Abstract

This Thesis presents experimental results of quantum transport measurements on high quality (HQ) suspended graphene devices. A high-precision transfer technique for graphene flakes was developed and used to fabricate a suspended HQ graphene device with additional bottom gate structure. The behavior of such device is consistent with the presence of a pn junction, and electronic transport occurs in ballistic regime over a length of 1 micron. As compared to the previously measured devices, the ones produced by this technique show one order of magnitude longer ballistic transport. Using the developed method, HQ tetralayer graphene (4LG) multiterminal devices were fabricated, their quality confirmed by early onset of Quantum Hall Effect. At low temperature, 4LG shows thermally activated insulating behavior around charge neutrality. Based on similarity of 4LG with insulating bilayers, staggered exchange potential mechanism of interaction-induced insulating state is proposed. Even-odd effect of interactions in graphene multilayers is suggested.

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QUANTUM TRANSPORT IN HIGH QUALITY SUSPENDED GRAPHENE

THÈSE

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Post tenebras lux

"After the darkness, light" - motto introduced by Jan Calvin for the Reformism movement and later also taken by the city and the University of Geneva

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I have chosen this epigraph because the work presented in this Thesis has been conducted at the University of Geneva. Besides, the translation of this Latin idiom to Russian language resembles a famous statement made by a Russian Empire Generalissimo, Alexander Suvorov: "Learning is the light and ignorance is the darkness..." – which summarizes my motivation for learning and doing research.

After months in the lab and hundreds meters of scotch tape, one day, I finally saw the signature resistance peak around charge neutrality point which meant: I had a good device which probably would show something interesting. I have arrived to the point of writing a preface for my Thesis, so few devices have indeed shown something interesting. It was not an easy project and I am very happy it has come to a meaningful final point. There are many people to whom I feel very grateful for sharing their knowledge and for their support, help and inspiration. Below, some of them are mentioned, but the list is by no means exhaustive!

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Chapter 1

Introduction

1.1 Carbon and its allotropes

Carbon is the fourth most abundant element (by mass) on our planet and in the whole Universe, after Hydrogen, Helium and Oxygen. It is fundamental to the human life in a literal sense as our bodies incorporate a multitude of carbon-based molecules. Pure Carbon is also abundant and can be found in different forms, which are widely used both on industrial and individual level.

Carbon-only materials differ by how many chemical bonds atoms form with each other, and follow the definition of allotrops – different crystal configurations with the same chemical composition. In diamond, all Carbon atoms are \( sp^3 \)-hybridized, forming \( \sigma \)-bonds with other 4 atoms (see Fig. 1.1a-b), producing an exceptionally hard transparent material. Amorphous Carbon, or coal, features a mixture of \( sp^3 \) and \( sp^2 \)-hybridized atoms, without strongly defined crystallographic structure. Carbon allotropes where all atoms are \( sp^2 \)-bonded to other 3 Carbons, include graphite, graphene, carbon nanotubes and fullerenes, covering all dimensionalities. Graphite, a stack of graphene layers, is 3-dimensional (Fig. 1.1c). Graphene is a 2-dimensional crystal with a honeycomb-shaped lattice (Fig. 1.1d) and is a major subject of this work. Carbon nanotubes are 1-dimensional objects formed by rolling graphene sheets. One distinguishes single- and multiwall nanotubes (Fig. 1.1e) and arm-chair and zig-zag nanotubes, depending on along which direction the tube is rolled (Fig. 1.1d). Spherically-shaped fullerene or a buckyball is 0-dimensional (Fig. 1.1f), it can be obtained if some honeycombs contain 5 or 7 atoms instead of 6, which causes the crystal plane to curve. All Carbon allotropes feature interesting electronic, mechanical and chemical properties and have been an important subject of Condensed Matter Physics.
Introduction

![Carbon allotropes](image)

**Figure 1.1:** Carbon allotropes. **a**, Crystal structure of diamond; **b**, Raw diamond crystal; **c**, Graphite crystal; **d**, Graphene crystal honeycomb lattice; zig-zag and armchair edges are indicated; **e**, Single- and multiwall Carbon nanotubes; **f**, Structure of a fullerene (buckyball).

[1, 2]. The low-energy electronic properties of graphene have recently attracted an intense attention of the research community, for they are unique in many aspects, some of which will be covered in this Manuscript.

### 1.2 Dirac fermions in graphene

Pristine graphene has been isolated some 10 years ago in the group of Andre Geim and Kostya Novoselov, who have succeeded to cleave graphite crystals by scotch tape. The serendiptious finding has led to a robust method to obtain good quality graphene, opening a vast horizon of new physics and potential applications to explore [3–5]. Scotch-tape exfoliation, also known as mechanical microcleaving, is the most reliable method to obtain ultra-high quality graphene flakes till nowadays.

Unique properties of graphene originate from its electronic structure. The charge carriers form a 2-dimensional electron gas (2DEG) with zero-gap semiconductor band structure. At low energy, around the charge neutrality point (CNP), where the valence and conduction bands touch, the energy-momentum dispersion is linear, *i.e.* the charge carriers are relativis-
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tic: massless and chiral [3, 6]. As a consequence, graphene exhibits a unique half-integer quantum Hall effect (QHE) due to the additional Berry’s phase acquired by the charge carriers in magnetic field [4, 5]. Another interesting implication of relativistic and chiral nature of the charge carriers in graphene and electron-hole symmetric low-energy spectrum is Klein tunnelling [7]. In the ideal case of an atomically sharp barrier a relativistic particle does not backscatter from a potential barrier crossing it as its antiparticle instead, without a significant loss of the transmission probability for many angles of incidence. In reality, however, the potential is smooth so there is a loss of the transmission probability as the charge carriers pass the region with a potential gradient and only the ones with the incidence close to normal pass the barrier as carriers of the opposite charge [8].

In the first part of the work presented here, the procedure for high-precision transfer of graphene flakes has been adopted from [9] to produce a suspended graphene device with a $p_n$ junction. Between the junction and sufficiently reflective contacts, a Fabry-Pérot cavity for the charge carriers is formed. Due to the ballistic regime of the electronic transport on the scale of the cavity, the phase of electrons inside it is preserved, leading to an interference pattern. An indication of Klein tunnelling across the potential barrier has been observed: only the charge carriers with the incidence close to normal are not backscattered and enter the cavity. When a perpendicular magnetic field is applied their trajectory inside the cavity is bent by the Lorentz force and, having completed one ”round” inside the cavity, they pick up the Berry’s phase so the interference pattern is shifted with a phase of $\pi$. Our observations indicate that the method we used indeed produces high quality ballistic samples on $\mu$m scale. High quality devices with local control of the electrostatic field allow one to engineer nanostructures for Veselago lensing [10] or charge carrier collimation [11]. Using similar structures with graphene $p_n$-junctions ballistic on the device scale in magnetic field opens possibilities to realize interesting ”optics for electrons” configurations including electron guiding due to the snake states [12, 16].

1.3 Many-body effects in graphene and its multilayers

Graphene and its layers also exhibit many-body physics effects which modify their electronic structure or lead to symmetry-broken states in the magnetic field. Due to the vanishing density of states at the charge neutrality point, electron-electron interactions in pristine samples of very high quality have
been shown to modify the Fermi velocity near the charge neutrality \cite{17, 18}. Stacks of graphene offer an even richer behavior manifesting many-body physics, which will be a subject of the second part of this work.

The electronic structure of few-layer graphene depends on the way graphene planes are stacked. Different stacking orders can be found, among which the Bernal stacking is the most thermodynamically stable, and here we focus on the properties of Bernal-stacked few-layer graphene. Bilayers have a parabolic energy-momentum dispersion, and the charge carriers become massive, yet they preserve their chirality. A unique property of bilayer graphene is that a gap between the conduction and the valence band can be opened and tuned by a perpendicular electrostatic field \cite{19, 20}. Since the ground state in bilayer graphene is highly degenerate and hosts charge carriers of both polarities, many-body effects can lead to symmetry breaking. A substantial experimental and theoretical effort has been made to explain the observed phenomena, e.g., an insulating gapped state close to the charge neutrality in the absence of the magnetic field \cite{21–23}. A behavior consistent with different ground states has been observed \cite{24, 25}, and how exactly the ground state of the system depends on the microscopic details remains an open question.

Thicker graphene stacks also show interesting properties. The electronic structure of few-layer Bernal stacks can be considered as a combination of a linear and parabolic sub-bands for odd number of layers $N$ and parabolic sub-bands in case the $N$ is even \cite{26–29}. Bernal-stacked trilayers have been shown to be conducting even at low temperatures with a tunable conduction and valence band overlap, which is attributed to the presence of the linear sub-band in the electronic structure of the system \cite{30}.

In the second part of this work, having developed the expertise to fabricate multiterminal suspended devices, we study the physics close to the charge neutrality in suspended few-layer graphene samples. The main focus is on the properties of high quality tetralayer graphene, the experimental evidence on which has been so far limited, since it is not straightforward to confirm the sample thickness for graphene stacks thicker than trilayers. We observe an unexpected strongly insulating behavior in the vicinity of charge neutrality at $B = 0$ in high quality samples. To explain such behavior in tetralayer graphene we generalize the approach to the similar insulating behavior in bilayers, which is based on electron-electron interactions producing a staggered exchange potential. Moreover, the presence of a staggered exchange potential consistently explains the behavior trilayer Bernal-stacked graphene which remains conducting around the CNP even at low temperatures, suggesting an even-odd effect of electron-electron interactions close to the charge neutrality point in high quality suspended few-layer graphene samples. These observations present an unexpected finding that electron-
electron interactions are affecting thicker graphene stacks even stronger than bilayers. Intuitively, one would expect their electronic properties to converge to the ones of graphite, therefore we suggest that the transport in the latter might be dominated by defects of stacking, at least near the charge neutrality point.

