_φ [nm]
iGr_{drop}	1	266 000	0.1	5.0	7.5	0.15	14
iGr_{film}	1	1858	10	2.2	2.8	0.135	22.8
iGr_{film}	2	2135	7	2.38	2.26	0.115	23.7
iGr_{film}	5	866	20	2.12	2.4	0.158	22.4
iGr_{film}	10	468	31	2.3	2.3	0.16	23.3

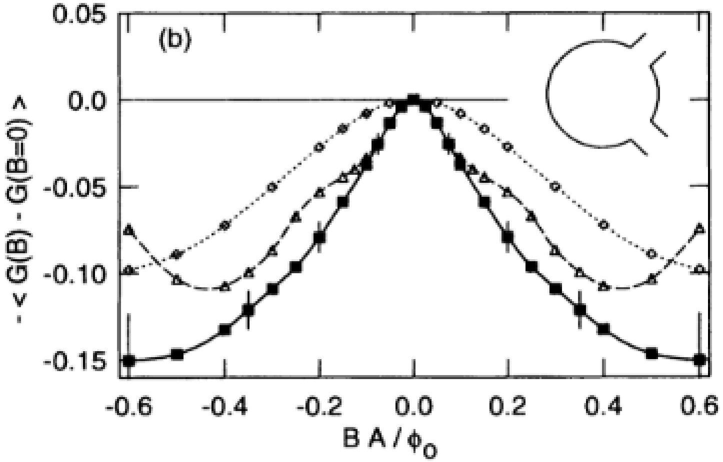
Feiran Wang et al., Adv. Funct. Mater 2007478 (2020)

Dephasing length , $L_\varphi \approx 20$nm is achieved for electron trajectories close to the edge of the flake (average flake size ≈ 50nm).

Geometry of liquid exfoliated flakes is close to oval with aspect ratio *W/L*<2



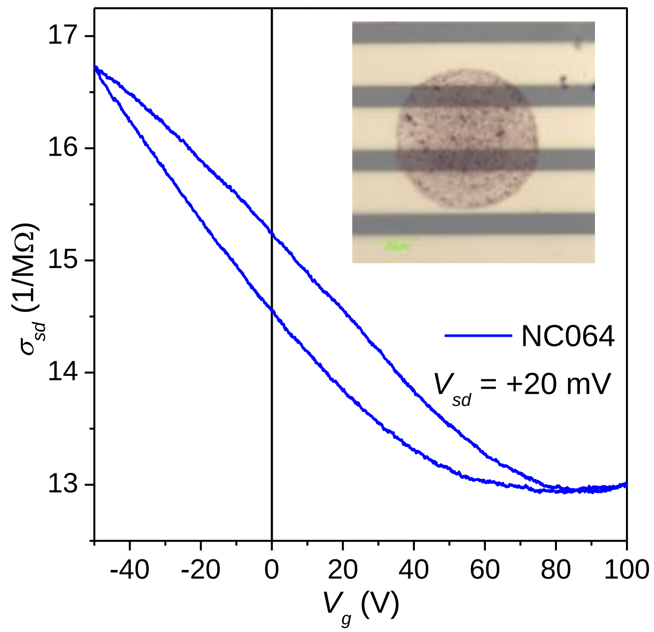
And WL in small disks results in linear *R(B)* !