1.4 Suspended graphene

The experimental scope of the work presented in this manuscript is focused on the fabrication and characterization of high quality suspended graphene devices. Decoupling from the substrate has two important implications for graphene, both of which are key to this Thesis. Primarily, suspended devices can be cleaned to reach ultra-high quality so the electronic transport is essentially ballistic. We have confirmed that the acid-free method [31] indeed produces high quality graphene which can be annealed to achieve ballistic transport on scale of few µm (see the Section 1.2). This is one order of magnitude longer ballistic samples as compared to the best previously reported devices supported on Si/SiO$_2$ substrate, which have a mean-free path $l_{MFP}$ of few hundred nm [32]). It is a step towards more complex device configurations, since longer $l_{MFP}$ allows more freedom in the choice of the gate geometry and it revokes the necessity to minimize gate dimensions, also simplifying the fabrication.

Secondly, very clean suspended graphene devices allow one to probe the physics close to the charge neutrality point because they reach an unprecedented low density of charged inhomogeneities ($n^* < 10^9$ cm$^{-2}$) [17] and they are decoupled from the substrate. In order to obtain samples of this quality, they need to be current annealed. As the voltage is ramped across the sample, it heats so the residues remaining from the fabrication process diffuse from the bulk of the sample towards the contacts [33]. Successful annealing is a very tricky procedure with high chances of breaking a device. An additional complication in this case appears from the sample geometry: due to invasive nature of metallic contacts it is not trivial to homogeneously current anneal suspended Hall bar samples which are optimal for characterization of such transport phenomena as quantum Hall effect [34, 35]. We have developed and optimized a cross-like four-probe geometry which has allowed us to successfully anneal several few-layer graphene devices [36, 38] and is advantageous for device characterization as compared to the two-terminal geometry.
Introduction

Outline

This manuscript has the following structure: the Preface and the Chapter 1 – this Introduction – are followed by the Chapter 2, which presents a theoretical overview of the electronic structure of mono- and few-layer Bernal graphene stacks and of their electronic properties. Further, the field effect and quality assessment in different types of graphene devices are discussed, followed by magnetotransport in graphene and its stacks. Next, Klein tunnelling and quantum transport in Fabry-Pérot cavities in graphene is discussed. After that, the symmetry breaking by electron-electron interactions close to the charge neutrality in the absence of magnetic field in bilayers is reviewed.

Next Chapters present experimental findings of this Thesis. Chapter 3 is dedicated to the experimental details of the work presented here. Sample fabrication methods are presented, followed by the discussion of the current annealing procedure and concluded by methods to assess the sample thickness: Raman and magneto-Raman spectroscopy. In Chapter 4, monolayer graphene suspended over an additional gate is used to induce a $pn$ junction interface. We demonstrate ballistic electronic transport on $\mu$m scale and observe the phase shift of electrons interfering inside a $\sim 1 \mu$m large Fabry-Pérot cavity in the perpendicular magnetic field. In Chapter 5, using a similar fabrication method, we successfully fabricate and anneal ultra-high quality suspended multiterminal tetralayer devices which turn out to be insulating around the charge neutrality, see the Section 1.3. The experimental findings are followed by a Résumé, which concludes this manuscript.
Chapter 2

Electronic transport properties of graphene and its stacks

2.1 Electronic spectrum of graphene: the tight-binding approach

In this Section, the electronic structure of mono- and few layer graphene will be discussed. First, in the Subsection 2.1.1 a tight-binding approach to monolayer graphene band structure will be shown. Secondly, low-energy properties of graphene will be discussed in the Subsection 2.1.2 with special focus on relativistic chiral properties of the charge carriers. Similar approach will be outlined for bilayer and few-layer graphene. Subsection 2.1.3 presents the electronic structure of bilayers and discusses the biased bilayer case. Subsection 2.1.4 shows how the electronic structure of few-layer graphene can be decomposed in linear and parabolic sub-bands and applies this approach to tri- and tetralayer graphene.

2.1.1 Band structure of mono-layer graphene

Graphene is an atomically thin layer of carbon atoms arranged in a honeycomb lattice, as sketched in Fig.2.1. Each Carbon atom forms three in-plane $\sigma$-bonds with its neighbors. One electron of an out-of-plane $p_z$-orbital is left to form $\pi$-bonds. The energy of $\sigma$-bonds is much larger then the one of the $\pi$-bond, and as far as in this work, we are interested in electronic transport at low energies, we can focus only on electrons from $p_z$-orbitals.

The energy spectrum of monolayer graphene can be obtained using the tight-binding approach, which takes into account hopping between neighboring atoms in the crystal. Here we consider only the hopping between the
Electronic transport properties of graphene and its stacks

Figure 2.1: Graphene crystal structure. a, Graphene lattice; the dashed lines mark the unit cell, consisting of sublattice atoms A and B; lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ describe the location of atoms in a sublattice; $\delta_1$, $\delta_2$ and $\delta_3$ show the shift of the sublattice B with respect to the sublattice A; b, Brillouin zone (BZ) of monolayer graphene: $\mathbf{b}_1$ and $\mathbf{b}_2$ are reciprocal lattice vectors, $K$ and $K'$-points mark two independent sets of BZ corners, or valleys.

nearest sites and just shortly mention how including the next-nearest hopping modifies the electronic structure of graphene and its stacks [2, 4, 6, 39].

The unit cell of a honeycomb lattice consists of two identical Carbon atoms with a length of a conjugated bond between them $a = 1.42$ Å. The two atoms are conventionally labelled as $A$ and $B$, marked red and blue in Fig. 2.1a. This crystal structure can be considered as two superposed triangular sublattices, with the lattice vectors in real and reciprocal space given by

$$\mathbf{a}_1 = \frac{a}{2}(3, \sqrt{3}), \quad \mathbf{a}_2 = \frac{a}{2}(3, -\sqrt{3}),$$

$$\mathbf{b}_1 = \frac{2\pi}{3a}(1, \sqrt{3}), \quad \mathbf{b}_2 = \frac{2\pi}{3a}(1, -\sqrt{3}).$$

The periodicity of the crystal lattice allows us to construct a Bloch wavefunction for electrons localized on each sublattice (not including spin):

$$\phi_A = \sum_A e^{2\pi i \mathbf{k} \cdot \mathbf{r}_A} \psi_A(\mathbf{r} - \mathbf{r}_A)$$

$$\phi_B = \sum_B e^{2\pi i \mathbf{k} \cdot \mathbf{r}_B} \psi_B(\mathbf{r} - \mathbf{r}_B).$$

Here, $\mathbf{k}$ is a wave vector, $\mathbf{r}_A, \mathbf{r}_B$ indicate the positions of atoms belonging to $A$ and $B$ sublattice, $\psi_A$ and $\psi_B$ are atomic wavefunctions for electrons sitting
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on each site, respectively. \( \phi_i(r), i = A, B \) are normalized and do not overlap, i.e. \( \langle \phi_A | \phi_A \rangle = \langle \phi_B | \phi_B \rangle = 1 \), and \( \langle \phi_A | \phi_B \rangle = \langle \phi_B | \phi_A \rangle = 0 \). Using these wavefunctions we can construct a trial wavefunction (a linear combination of \( \phi_A(r) \) and \( \phi_B(r) \))

\[
\Psi(r) = c_A \phi_A(r) + c_B \phi_B(r), \tag{2.4}
\]

where \( c_A \) and \( c_B \) represent the wavefunction amplitude on each sublattice.

We start solving the Schrödinger equation \( H \Psi = E \Psi \) by multiplying it with \( \phi_A, B \)

\[
\langle \phi_A | H | \Psi \rangle = c_A \langle \phi_A | H | \phi_A \rangle + c_B \langle \phi_A | H | \phi_B \rangle = E \langle \phi_A | \Psi \rangle \\
\langle \phi_B | H | \Psi \rangle = c_A \langle \phi_B | H | \phi_A \rangle + c_B \langle \phi_B | H | \phi_B \rangle = E \langle \phi_B | \Psi \rangle \tag{2.5}
\]

Here, \( \langle \phi_A | H | \phi_A \rangle \) and \( \langle \phi_B | H | \phi_B \rangle \) represent the on-site energy \( E_0 \), which can be set to 0 without loss of generality. The nearest neighbor hopping is described by \( \langle \phi_A | H | \phi_B \rangle \) and \( \langle \phi_B | H | \phi_A \rangle \), which can be equivalent to \( \gamma_0 S(k) \), representing the hopping to the other sublattice and taking into account the corresponding phases:

\[
S(k) = \sum_{i=1,...,3} e^{ik\delta_i} = 2e^{\frac{1}{2}ia_k \cos \left( \frac{\sqrt{3}ak_y}{2} \right)} + e^{ia_k}, \tag{2.6}
\]

with the nearest neighbor (see Fig.2.1b) vectors given by

\[
\delta_1 = \frac{a}{2}(1, \sqrt{3}), \quad \delta_2 = \frac{a}{2}(1, -\sqrt{3}), \quad \delta_3 = a(-1, 0), \tag{2.7}
\]

The notation for the nearest neighbor hopping energy \( \gamma_0 \) (often \( t \) in the literature) is adopted from Slonczewski-Weiss-McClure (SWM) model \[40–42\] and will be used in this manuscript to maintain a consistent notation convention. From density functional theory (DFT) calculations, the estimate for its value ranges between \( \gamma_0 \approx 2.8 - 3.1 \text{eV} \) \[43–45\], in agreement with the value experimentally determined for the in-plane hopping in graphene by the photoemission, Raman and infrared spectroscopy \[46–49\].