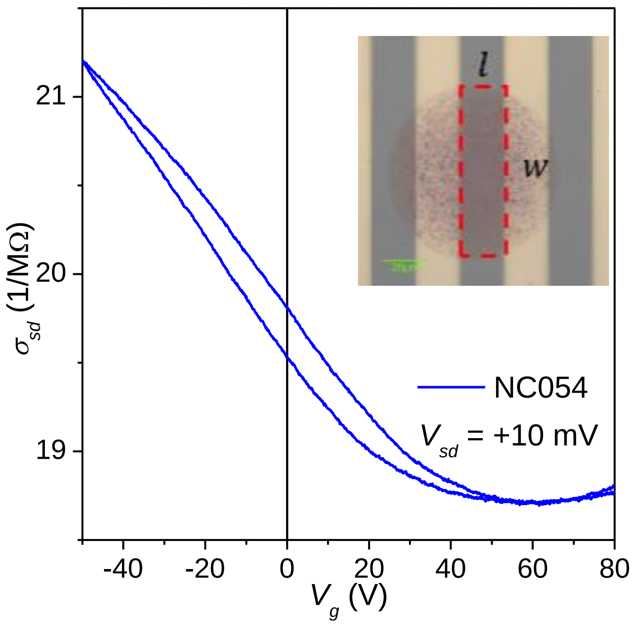


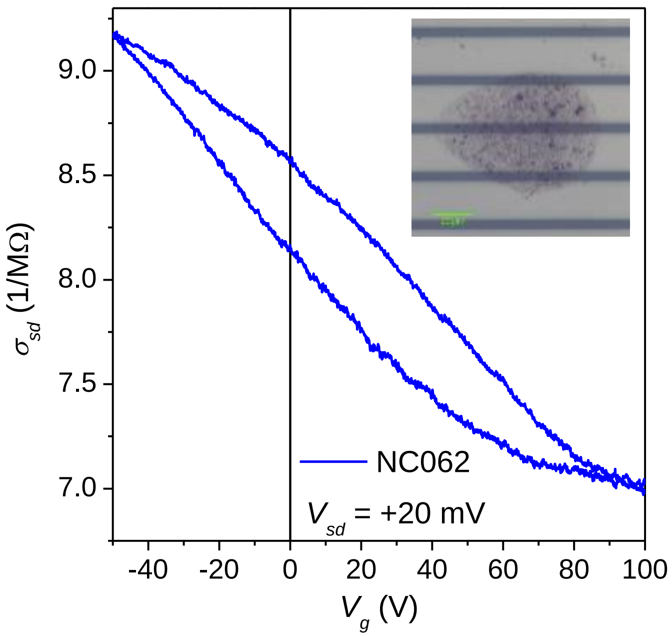
H.Chacham et al., ACS Appl. Nano Mater. 3, 12095 (2020)

A.M. Chang et al., PRL 73, 2111 (1994)

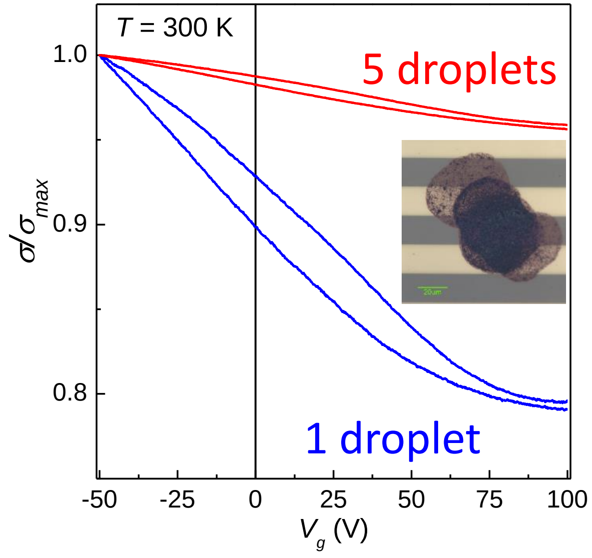
Gate voltage effect in zero magnetic field.