With the expression (2.6), the Hamiltonian \( H \) describing hopping between the two sublattices can be written as a \( 2 \times 2 \) matrix,

\[
H = \begin{pmatrix}
0 & \gamma_0 S(k) \\
\gamma_0 S^*(k) & 0
\end{pmatrix} \tag{2.8}
\]

and the eigenvalue problems takes the form:

\[
H \begin{pmatrix}
a_k \\
b_k
\end{pmatrix} = E_k \begin{pmatrix}
a_k \\
b_k
\end{pmatrix} \tag{2.9}
\]
Solving (2.9) we arrive to the energy dispersion relation

\[ E(k_x, k_y) = \pm \gamma_0 \sqrt{1 + 4 \cos \left( \frac{3ak_x}{2} \right) \cos \left( \frac{\sqrt{3}ak_y}{2} \right) + 4 \cos^2 \left( \frac{\sqrt{3}ak_y}{2} \right)} . \]

(2.10)

The Brillouin zone corresponding to a triangular lattice has a hexagonal shape (Fig. 2.1b). We can see that \( S(\mathbf{k}) \) takes zero values in the corners of the Brillouin zone, which fall in two inequivalent sets, also called valleys, usually labelled as \( K \)- and \( K' \)-points;

\[ K = \frac{2\pi}{3a}(1, \sqrt{3}), \quad K' = \frac{2\pi}{3a}(1, -\sqrt{3}). \]

(2.11)

The band structure generated by the energy-momentum dispersion (2.10) is shown in Fig. 2.2a. The sign \( \pm \) corresponds to the conductance and valence bands. Each carbon atom contributes one \( \pi \) electron, and, given there are two identical atoms in a unit cell and two possible spin orientations, the Fermi level of undoped graphene is located where the bands touch – charge neutrality point (CNP), which makes it a zero-gap semiconductor. If \( A \) and \( B \) atoms of the unit cell are not identical then the sublattice symmetry is broken, as the on-site energy is different. This would result in non-zero different diagonal elements in Eq. (2.8), producing a band structure with a gap.
2.1.2 Low-energy dispersion of massless Dirac fermions

The low energy electronic transport regime in graphene is defined by the nearest-neighbor hopping parameter: \( E < \gamma_0 \). Expanding the Hamiltonian \((2.8)\) near the corners of Brillouin zone, \( \mathbf{k} = \pm \mathbf{K} + \mathbf{q} \), where \( |\mathbf{q}| \ll |\mathbf{K}, \mathbf{K}'| \), we obtain an effective low-energy Hamiltonian \([2, 39]\)

\[
\hat{H}_{K,K'}(\mathbf{q}) = \hbar v_0 \begin{pmatrix} 0 & q_x \mp iq_y \\ q_x \pm iq_y & 0 \end{pmatrix}, \tag{2.12}
\]

Here, \( v = \frac{3a\gamma_0}{2} \) is Fermi velocity, which is estimated to be \( \sim 10^6 \text{ ms}^{-1} \). The effective Hamiltonian \((2.12)\) produces an energy-momentum dispersion

\[
E(\mathbf{q}) \approx \pm v_F |\mathbf{q}| + \mathcal{O}(\mathbf{q}/K)^2 \tag{2.13}
\]

The result of this expansion is what makes graphene stand out from other 2DEG systems: the velocity of charge carriers does not depend on the momentum, i.e. they are described using the Dirac equation for relativistic fermions, with Fermi velocity \( v_F \) instead of the speed of light \( c \), and with zero effective mass \([4]\).

We can rewrite the effective Hamiltonian for monolayer graphene \((2.12)\) for each valley:

\[
\hat{H}_K = -iv_F \sigma \nabla, \quad \hat{H}_{K'} = iv_F \sigma \nabla. \tag{2.14}
\]

Here, \( \sigma = (\sigma_x, \sigma_y) \) are Pauli matrices constructed in the sublattice basis. The sublattice contributions to graphene’s wavefunction – two-component spinors – are very similar to the one of a spin in their formalism, so they are called pseudospin degrees of freedom:

\[
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}. \tag{2.15}
\]

The wavefunctions around \( K \) and \( K' \)-points are related by time-reversal symmetry \( \psi_K(\mathbf{k}) = \psi_K'(\mathbf{-k}) \):

\[
\psi_{\pm,K}(\mathbf{k}) = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-i\theta_k/2} \\ \pm e^{i\theta_k/2} \end{pmatrix},
\]

\[
\psi_{\pm,K'}(\mathbf{k}) = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{i\theta_k/2} \\ \pm e^{-i\theta_k/2} \end{pmatrix}, \tag{2.16}
\]

where \( \theta_k = \arctan \frac{k_x}{k_y} \) is the polar angle of \( \mathbf{k} \). Noticing that charge carriers in different valleys have the opposite chirality, we define a helicity operator
as a pseudospin projection on the direction of the momentum \[ \hat{h} = 1/2\sigma \frac{p}{|p|}, \] (2.17)

Around the \( K \)-point, such projection \( \langle \psi | \hat{h} | \psi \rangle \) points outside of the valence band cone and points inside it in the conduction band, and vice-versa around the \( K' \)-point, as illustrated by the Fig.2.2b. The chiral nature of charge carriers in graphene has important consequences regarding the Berry’s phase. A full rotation of \( 2\pi \) completed by the pseudospin projection around the origin, \( i.e. K- \) or \( K' \)-point, leads to the wavefunction changing its sign, see the Eq.(2.16), which corresponds to Berry’s phase \( \pi \). The most notable consequence of Berry’s phase acquisition is the so-called half-integer or anomalous quantum Hall effect, which will be discussed in detail in Section 2.3.1.

2.1.3 The band structure of bilayer graphene

The electronic structure of bilayer graphene is different from the one of monolayer and has unique properties, too. Bilayer graphene is a system composed of two graphene planes. Bernal, or AB, stacking is the most thermodynamically stable way to stack graphene layers, is illustrated in Fig.2.3: the atom \( A_1 \) is located under the \( B_2 \) and the \( B_1 \) and \( A_2 \) are under (on top of) the centers of corresponding hexagons of another layer.

The bilayer graphene unit cell consists of four atoms, as shown in Fig.2.3 which can be labelled as \( A_1, B_1, A_2, B_2 \) counting two sublattices of the two layers. Notations for the hopping parameters \( (\gamma_0, \gamma_1, \gamma_3) \) are adopted from
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the SWM model \[40\,\text{and}\,42\]. The arrows in Fig 2.3 illustrate the meaning of this notation. \(A_1\) and \(B_2\) are located under each other, so they are referred to as dimer sites (shown in Fig 2.3 with a dashed line). \(A_2\) and \(B_1\) are located under the hexagon centers of the other layer so they are called non-dimer sites. We can construct the following tight-binding Hamiltonian for the bilayer graphene in the basis \(A_1, B_1, A_2, B_2\):

\[
H_K \equiv \begin{pmatrix}
0 & \gamma_0 S(k) & 0 & \gamma_1 \\
\gamma_0 S^*(k) & 0 & 0 & 0 \\
0 & 0 & 0 & \gamma_0 S^*(k) \\
\gamma_1 & 0 & \gamma_0 S(k) & 0
\end{pmatrix},
\]

(2.18)

where \(S(k)\) is the same as in (2.6). Such tight-binding Hamiltonian produces the following energy-momentum dispersion:

\[
E(k) = \pm \frac{1}{2} \gamma_1 \pm \sqrt{\frac{1}{4} \gamma_1^2 + \gamma_0^2 |S(k)|^2}.
\]

(2.19)

This expression produces an electron-hole symmetric energy-momentum dispersion with four parabolic bands \[51\,\text{and}\,52\]. Two of these bands touch at charge neutrality point where the Fermi level of undoped BLG is, and the two other bands are separated from them by \(\gamma_1 \approx 0.4\,\text{eV}\) \[53\].

Expanding the spectrum near the \(K\) and \(K'\) points in the low energy limit yields \[51\,\text{and}\,52\]

\[
E_{1,2}(k) \approx \pm \frac{\gamma_0^2 |S(k)|^2}{\gamma_1} \approx \pm \frac{\hbar^2 q^2}{2m^*},
\]

(2.20)

with the effective mass \(m^*\) being

\[
m^* = |\gamma_1|/(2v_F^2) \approx 0.054m_e,
\]

(2.21)

where \(m_e\) is a free electron mass.

Using operators \(\hat{p}_x = \xi \hat{p}_x + \hat{p}_y\) and \(\hat{p}_- = \xi \hat{p}_x - \hat{p}_y\), where \(\xi = \pm 1\) for \(K\)- and \(K'\)-point correspondingly, and

\[
\hat{p}_x = -i\hbar \frac{\partial}{\partial x}, \quad \hat{p}_y = -i\hbar \frac{\partial}{\partial y},
\]

(2.22)

we obtain an effective Hamiltonian for the bilayer graphene in the basis of \(A_2\) and \(B_1\):

\[
\hat{H}_K = \frac{1}{2m^*} \begin{pmatrix}
0 & \hat{p}_x^2 \\
\hat{p}_x^2 & 0
\end{pmatrix}.
\]

(2.23)
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Figure 2.4: Band structure of bilayer graphene. a, Low energy limit of the band structure obtained in the nearest-neighbor tight-binding approach; b, The band structure calculated using the tight-binding approach including next-nearest neighbor hopping parameters; the inset shows the low-energy dispersion near $K$ and $K'$-points \[52\]; c, Energy-momentum dispersion with effect of trigonal warping: three satellite Dirac cones appear around the original one \[52\]

This gives us the energy-momentum dispersion $E_{\pm} = \pm \frac{\hbar^2 k^2}{2m^*}$, where plus and minus correspond to the conduction and valence bands respectively and the wave function (2.16) for the charge carriers in each band and valley can be written as

$$\psi_{\pm, \xi}(k) = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{-\xi \theta_k} \\ \pm e^{\xi \theta_k} \end{pmatrix}. \quad (2.24)$$

We can see that the charge carriers in bilayer graphene are also chiral; parabolic energy-momentum dispersion of chiral massive fermions places bilayer graphene in a special place with respect to other 2DEGs and leads to a new type of quantum Hall effect observed in BLG, which will be discussed in the Subsection 2.3.1.

Biased bilayer graphene

Thanks to electronic states localized on different sublattices on each layer, breaking the sublattice symmetry in bilayer graphene can be achieved by breaking the layer symmetry, e.g. by introducing an electrostatic potential $V$ perpendicular to the sample surface (Fig 2.5a). In case $V \ll \gamma_1$, a term $\pm V/2$ is added to the diagonal elements of the effective low-energy Hamilto-
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Figure 2.5: A perpendicular electrostatic field opens a gap in bilayer graphene. a, Sketch of the bilayer graphene crystal with a perpendicular electrostatic field; b, Low energy band structure of the unbiased bilayer graphene as compared to the one of the biased; c, Sketch of the BLG device with double gating; d, Tuning the gap size in a double gated bilayer at 50 mK: 3D square resistance $R_{\square}$ as a function of top and bottom gate; inset is a color plot of the same data and shows the suppression of conductance $1/R$ with applied electrostatic field [19].

The Hamiltonian (2.23) (signs correspond to different layers), creating therefore a gap $V$ between the valence and conduction bands, as illustrated in Fig.2.5b:

$$E_{\pm} = \pm \sqrt{V^2 / 4 + \left( \frac{\hbar^2 k^2}{2m^*} \right)^2}$$

This property allows the gap to be induced and tuned by applying an electrostatic potential up to 300 meV [52, 54, 56]. Experimentally, this can be achieved by chemical doping or by double gating the device, see Fig.2.5c: one of the gates is used to control the charge carrier density and the other one – to induce an electrostatic potential to open a gap. Doubly gated structures have been realized by several groups, both with supported and with suspended graphene bilayers [19, 20, 47, 57]. Fig.2.5d shows a sharp increase of the square resistance as the electrostatic field is getting larger in a doubly gated sample, with the black area on the inset corresponding to the insu-
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Biased graphene is used to create device with electrostatic confinement, full or partial, such as quantum dots and constrictions [20, 58].

2.1.4 Band structure of few-layer graphene: the effective sub-band model

Here, we discuss how the low energy band structure of few-layer graphene can be described as a composition of effective sub-bands [26, 27, 59–61], also confirmed by the DFT calculations [43]. This Subsection is devoted to the electronic structure for tri- and tetralayer graphene discussed in the framework of the suggested approach.

To outline the principle behind the effective sub-band approach adopted from [26–29] and the Supplementary information from the Ref. [38], we write down the most general form of a Hamiltonian of \( N \)-layer graphene that takes into account only the nearest-neighbor hopping. The basis states \( A_j \) and \( B_j \) atoms on the layer \( j = 1, \cdots, N \) – are sorted as \( |A_1\rangle, |B_1\rangle; |A_2\rangle, |B_2\rangle; \cdots; |A_N\rangle, |B_N\rangle; \)

\[
\mathcal{H} = \begin{pmatrix}
H_0 & V \\
V^\dagger & H_0 & V^\dagger \\
& \ddots & \ddots & \ddots \\
\end{pmatrix},
\]

(2.26)

with

\[
H_0 = \begin{pmatrix}
0 & v\hat{p}_- \\
v\hat{p}_+ & 0
\end{pmatrix}, \quad V = \begin{pmatrix}
0 & 0 \\
\gamma_1 & 0
\end{pmatrix},
\]

(2.27)

where \( v \) is the band velocity of monolayer graphene, \( \hat{p}_\pm = \xi \hat{p}_x \pm i \hat{p}_y \) with the in-plane momentum \( \hat{p}_x, \hat{p}_y \) and the valley index \( \xi = \pm 1 \) (+ for \( K \) and − for \( K' \)), and \( \gamma_1 \) is the nearest interlayer coupling. \( H_0 \) describes the monolayer Hamiltonian, and \( V \) defines the interlayer coupling between the dimer states.

The Hamiltonian (2.26) can be diagonalized in a basis constructed of states localized on even and odd layers. Let us introduce such basis, with a quantization of \( \mathbf{k} \) along the layer-stacking direction,

\[
|X_n^{(\text{odd})}\rangle = c_n \sum_{j=\text{odd}} (\sin \kappa_{n,j}) |X_j\rangle, \\
|X_n^{(\text{even})}\rangle = c_n \sum_{j=\text{even}} (\sin \kappa_{n,j}) |X_j\rangle,
\]

(2.28)
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where
\[ \kappa_n = \frac{n\pi}{N+1}, \quad n = 1, 2, \cdots, \left\lfloor \frac{N+1}{2} \right\rfloor, \] (2.29)

\( X = A \) or \( B \), and the normalization factor \( c_n = 1/\sqrt{2(N+1)} \) when \( \kappa_n = \pi/2 \), and \( c_n = 1/\sqrt{N+1} \) otherwise. A superscript such as \( \text{(odd)} \) indicates that the wave function has its amplitude only on \( |A_j\rangle \) sites in odd \( j \) layers. By grouping the basis states as \( \vec{u}_n = \{ |A^{(\text{odd})}_n\rangle, |B^{(\text{odd})}_n\rangle, |A^{(\text{even})}_n\rangle, |B^{(\text{even})}_n\rangle \} \), the Hamiltonian (2.26) is block-diagonalized with a sub-Hamiltonian

\[
\mathcal{H}_n = \begin{pmatrix}
0 & \hat{v} \hat{p}_- & 0 & 0 \\
\hat{v} \hat{p}_+ & 0 & \tilde{\gamma}_1 & 0 \\
0 & \tilde{\gamma}_1 & 0 & \hat{v} \hat{p}_- \\
0 & 0 & \hat{v} \hat{p}_+ & 0 \\
\end{pmatrix},
\] (2.30)

which resembles the one of the bilayer graphene (see the Subsection 2.1.3) with modified interlayer coupling:

\[ \tilde{\gamma}_1 = (2 \cos \kappa_n) \gamma_1. \] (2.31)

The case of \( \kappa_n = \pi/2 \) which appears in multilayers with odd number of layers \( N \) is special, as the even bases \( |\phi^{(X,\text{even})}_n\rangle \) are identically zero and only two bases \( \{ |\phi^{(A,\text{odd})}_n\rangle, |\phi^{(B,\text{odd})}_n\rangle \} \) survive. The matrix for these two remaining bases is

\[
\mathcal{H}_n = \begin{pmatrix}
0 & \hat{v} \hat{p}_- \\
\hat{v} \hat{p}_+ & 0 \\
\end{pmatrix}
\] (2.32)

which is equivalent to the Hamiltonian of monolayer graphene, with the wave bases localized only on the odd layers \( (1^{\text{st}}, 3^{\text{rd}}, 5^{\text{th}}, \ldots) \).

Solving the eigenstate problem similarly to the case of mono- and bilayer graphene in Subsection 2.1.1 and 2.1.3 we obtain an electron-hole symmetric energy-momentum dispersion with linear or parabolic bands, depending on the values of \( \kappa \):

\[
E(\mathbf{k}, \kappa_n) = \pm \gamma_1 \cos \kappa_n \pm \sqrt{\gamma_0^2 |S(\mathbf{k})|^2 + \gamma_1^2 \cos^2(\kappa_n)}. \] (2.33)

Let us now consider the electronic structure produced by this low-energy energy dispersion for tri- and tetralayer graphene.

Electronic structure of Bernal-stacked trilayer graphene

For the Bernal-stacked trilayer graphene \( N = 3 \) (see the crystal structure in Fig. 2.6a,b) this approach produces \( \cos \kappa_3 = 0, \pm 1/\sqrt{2} \) so the electronic
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Figure 2.6: Crystal structure of trilayer graphene. a, Bernal-stacked trilayer graphene and hopping parameters; b, Structural difference between graphene with Bernal and rhombohedral stacking order: the former has a mirror symmetry with respect to the second layer, the latter has an inversion symmetry center shown as an encircled dot.

structure is described as:

\[
E(k) = \begin{cases} 
\pm \gamma_0 |S(k)|, & \cos \kappa = 0 \\
\pm \gamma_1 / \sqrt{2} \pm \sqrt{\gamma_0^2 |S(k)|^2 + \gamma_1^2 / 2}, & \cos \kappa = \pm 1 / \sqrt{2}.
\end{cases}
\] (2.34)

We see that the energy-momentum dispersion is decomposed in a linear and parabolic sub-band sets, shown in Fig.2.7a, illustrating that a trilayer graphene is a zero-gap semiconductor. Unlike in the case of bilayer graphene, biased Bernal-stacked trilayers do not exhibit insulating behavior. The electrostatic field shifts the linear sub-band with respect to the Fermi energy hence the trilayer remains conducting [62]. Including the next-nearest neighbor hopping parameters results in a more complex electron-hole asymmetric band structure shown on Fig.2.7b.

Here, the rhombohedral stacking (ABC) in graphene is not considered in detail, however few structural differences and its distinct electronic properties can be mentioned. Structurally, ABC stacks are obtained by rotating the third layer by 120° with respect to the second one (in Bernal stacking, the third layer is rotated by −120° with respect to the second one, so the first one is exactly under it), so ABC stacks always obey inversion symmetry, see Fig.2.6: [64]. In the case of trilayer graphene with rhombohedral stacking, the low-energy band structure is shown on Fig.2.7: [65] with a cubic dispersion.
Figure 2.7: Electronic structure of trilayer graphene \footnote{63}. a, Bernal stacking, tight-binding approach; b, Bernal stacking, SWM model including next-nearest neighbor hoppings; c, Rhombohedral stacking.