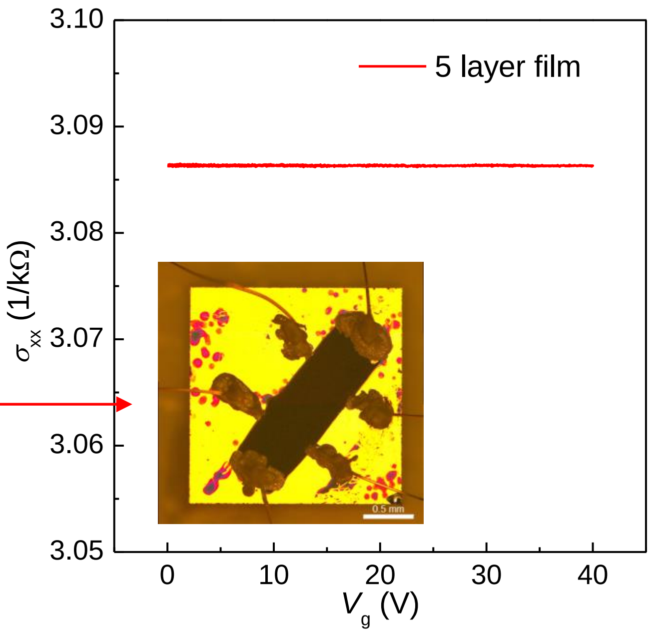


Doping level ~10^{13} cm^{-2}, Mobility ~10 cm^2/Vs

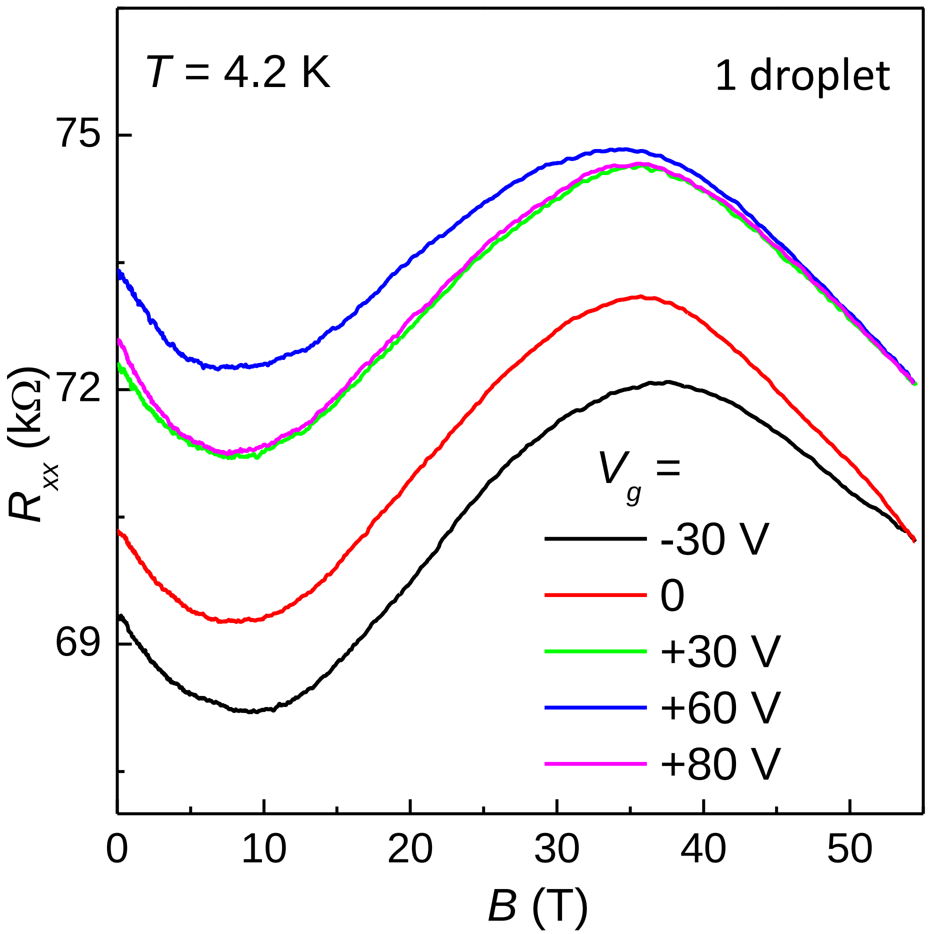


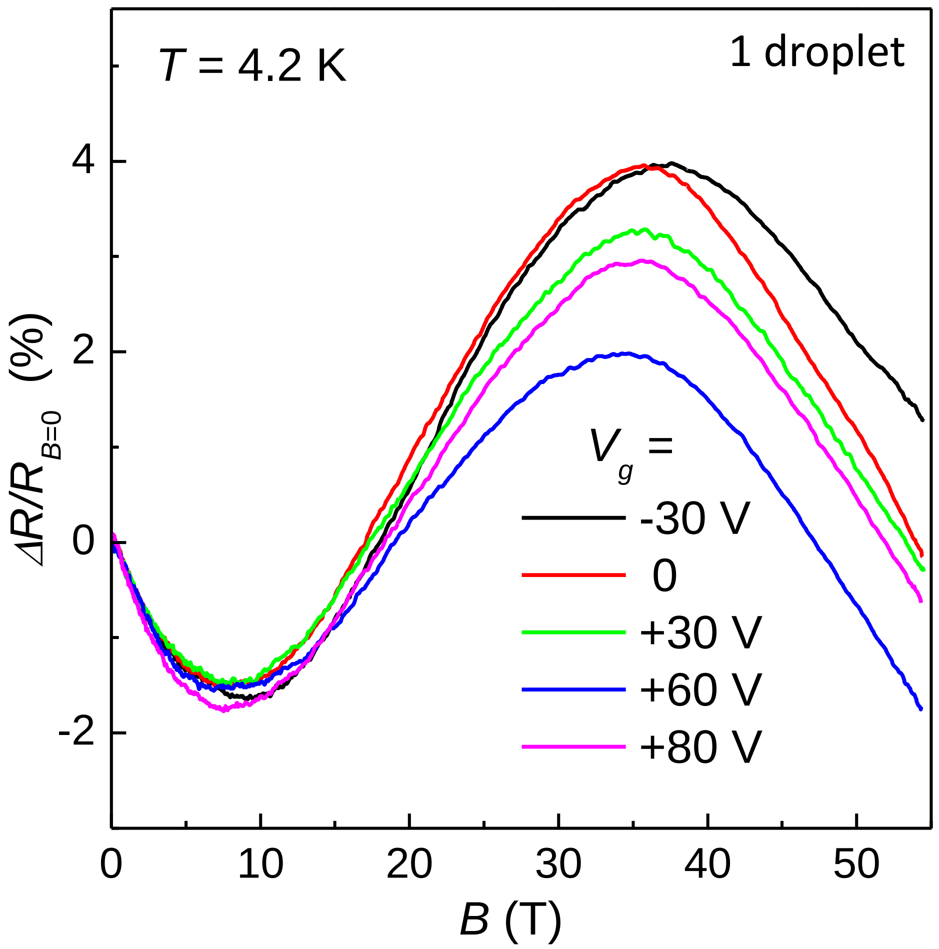
With increasing number of overlapping droplets the effect of V_g on device conductivity becomes weaker.

No gating effect in the films



Droplets. Gate voltage effect in strong magnetic field.





Relative $\Delta R/R_{B=0}$ magnetoresistance at $B > 35$ T demonstrates the same slope for all the values of applied V_g, suggesting that linear negative MR is independent of the carrier density.

N. Cottam et al., Small 2311416 (2024)

Do we see quantum effects in iGraphene?

- Very low mobility does not allow Landau quantisation: $\mu B = 1$ at $B > 100$ T
- No observations of SdH oscillations of Quantum Hall Effect

- Very small size of the flakes (~50nm) with respect to the device size (>1000 nm)
- Percolation transport through a complicated network

- Thin (<3 printed layers) stripe devices demonstrate irreproducible resistance and unmeasurable Hall voltage.
- Thick (>10 printed layers) layers have typical thickness >100nm (3D material?).

- Typical graphene gate voltage dependence of conductivity

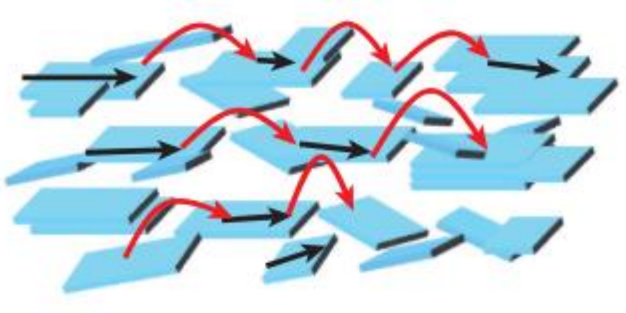
- Weak localisation effect.

- Negative magnetoresistance in DROPLETS.

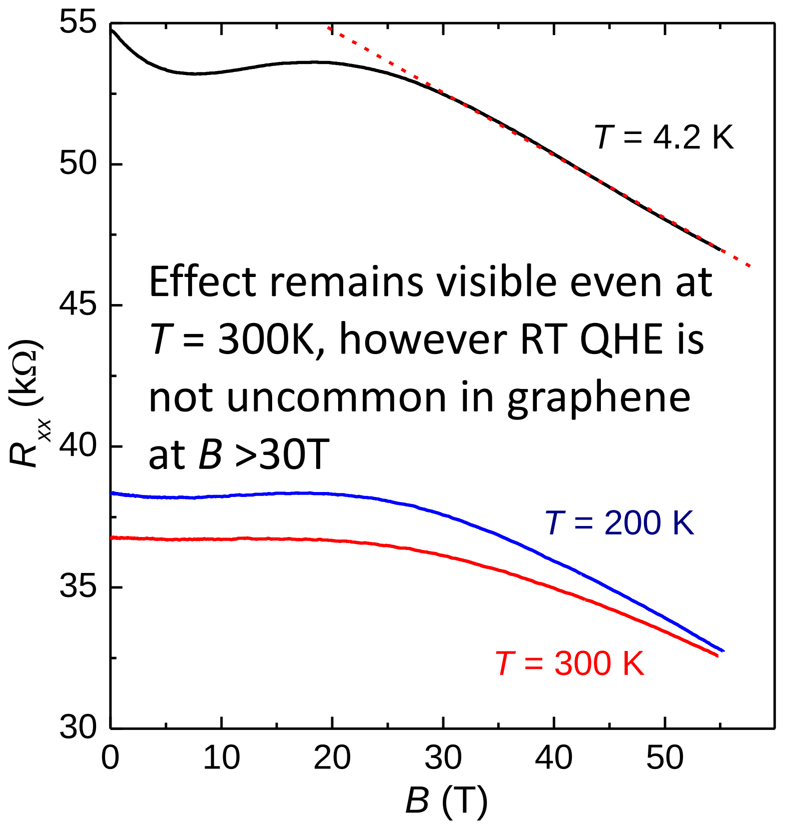
Droplets are more reproducible than thin films. Thinner, more uniform, no coffee rings, etc.

Model of local quantum transport

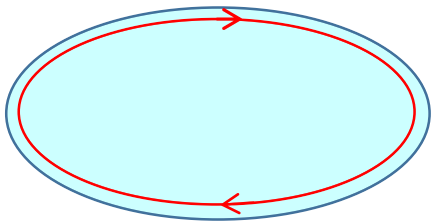
Conventional intra- inter-flake hopping transport model.