Figure 2.8: Crystal structure of tetralayer graphene. a, Four layers with nearest-neighbor hopping parameters $\gamma_0$ and $\gamma_1$ indicated by arrows; b, Bernal stacking order in the tetralayer, with the inversion center shown as an encircled dot.

close to the $K$ and $K'$-points. It is evident that such electronic structure cannot be obtained using effective subband model; the same is true for thicker ABC-stacked graphene flakes as well.
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Electronic structure of Bernal-stacked tetralayer graphene

The crystal structure of Bernal-stacked tetralayer graphene (4LG) is presented in Fig. 2.8a. It consists of four ABAB-stacked graphene layers and follows the inversion symmetry around the center located between the second and the third layer (Fig. 2.8b). Its electronic structure can be obtained following the effective subband approach outlined above, in a similar manner as for 3LG. From (2.33) with $N = 4$, $\kappa_4 = \pi/5, 2\pi/5, 3\pi/5, 4\pi/5$ with $\cos \kappa_{4,1} = \pm 1/4(1 + \sqrt{5})$ and $\cos \kappa_{4,2} = \pm 1/4(-1 + \sqrt{5})$ correspondingly. Plugging them in Eq. (2.33) produces the following dispersion relations:

$$
E(k) = \begin{cases} 
\pm \frac{1}{4}(1 + \sqrt{5})\gamma_1 \pm \sqrt{70^2|S(k)|^2 + \gamma_1^2 \frac{1}{8}(3 + \sqrt{5})}, & \cos \kappa = \pm 1/4(1 + \sqrt{5}), \\
\pm \frac{1}{4}(-1 + \sqrt{5})\gamma_1 \pm \sqrt{70^2|S(k)|^2 + \gamma_1^2 \frac{1}{8}(3 - \sqrt{5})}, & \cos \kappa = \pm 1/4(-1 + \sqrt{5}).
\end{cases}
$$

(2.35)

As Eq. (2.35) shows, the electron-hole symmetric electronic structure of 4LG consists of two bilayer-like sets of sub-bands, with different effective masses. The band structure generated by this rather simple consideration is shown in Fig. 2.9a. At low energy, parabolic sub-bands touch at the Fermi energy. Including next-nearest neighbor hopping parameters $\gamma_2 - \gamma_5$ modifies the band structure, as shown in Fig. 2.9b. The energy-momentum dispersion is not electron-hole symmetric any more and the exact energy landscape at the energy scale $E \ll \gamma_1$ strongly depends on the exact values of next-nearest neighbor hopping parameters.

2.2 Electronic transport in graphene devices

This Section is dedicated to the electronic properties of graphene devices and comparison of supported and suspended graphene. Subsection 2.2.1 is focused on the field-effect in graphene devices and the parameters indicating device quality. In Subsection 2.2.2 high quality graphene field effect devices are presented and compared: graphene supported on hexagonal Boron Nitride, and suspended graphene. It is shown that the latter is the most suitable type of devices for studying many-body interactions effects close to the charge neutrality.
Figure 2.9: Electronic structure of tetralayer graphene. a, Energy-momentum dispersion of tetralayer graphene with Bernal stacking, using the tight-binding approach with only the nearest-neighbor hopping included; b, Energy-momentum dispersion of tetralayer graphene with Bernal stacking, using the SWM model including next-nearest neighbor hoppings [29].

Figure 2.10: Graphene sample supported on Si/SiO$_2$ is etched in a 6-terminal Hall bar geometry [3].

2.2.1 Electric field effect and resistance peak at CNP

Field effect in graphene can be induced and controlled by applying voltage $V_G$ to an external top or bottom gate separated from graphene by a layer of dielectric. The electron-hole symmetric spectrum with touching valence and conduction bands (Fig. 2.11a) makes the field effect in graphene ambipolar [3]. The hallmark feature of graphene field effect is the so-called Dirac peak (DP) – the resistance peaks when the Fermi level approaches the charge neutrality.
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Figure 2.11: Typical resistance peak at charge neutrality. **a**, Sketch of the energy-momentum dispersion near the CNP in graphene, horizontal lines illustrate Fermi levels corresponding to different polarity of the gate voltage \( V_G \), shaded area corresponds to the potential fluctuations from charged inhomogeneities with density \( n^* \); **b**, Resistance as a function of gate voltage \( R(V_{BG}) \) measured in monolayer graphene at 4 K; **c**, Conductance as a function of carrier density in a log-log scale \( G(n) = 1/R \) provides an estimation of the resistance peak width, charge carrier density \( n \) is extracted from the QHE plateau evolution with the field and \( n^{[66]} \), arrow indicates the charged inhomogeneities density \( n^* \).

First graphene devices were fabricated on Si/SiO\(_2\) substrates, – highly doped Si crystal wafer covered by \( \sim 300 \) nm of insulating SiO\(_2\) as a back gate (Fig.2.10). The parallel capacitor model is useful to estimate the charge carrier density induced by such back gate:

\[
n = \alpha(V_{BG} - V_{CNP}). \tag{2.36}
\]

Here, \( \alpha \) is the gate capacitance per unit area divided by the elementary charge:

\[
\alpha = \frac{\epsilon_0 \epsilon_r}{ed}. \tag{2.37}
\]

\( \epsilon_0 \) is the vacuum dielectric constant, \( e \) stands for the elementary charge, \( \epsilon_r \) is the relative dielectric permittivity of the gate insulator, and \( d \) is its thickness. \( d \) can be known with a good precision for supported graphene samples. The
maximum charge carrier density in a device supported on Si/SiO$_2$ ($\sim$ 300 nm) is limited by the gate insulator breakdown voltage $V_{BD} \approx 150$ V. In case of Si/SiO$_2$ devices, $n_{\text{max}} = \alpha_{\text{SiO}_2} n V_{BD} \approx 1 \times 10^{13}$ cm$^{-2}$.

Charge carriers mobility is one of the typical parameters reflecting the device quality. Away from the charge neutrality, it can be estimated from the Drude formula for disordered systems:

$$\mu_{\text{FE}} = \frac{1}{e} \frac{d\sigma}{dn}$$

In graphene devices supported on Si/SiO$_2$, mobility values can reach 10-20 $10^{3}$ cm$^2$V$^{-1}$s$^{-1}$. In high quality devices, where the transport is essentially ballistic, the Drude definition of mobility for diffusive systems is not meaningful.

Another important indication of sample quality is the resistance peak width, which directly reflects the amount of charge inhomogeneities in the sample. The width of the peak can be estimated from a log-log plot of the conductance as a function of gate voltage, $G(V_G)$ as shown on Fig.2.11. Close to the charge neutrality, potential fluctuations caused by charged impurities define the carrier density $n < n^*$, so changing the gate voltage does not affect the carrier density in the device. Once $n > n^*$, the field effect dominates the transport and the charge density is tuned by the applied electrostatic field. Typical values of $n^*$ in devices supported on Si/SiO$_2$ are of the order of $10^{11}$ cm$^{-2}$, which is not low enough to observe the phenomena close to the CNP.

Many of characteristic graphene properties can be observed in devices on Si/SiO$_2$ where the transport is diffusive on the scale of few $\mu$m (e.g. Dirac peak, QHE up to the room temperature and broken symmetry states at $B > 9T$ [4, 67, 68]), however higher quality devices are required to observe phenomena close to the charge neutrality or study the ballistic transport properties in graphene.

### 2.2.2 High quality graphene devices

**Graphene on h-BN**

One way to improve the device quality is to reduce the amount of impurities trapped between the graphene sheet and the substrate as well as to minimize the surface roughness effect by using a clean, flat substrate. A good substrate for this method is hexagonal Boron Nitride, h-BN, an insulating crystal with hexagonal lattice, which can be also microcleaved to obtain atomically flat surface. To transfer a graphene flake on top of h-BN is a delicate procedure,
Figure 2.12: Graphene on h-BN. \(a\), Hexagonal Boron Nitride crystal structure; \(b\), Graphene sample is supported on hBN is etched in a Hall bar geometry \([9]\)

similar to the graphene transfer on top of the predefined gate structure described in the Subsection 3.1.3 \([9]\). h-BN supported devices generally show better quality than their Si/SiO\(_2\) counterparts, however hydrocarbon bubbles trapped between the flakes strongly limit the sample quality. If the bubble-free area is large enough to fabricate a device then the rest of the flake can be etched away. To improve the sample quality, a series of consecutive annealings and atomic force microscopy (AFM) ironing can be used.

Best reported supported samples on h-BN allow to tune the charge carrier density down to \(\sim 10^{10}\) cm\(^{-2}\) so the transport properties of graphene close to CNP still remain inaccessible. However, many interaction effects such as fractional quantum Hall effect and Dirac peak reshaping have been reported on such samples \([69, 70]\). More interesting phenomena originating from interaction with the substrate, such as satellite Dirac peaks emerging from the Moiré lattice \([71]\) and Hofstadter butterfly fractal modification of the energy spectrum by the emerging periodic potential in the applied magnetic field \([72, 73]\), have been observed in clean graphene on h-BN substrate.

**Suspended graphene**

Suspending graphene flakes over the substrate helps to avoid substrate-related disorder and artefacts, as the flakes become decoupled from the environment. Suspending a graphene sheet can be done either by exfoliation on top of prepatterned substrate with holes or trenches \([74]\) or by selectively etching the substrate out from under the flake \([66, 75]\). The latter fabrication method is discussed in detail in the Section 3.1. This approach, in combination with
current annealing, allows one to obtain devices with the charged impurities density of only $n^* \approx 10^9 \text{ cm}^{-2}$ in monolayer graphene, which corresponds to only few electrons per $\mu\text{m}^2$ [17]. Remarkably low density of charge inhomogeneities in successfully annealed samples makes suspended graphene devices the most suitable type of samples to observe many-body interactions effects close to the charge neutrality. Subsection 2.5.1 presents a discussion why interactions in such samples are few times stronger than in supported samples.

On the downside, suspended graphene devices are very hard to fabricate, as discussed in the Introduction and the Section 3.1 and fragile – high $V_G$ can mechanically break the flake due to the electrostatic attraction to the gating substrate. This limits the accessible charge carrier density range in suspended graphene devices to $n < 10^{12} \text{ cm}^{-2}$. On top of that, suspended graphene devices have strong limitations of their size and geometry. Specifically, most of reported successfully annealed samples have dimensions of the order of 1-3 $\mu\text{m}^2$, and with very few exceptions, they are two-terminal. If a Hall bar similar to the one shown for graphene on Si/SiO$_2$ in Fig. 2.10 is suspended in few $\mu\text{m}$ large device, the Hall probes would have to be too close to the source and drain contacts, so they would effectively short the contacts [75]. Moreover, homogeneous current annealing is another limiting factor for such device geometry: in a suspended Hall bar, it is very difficult to avoid the impurities shorting the probes or clustering in one place, so the transport across the device depends on which probes are used. A way around this is...
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described in detail in the Section 3.1: a cross-like geometry allows the independent probing of longitudinal and transversal conductance, and fragments of the edges which are typically contaminated and lead to inhomogenous transport can be etched away (see the Fig. 3.1).