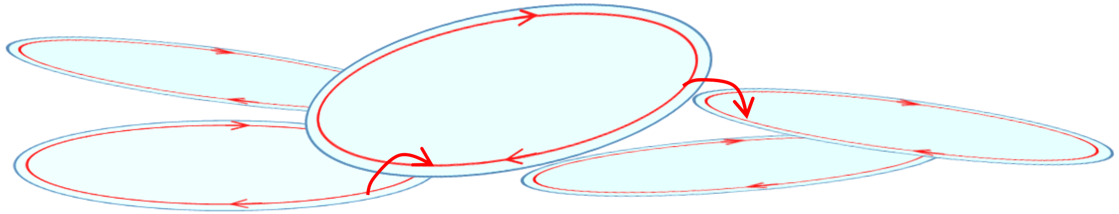
Assumption:
Intra-flake mobility is high μ_{intra} ~ 1000 cm^2/Vs



In high magnetic fields Landau levels and edge states are formed inside individual flakes of ~50nm diameter.



In increasing high magnetic fields the density of states at the Landau level increases enhancing flake-to-flake transport and leading to the negative magnetoresistance.

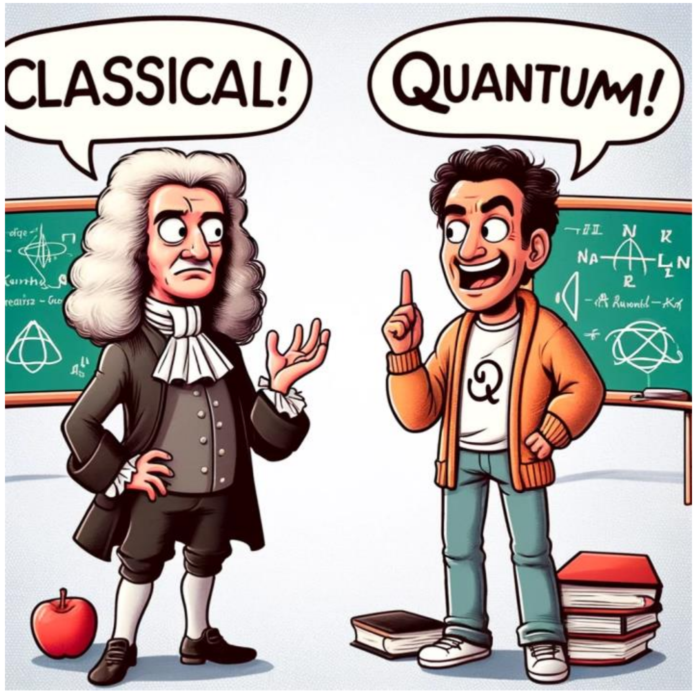


Percolation through a Quantum Hall network?
Quantum iGraphene model is required.

Negative MR is independent of the V_g (carrier density), all electrons in the first Landau level?

CONCLUSIONS

- Possible quantum effects in iGraphene transport in high magnetic fields.
- Unusual Weak Localisation behaviour can be explained by the flake shape and size.
- Negative magnetoresistance in high magnetic fields can be relevant to the formation of quantum edge states in individual flakes due to high intra-flake mobility.
- Droplet devices (created by 1-5 individual graphene ink droplets) demonstrate surprising reproducibility and very different behaviour in strong magnetic fields.



Check f

RESEARCH ARTICLE

NANO · MICRO small
www.small-journal.com

Quantum Nature of Charge Transport in Inkjet-Printed Graphene Revealed in High Magnetic Fields up to 60T

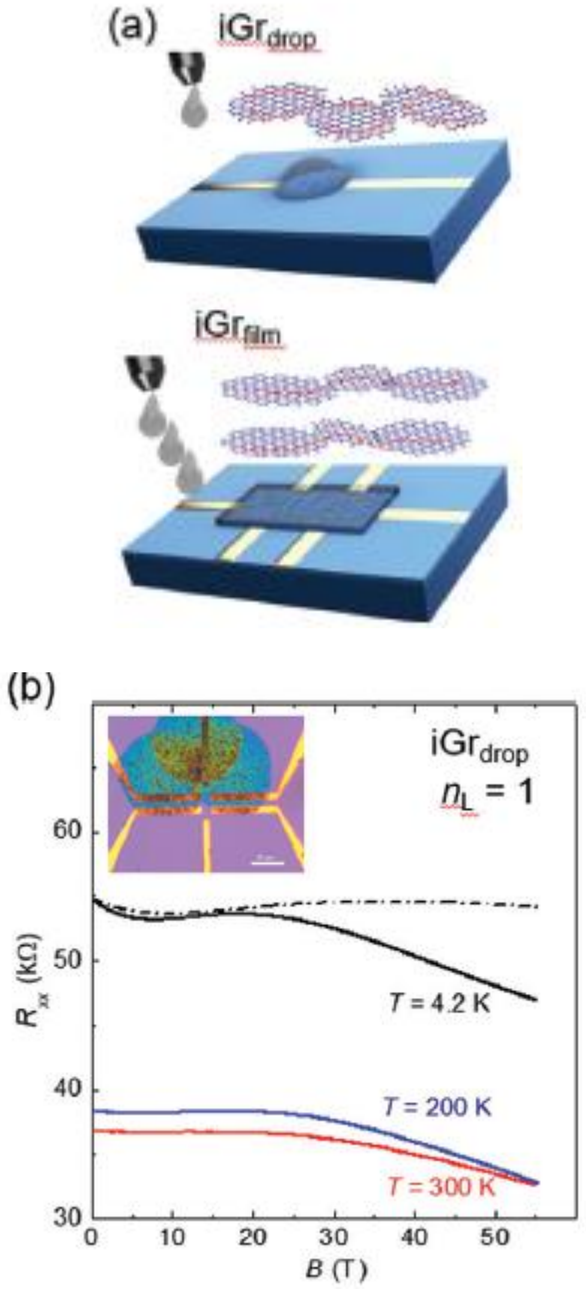
Nathan D. Cottam, Feiran Wang, Jonathan S. Austin, Christopher J. Tuck, Richard Hague, Mark Fromhold, Walter Escoffier, Michel Goiran, Mathieu Pierre, Oleg Makarovsky, and Lyudmila Turyanska**

Inkjet-printing of graphene, iGr, provides an alternative route for the fabrication of highly conductive and flexible graphene films for use in devices. However, the contribution of quantum phenomena associated with 2D single layer graphene, SLG, to the charge transport in iGr is yet to be explored. Here, the first magneto-transport study of iGr in high magnetic fields up to 60 T is presented. The observed quantum phenomena, such as weak localization and negative magnetoresistance, are strongly affected by the thickness of the iGr film and can be explained by a combination of intra- and inter-flake classical and quantum charge transport. The quantum nature of carrier transport in iGr is revealed using temperature, electric field, and magnetic field dependences of the iGr conductivity. These results are relevant for the exploitation of inkjet deposition of graphene, which is of particular interest for additive manufacturing and 3D printing of flexible and wearable electronics. It is shown that printed nanostructures enable ensemble averaging of quantum interference phenomena within a single device, thereby facilitating comparison between experiment and underlying statistical models of electron transport.

1. Introduction

Isolation of single layer graphene (SLG) triggered disruptive changes in the fundamental science of 2D materials and device applications,[1,2] and enabled observation of novel quantum effects, such as the Quantum Hall Effect at temperatures as high as 300 K,[3] weak localization and antilocalization phenomena.[4–8] Pronounced quantum effects in SLG are attributed to its high carrier mobility[1,2] and linear Dirac cone-shaped dispersion, which lead to large energy gaps between the Landau levels that form in a quantizing magnetic field and enables control of both the carrier type and concentration in graphene field effect transistors (GFETs).[1,2,9]

Liquid exfoliation of graphene offers an alternative route for production of 2D materials,[10–12] which can be used to formulate inks for scalable deposition by drop-on-demand inkjet additive manufacturing.[13]



N. Cottam et al., Small 2311416 (2024)