2.3 Quantum Hall effect in graphene and its stacks

This Section is dedicated to a characteristic magnetoresistance property of two-dimensional electron gas (2DEG) systems – quantum Hall effect, which determines the electronic transport in perpendicular magnetic field. In the Subsection 2.3.1, the general principles of quantum Hall effect (QHE) are outlined, and the dispersion of Landau levels for mono- and bilayer graphene is derived. Further, we discuss the anomalous QHE in monolayer and bilayer graphene and present the QHE of tri- and tetralayer Bernal-stacked graphene.

Subsection 2.3.2 is focused on broken symmetry states due to many-body interactions in mono- and bilayer graphene subjected to high magnetic field, which are manifested as additional integer values of QH plateaus to what is expected in case of the single particle picture for graphene.

2.3.1 Transport properties of graphene in high magnetic fields

Quantum Hall effect

When a 2DEG system is placed in a sufficiently strong perpendicular magnetic field $B$ the electron motion in the bulk of a sample is confined to circular orbits due to the Lorentz force (2.39), and the continuous energy spectrum splits into so-called Landau levels (LLs) with energies corresponding to the quantized cyclotron frequency values. In order to understand this behavior better, we start with the classical Hall effect, which occurs when the Lorentz force $F_L$ bends the trajectories of electrons moving from source to drain with the velocity $v$: 

$$F_L = e(E + \frac{1}{c} v \times B), \quad (2.39)$$

where $e$ is the elementary charge, $E$ is electric field and $c$ is the speed of light. The velocity of the charge carriers obtains a transversal component: $v_{xy} = cE/B$, the direction being defined by the carrier polarity, see Fig. 2.14a for electrons. In this case, electrons are accumulated on one edge of the sample, therefore resulting in a transversal potential drop $V_H$ called Hall
Figure 2.14: a, Sketch of a typical Hall bar geometry, similar to the one presented in Fig 2.10: longitudinal voltage drop is measured between source and drain contacts and transversal Hall voltage is measured between the perpendicular contacts; b, Sketch of the semiclassical ”skipping orbits” description.

To directly measure $V_H$ a pair of voltage probes located on the edges is necessary, as shown in Fig 2.14a, which illustrates probes configurations for measuring the longitudinal and transversal voltage drop across the device.

In clean 2DEGs, a strong perpendicular magnetic field confines the charge carriers in the bulk to the cyclotron orbits. Edge states going around the perimeter of the sample in a semiclassical approach can be thought of as ”skipping” orbits of the charge carriers which are reflected from the edge, see the Fig 2.14b. Solving the two-dimensional problem of an electron in magnetic field we obtain the energy spectrum of a 2DEG quantized as

$$E_n = \hbar \omega_c(n + \frac{1}{2})$$  \hspace{1cm} (2.40)

Here, $\omega_c = eB/m^*$ is a cyclotron frequency. ”Clean 2DEG” means that electrons can complete a cyclotron orbit before being scattered, and the bulk becomes insulating. This condition can be written as $\omega_c \tau > 1$, where $\tau$ is the single-particle lifetime, or the time that an electron survives without collisions. At the edges of a sample, which can be interpreted as a confining potential, Landau levels bend upwards (for electrons) or downwards (for holes), see Fig 2.15a. When the Fermi energy ($E_F$) crosses LLs at the edges of the sample it produces a conducting channel, or an edge state per LL crossed. Here, it is convenient to define the filling factor

$$\nu = \frac{n}{eB/h},$$  \hspace{1cm} (2.41)
Figure 2.15: Landau levels spectrum. a, Potential profile across the sample in transversal direction (following the convention from Fig 2.14): each time $E_F$ crosses a Landau level, one more conduction channel contributes to the transversal conductance; b, Widening of Landau levels due to disorder, different filling refers to localized (shaded area) and extended states, red trace shows a corresponding $\sigma_{xy}$.

where $n$ is charge carrier density and the denominator corresponds to the magnetic flux density, where $\hbar/e$ is a flux quantum and $B$ is magnetic field. When $E_F$ is tuned between the LLs the states remain localized (shaded area in Fig 2.15b) due to the disorder until they become extended (white area in Fig 2.15b) and the conductance grows until the system reaches the next Landau level. This constitutes the Quantum Hall effect (QHE): the transversal conductance $\sigma_{xy}$ is changing in a step-like manner as the magnetic field or charge carrier density is increased (see the sketch of DOS(E) for monolayer graphene on Fig 2.15b), while the longitudinal conductance $\sigma_{xx}$ undergoes concomitant zeros.

**Electron states of monolayer graphene in magnetic field**

Quantum Hall effect is not sample specific, instead it reflects the properties of charge carriers in a system with a given band structure. Electronic properties of graphene are unique in many ways, as was discussed in the Subsection 2.1.1 and the QHE in graphene reveals some consequences of this uniqueness.

Let us start by considering the energy spectrum of monolayer graphene placed in a perpendicular magnetic field. This spectrum can be obtained using the effective low energy Hamiltonian for monolayer graphene in magnetic field using Eq. (2.14) from the Subsection 2.1.2

$$\hat{H}_{\text{eff}} = \sigma \hbar v_F (\hat{p} - \frac{e}{c} \hat{A}),$$

(2.42)
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where $\sigma$ stands for the Pauli matrices (like the ones defined for Eq. (2.14)), $\hat{p} = -i\hbar \nabla$ and $A$ is a vector potential, $B = \nabla \times A$. The Schrödinger equation in this case reads

$$\sigma \hbar v_F (\hat{p} - \frac{e}{c} A) \psi = E \psi. \quad (2.43)$$

For further convenience we can define $\hat{\pi} = \hat{p} - \frac{e}{c} A$ and

$$\hat{\pi}_- = \hat{\pi}_x - i \hat{\pi}_y = \sqrt{2} \hbar B \hat{b},$$
$$\hat{\pi}_+ = \hat{\pi}_x + i \hat{\pi}_y = \sqrt{2} \hbar B \hat{b}^+, \quad (2.44)$$

where $\hat{b}$ and $\hat{b}^+$ are Bose operators and $[\hat{b}, \hat{b}^+] = 1$. Solving an eigenstate problem for such operators will result in harmonic oscillator states, with $\hat{\pi}_+$ and $\hat{\pi}_-$ acting as raising and lowering operators correspondingly.

The complete energy spectrum can be obtained from

$$\hat{b}^\dagger \hat{b} \psi_B = \epsilon^2 \psi_B, \quad (2.45)$$

where the eigenvalues are $\epsilon^2_n = n = 0, 1, 2, \ldots$, using which we can write down the eigenvalues of massless Dirac fermions in the magnetic field:

$$E_n^\pm = \hbar \omega_c \sqrt{n} \quad (2.46)$$

with the cyclotron quantum $\omega_c = \sqrt{2\hbar v_F/l_B}$. The solution for each valley is sublattice-polarized (around $K$-point, for $B > 0$, only states localized on the sublattice $A$ have non-zero amplitude) [2].

One can immediately see from this dispersion relation that it is very different from the typical 2DEG with a parabolic energy-momentum dispersion, Landau level spectrum of which has a form of $E_n = \hbar \omega_c (n + 1/2)$. In contrast with such 2DEG systems, Landau levels in graphene are not equidistant, and the zero energy LL is shared by holes and electrons (by the electron-hole symmetry of the solution) and because of this it is addressed as anomalous.

**Anomalous QHE in mono- and bilayer graphene**

QHE in graphene provides a solid evidence of the Dirac nature of charge carriers [4, 5] and is so robust that it can be observed at room temperature [67]. Due to the spin and valley degeneracy $g_s$ and $g_v$, each contributing Landau level has 4 conduction channels of $e^2/h$. For each polarity of charge carrier, the 0th Landau level is half-filled, so the plateau sequence is

$$\sigma_{xy} = g_s g_v (n + \frac{1}{2}) \frac{e^2}{h}, \quad (2.47)$$
Figure 2.16: Quantum Hall effect in monolayer graphene. a, Transversal resistance $R_{xy}$ (black) and longitudinal resistance $R_{xx}$ (red) as a function of magnetic field $B$ at $V_G = 15$ V, arrows indicate the filling factor $\nu = \hbar n/eB$ corresponding to plateaus of $R_{xy}$ and zeroes of $R_{xx}$; b, Hall resistance (black) and longitudinal resistance (orange) as a function of back gate voltage $V_G$ at $B = 9$ T.

Figure 2.17: Quantum Hall effect in bilayer graphene. a, Transversal resistivity $\rho_{xy}$ (blue) and longitudinal resistivity $\rho_{xx}$ (red) as a function of magnetic field $B$ at $n \approx 2.5 \times 10^{12}$ cm$^{-2}$; b, Transversal conductivity $\sigma_{xy}$ as a function of charge carrier density at fixed magnetic field.

for this reason, the quantum Hall effect in monolayer graphene is also called half-integer and results in a plateau sequence different from non-relativistic 2DEG systems, where QHE plateaus start at $\nu = 4$ and are equidistant, i.e. $\sigma_{xy}$ plateaus take values of 2, 6, 10, $\ldots$, $e^2/h$, as shown in Fig 2.16.
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The case of bilayer graphene differs from the one of the monolayer because the charge carriers are massive and the energy-momentum dispersion is parabolic. Following the same approach as for monolayer graphene [52], we can obtain the Landau level spectrum for bilayer graphene in the low-energy approximation $E \ll \gamma_0$:

$$E = \pm \hbar \omega_c^* \sqrt{n(n-1)}, \quad \text{where} \quad \omega_c^* = \frac{|e|B}{m^*c} \quad \text{and} \quad n = 0, 1, 2, \ldots, \quad (2.48)$$

where $m^*$ is the effective mass (2.21). As can be seen from (2.48), $n = 0$ and $n = 1$ are both zero-energy solutions, so the zero-energy state acquires 8-fold spin, valley and orbital degeneracy and is shared by electrons and holes. QHE in bilayer, therefore, is unique with respect to both conventional 2DEG and monolayer graphene: there is no plateau at 0 energy and it is not half-integer. The plateau sequence follows $\nu = 4(n + 1)$, as it was confirmed in numerous experiments (See Fig.2.17b). Similar to the case of monolayer graphene, such unusual QHE is related to the non-trivial Berry phase of $2\pi$ in bilayer graphene.

QHE in tri- and tetralayer graphene

The electronic structure of trilayer graphene, as demonstrated in the Subsection 2.1.4, can be considered as an effective combination of mono- and bilayer-like sub-bands. In this case, the degeneracy of the zero-energy LL corresponds to the their combined degeneracies amounting to $4 + 8 = 12$. The QH plateaus for trilayer graphene are expected at $\nu = \pm 6, \pm 10, \pm 14 \ldots$ [28, 55, 60, 64, 78] and have been obtained experimentally [79, 80]. Moreover, crossings of linear and parabolic sub-bands are observed, too: the 4-fold degeneracy of a LL increases to 8-fold at the crossing in clean samples [63].

The electronic structure of tetralayer graphene, in the simplest approximation based on the effective bilayer model which is described in Subsection 2.1.4 as consisting of two bilayer-like sub-bands. Therefore in tetralayers, it is expected to have a half-filled 16-fold degenerate $E = 0$ state, resulting in the filling factor sequence $\nu = \pm 8, \pm 12, \pm 16, \pm 20 \ldots$ [60]. Taking into account more hopping parameters, however, suggests modifications of the band structure at low energy $E \ll \gamma_1$ which would result in a different sequence, depending on the interplay between the values of the next-nearest neighbor hoppings, see Fig.2.18b [28]. More details regarding QHE in 4LG will be presented in Chapter 5 which is dedicated to experimental results on 4LG.
Electronic transport in graphene devices

Figure 2.18: Quantum Hall effect in tetralayer graphene. a, Hall conductivity as a function of Fermi energy calculated for different stacking orders with only nearest-neighbor hopping parameters included in the tight-binding model [60]; b, Color plot of density of states as a function of charge carrier density and magnetic field \( B \) calculated for Bernal-stacked tetralayer graphene with all hopping parameters included [28].

2.3.2 Broken symmetry states in QH regime

Symmetry breaking in graphene in high magnetic field has been observed in both mono- and bilayer graphene [68, 81, 82] and the experimental observations are in line with the theoretical expectations for lifting of degeneracies by electron-electron interactions. In principle, the SU(4) symmetry of graphene (spin and valley flavors) can be broken following different mechanisms not related to many-body interactions, such as potential difference induced between graphene layers in thicker samples by electrostatic potential or chemical doping, see the Subsection 2.1.3 (i), spin splitting by Zeeman interaction (ii), or strain-induced lifting of the valley degeneracy (iii). In reported experiments, the broken symmetry states are observed in high quality samples with resistance peak close to \( V_G = 0 \), excluding (i) [56]. Zeeman interaction and strain-induced terms are estimated to be two orders of magnitude weaker than Coulomb interaction, excluding (ii) and (iii) as the dominating symmetry-breaking mechanisms [50, 83, 84].

In monolayer graphene in high perpendicular magnetic field (strength of which depends on the disorder present in the sample), the QHE sequence of \( \nu = \pm 2, \pm 6, \pm 10, \) is extended to \( \nu = 0, \pm 1, \pm 3, \pm 4, \ldots \) as shown in Fig 2.19a [68, 81, 87]. The \( \nu = 0 \) plateau has not been observed in 2DEGs with non-relativistic charge carriers. Another reason why the \( \nu = 0 \) plateau is unusual
Figure 2.19: Integer Quantum Hall effect in monolayer graphene.  

a, Two-terminal resistance $R$ as a function of filling factor $\nu$ is divergent around $\nu = 0$ [85]; b, Schematic of zero-energy LL degeneracies lifting as a function of magnetic field; c, Sketch of possible configurations of the ground state: quantum Hall ferromagnet (QHF) and canted antiferromagnet (CAF) [85]; d, Two-terminal conductance $G$ as a function of filling factor $\nu$ exhibits plateaus at $\nu = 0, 1, 3$ corresponding to broken symmetry states in graphene [85].

is that the longitudinal conductance $\sigma_{xx}$ does not go to zero and instead it corresponds to a diverging resistance, see the Fig.2.19a. The $n = 0$ LL is special with respect to $n > 0$ levels because it is shared by holes and electrons, therefore many-body effects breaking the symmetry are different from the ones in higher order LLs.

It has been a challenge to determine the ground state underlying the broken symmetry states which would correctly explain the measured behavior. Among proposed mechanisms, two scenarios are in line with the observations: quantum Hall ferromagnet (QHF) [88–90], suggesting that the symmetry within each Landau level breaks separately, and magnetic catalysis [90, 91], which considers an interplay between states from different LLs. The first one predicts spin-polarized counterpropagating edge states, so the system is expected to remain conducting, and the second suggests an excitonic gap generation due to the interaction between holes and electrons in the $N = 0$ LL, which renders the entire system insulating. In QHF, all integer values of $\nu$ are allowed, and the magnetic catalysis scenario allows only $\nu = \pm 1$ odd filling factor as a result of an interplay of the many-body effects with the Zeeman splitting, despite of its small energy scale. All filling factors have
Figure 2.20: Integer Quantum Hall effect in bilayer graphene. \textbf{a}, Transversal conductivity $\sigma_{xy}$ as a function of the back gate voltage $V_g$ at different values of magnetic field $B$ shows plateaus corresponding to broken symmetry states in bilayer graphene with $\nu = 0, 1, 2, 3$ [94]; Inset: The color plot of two-terminal conductance as a function of charge carrier density $n$ and magnetic field $B$ shows diverging insulating state corresponding to $\nu = 0$ [82]; \textbf{b}, Schematic of zero-energy LL degeneracies lifting as a function of magnetic field [94].

been observed [69] but the insulating behavior at the charge neutrality point is in contrast with QHF behavior. General scenario of breaking the symmetries is sketched in Fig.2.19c: So far, the best explanation of the observed behavior is given by a manifold of layered antiferromagnetic states (LAF), where spins on each sublattice cant with respect to each other [86, 92]. These configurations are sketched in Fig.2.19c [93].

Similar to the case of monolayer graphene, in high quality suspended bilayer samples, all ground state degeneracies are lifted: states at $\nu = 0, \pm 1, \pm 2, \pm 3$ shown in Fig.2.20a, and have been shown to originate from electron-electron interactions [82, 94]. Symmetries of higher energy LLs are broken in accord with the proposed scenario of the QH ferromagnet, \textit{i.e.} the $\nu = 5, 7, 9, \ldots$ have not been observed. The state $\nu = 0$ behaves like its counterpart in monolayer, showing a strongly divergent resistance, however the difference from the monolayer case is evident from (2.48): the lowest Landau level in bilayer graphene is 8-fold degenerate due to the additional orbital degeneracy, as Landau levels $n = 0$ and $n = 1$ have the same energy. The corresponding symmetry breaking order, sketched in Fig.2.20b, allows for 16 different configurations of the ground state with a rich phase diagram. To determine specifically which of them is realized is a hard task.
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requiring a close collaboration between theoreticians and experimentalists. Canted antiferromagnetic (CAF) ground state is so far the most consistent way to explain the broken symmetry states [95, 96], as will be presented in the Subsection 2.5.2 in more detail.

2.4 Ballistic transport in graphene p-n junctions

This Section is dedicated to the unique properties of chiral electronic transport in monolayer graphene. Subsection 2.4.1 is focused on Klein tunnelling in monolayer graphene. Subsection 2.4.2 discusses the Fabry-Pérot interference which occurs in ballistic samples bounce between potential barriers which form a cavity, and the Klein tunnelling in graphene pn junctions.

2.4.1 Klein paradox and Klein tunneling in graphene

Klein tunnelling is a manifestation of so-called Klein paradox: a relativistic particle incident on a potential barriers is transmitted under it as its antiparticle. A solution of the Dirac equation for relativistic particles incident on a potential barrier much higher than the particle rest energy $U_B \gg mc^2$ suggests that the particles cross the barrier without losing the amplitude (unlike in non-relativistic quantum tunnelling where the states under the barrier are described by evanescent waves) due to charge conjugation symmetry of Dirac particles. For massive relativistic particles, Klein tunnelling demands a potential barrier so high and sharp that it can be realized in supercritical atoms or black holes, where the particle creation regime would be dominating. In such conditions, it is hard to identify an observable consequence of such tunnelling, and therefore Klein tunnelling has long remained a gedanken experiment.

Realization of Klein tunnelling has become possible in graphene: charge carriers at low energy are described by the Dirac equation (see the subsection 2.1.2), and the spectrum is electron-hole symmetric. The charge carriers in graphene are massless so Klein tunnelling can be observed across a small potential barrier because the condition $U_B \gg mc^2$ is automatically satisfied [7]. In practice, conditions for such tunnelling are realized in the framework of a pn (or pnp) junction devices. The transmission through the barrier depends on the microscopic details of the potential profile, i.e. sharpness of the pn interface [7, 97].

Angular dependence of the transmission across a sharp potential barrier in graphene is shown in Fig 2.22. It illustrates the transmission probability
Ballistic transport in graphene p-n junctions

Figure 2.21: Schematic of the Klein tunnelling process through a \( pnp \) junction in monolayer graphene with a corresponding electronic structure: an electron is incident on a potential barrier and is transmitted across it as a hole, which turns back into electron once the barrier is left behind.

due to the Klein tunnelling for different charge carrier densities\([7, 98]\): in the conditions of prohibited backscattering from the barrier sharp on the scale of the lattice constant, the transmission can reach 100\% even at large incidence angles. However, a such sharp barrier leads to intervalley scattering\([99]\). In case of a smoother barrier, nearly full transmission occurs across the potential barrier at normal incidence (Fig.2.22b) and the transmission probability becomes highly sensitive to the angle of incidence and acquires an exponential component\([8]\).

In the case of graphene, the transmission across a \( pn \) junction is defined by an evanescent component which appears due to the finite smearing of a barrier with length \( L \) and width \( W \), and is dependent on the incident angle \( \theta \)\([8]\):

\[
k_F(x) = \begin{cases} 
-k_F/2 & x < 0 \\
F x & 0 \leq x \leq L \\
k_F/2 & x > L 
\end{cases}
\]

\[
|T|^2 \sim e^{(-2\pi^2 \frac{hv_F}{\lambda_F} \sin^2 \theta)} \tag{2.49}
\]

Here, \( F \) is the electric field \( F = V/L \). The Compton wavelength and the speed of light in the case of graphene are substituted by the Fermi wavelength \( \lambda_F = 2\pi/k_F \) and Fermi velocity \( v_F \).

The Landauer formula is useful to estimate the ballistic conductance of
Figure 2.22: Calculated angular dependence of the transmission coefficient across a potential barrier in graphene, red and blue colors stand for different charge carrier densities in the gated region. a, Infinitely sharp potential profile [7]; b, Realistic potential profile described by (2.49) [100]

A pn junction in graphene provided the mean free path $l_{MFP}$ is larger than the barrier length $L$,:

$$G = \frac{4e^2}{\hbar} \int d\theta \frac{Wk_F}{2\pi} |T(\theta)|^2 \approx \frac{2e^2}{\pi \hbar} W \sqrt{\frac{F}{\hbar v_F}} \quad (2.50)$$

In early Klein tunnelling experiments, the device quality was strongly limited by polymer residues from the sample fabrication and defects and impurities from the supporting substrate ($\mu \sim 1 - 5 \times 10^3$ cm$^2$/Vs), so pn junctions realized in graphene were rather diffusive. Still, the data and the calculations was suggesting that devices with a pn junction were more resistive than the ones without it [101, 102] and the conductance of the cleanest devices was in a reasonable agreement with the expression (2.50) [103, 104]. Without good quality ballistic samples and tools to probe the angle-resolved transport observation of Klein tunnelling was limited to a comparison with (2.50) until it was suggested that Klein tunnelling should explain the behavior of electrons in a Fabry-Pérot like cavity subjected to a magnetic field. This case will be the subject of the next subsection.
Ballistic transport in graphene p-n junctions

2.4.2 Fabry-Pérot interference in graphene pnp junctions

Observable consequences of Klein tunnelling can be probed in an electronic analogue of the Fabry-Pérot cavity. If contacts or pnp interfaces are sufficiently reflective then an interference pattern appears in the conductance map as a function of charge carrier density inside the cavity, as shown in Fig.2.24. Observation of direct consequences of Klein tunnelling in such a system presents a more unambiguous approach then comparing the measured conductance with (2.50).

Fabry-Pérot (FP) resonators can be realized in clean monolayer graphene devices between reflective contacts and in devices with pnp junctions. If the cavity-like region is smaller than the phase coherence length, electrons reflected from the potential barriers will interfere, resulting in transmission maxima and minima. In this case, the transport is dominated by the charge carriers incident at small angles, for which both transmission and reflection are non-negligible [106]. Let us consider that a potential barrier caused by a pn junction is parallel to the y-direction in the momentum space. Following the expression for the transmission probability (2.49), transport across such barrier will be restricted to charge carriers with \( k_y \approx 0 \), as the Fig 2.22 shows. Experimental observation of such interference is shown in Fig 2.23 where we can see a checker-board pattern from interferences occurring in two cavities formed between contacts and the pnp junction [105].
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Figure 2.24: Electron trajectories in a $pnp$ junction in weak magnetic field. 

a. Trajectories of electrons with different $k_y$ components in the momentum space: blue line corresponds to electron motion with finite $k_y$ at small magnetic field, which in higher $B$ develops into the trajectory indicated by the green line. Trajectory denoted by the orange line corresponds to the electrons with $k_y \approx 0$, which in finite $B$ enclose the origin of coordinates and acquire non-trivial Berry’s phase; 

b. Corresponding trajectories of electrons in the real space, same color convention as on the panel a; 

c. Color plot showing calculated resistance as a function of the potential depth and magnetic field. The phase shift corresponds to the contributions from the electrons with $k_y \approx 0$ \cite{106}.

When a magnetic field is applied in the direction perpendicular to the surface of the sample, as the Fig. 2.24a illustrates, charge carriers with different values of $k_y$ will have a different behavior in the FP cavity, as sketched on Fig. 2.24b. Tracking the quasimomentum trajectory of charge carriers with large $k_y$ which do not acquire Berry’s phase shows that they do not contribute to the interference due to the collimation. On the contrary, the charge carriers with $k_y \approx 0$ move almost perpendicularly with respect to the $pn$ junction, and acquire Berry’s phase, see Fig. 2.24b, causing the $\pi$-phase shift of the interference pattern, as they are dominating the contribution to the conductance, see Fig. 2.24c \cite{106}. Indeed, this behavior has been observed experimentally \cite{32,107}\ and is an indication of charge carriers collimation due to the Klein tunnelling.
2.5 Electron-electron interactions in suspended graphene close to the CNP at B=0

This Section is dedicated to the spontaneous symmetry breaking near the charge neutrality due to the electron-electron interaction effects in $B = 0$. First, Subsection 2.5.1 briefly discusses the strength of electron-electron interactions in mono- and bilayer graphene, demonstrating why suspended graphene is an optimal system for experimental observation of many-body effects. Subsection 2.5.2 is focused on possible mechanisms for opening a gap near charge neutrality in bilayer graphene and corresponding ground state configurations.

2.5.1 Electron-electron interactions are most pronounced in suspended graphene

Close to the charge neutrality point, the density of states (DOS) in monolayer graphene becomes vanishingly low, however strength of interactions with respect to the kinetic energy does not depend on carrier density as can be estimated from the Wigner-Seitz radius: \[ r_s = \frac{E_{\text{int}}}{E_F} = \frac{e^2}{\epsilon \hbar v_F}. \] (2.51)

where $E_{\text{int}}$ is the average energy of Coulomb interactions between electrons and $\epsilon$ stands for the dielectric permittivity of graphene environment. For $\epsilon > 1$, $r_s < 2.2$: it is evident that the strongest interaction effects are observed at $\epsilon = 1$, i.e. suspended graphene where the flake is not in contact with the substrate is the optimal system for observing the electron-electron interactions effects. Curiously, the expression (2.51) resembles strongly the definition of the fine constant $\alpha = e^2/\epsilon_0 \hbar c$, the only difference being that the speed of light $c$ is substituted for Fermi velocity $v_F$. For that reason, (2.51) is called graphene fine constant. It has been shown [17] that many-body interactions indeed result in Fermi velocity renormalization in suspended monolayer graphene.

In bilayer graphene, the DOS at charge neutrality has a finite constant value, so the effect of electron-electron interactions is different then in monolayers, which will be discussed in more details in the following Subsection. In the case of bilayers, $r_s$ is defined as

\[ r_s = \frac{2m^* e^2}{\epsilon \hbar^2 \sqrt{\pi n}}. \] (2.52)
In suspended bilayer of high quality, charge carrier density can be tuned down to $n \sim 1 - 5 \times 10^9 \text{cm}^{-2}$, which render $r_s \approx 100 - 200$, so the electron-electron interactions in bilayers are much stronger that in monolayers.

### 2.5.2 Insulating gap at CNP in bilayer graphene

In bilayer graphene, since the ground state is highly degenerate and contains both holes and electrons, and at low energy $E < \gamma_0$, the band structure has a parabolic energy-momentum constant DOS at CNP, the system becomes susceptible to perturbations due to many-body effects. Interactions allow the highly degenerate ground state to lower its energy by lifting degeneracies, which leads to a spontaneous symmetry breaking.

Experiments with ultra-high quality suspended graphene samples, some of which allow to probe the system at the charge carrier densities down to $1 - 5 \times 10^9$, have shed some light on which ground states can be realized. Some samples have been found metallic, and some – insulating, with a thermally activated insulating state, without any evident dependence on the sample quality [21]. Placed in a magnetic field, samples of both types have shown broken symmetry quantum Hall states, which result from electron-electron interactions, as discussed in the Subsection [2.3.2]. This suggests a possibility that different ground state configurations can be realized depending on the microscopic details of the samples.
E-e interactions in suspended graphene close to the CNP at B=0

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Table 2.1: AQH: Anomalous quantum Hall; QSH: quantum spin Hall; LAF: layered antiferromagnetic; CLP: charge layer-polarized; QVH: quantum valley Hall, adapted from [22].

At the mean-field level [22, 60, 108, 109], the low-energy properties of the symmetry-broken states in BLG are commonly described within a two-band model, in terms of a $2 \times 2$ matrix Hamiltonian of the type

$$H^{\text{BLG}} = -\frac{\hbar^2}{2m^*} (k_x^2 - k_y^2) \sigma_z \pm 2k_xk_y \sigma_y) - \Delta \sigma_z$$ (2.53)

for each valley and spin (the $\pm$ sign changes going from the $K$ to the $K'$ valley). The first term is the kinetic energy of the electrons ($m^*$ is the effective mass) and the second one represents the order parameter of the broken symmetry state ($\sigma_x, \sigma_y, \sigma_z$ are Pauli matrices acting on the layer degree of freedom). Different ground states emerge, depending on how the sign of the order parameter $\Delta$ changes upon switching valley or spin [22, 109], but, in all cases, the "bulk" of BLG is gapped (see Fig.5.8a) as the term $\sigma_z$ in the Hamiltonian has an opposite sign for each layer for any fixed spin and valley configuration.

Possible symmetry breaking mechanisms by electron-electron interactions include a layer-polarized manifold of ground states leading to an excitonic instability [108, 110–112]. Layer-polarized states are characterized by how flavors (spin, valley) are distributed between the layers due to the symmetry breaking: the exchange potential allows to lower the energy of the system. Some of the 16 possible configurations and their properties are listed in Table 2.1 adapted from [22]. In the framework of the layer-polarized ground state scenario, there are several configurations in which the bulk becomes insulating and the edge states are protected and therefore the samples show a finite conductivity [113, 114]. The experimental observations suggest that anomalous quantum Hall state (AQH), in which electrons occupy different valleys on each layer, is a likely candidate to explain the behavior of conducting bilayers [57, 115]. The behavior of insulating samples suggests the layer antiferromagnetic (LAF) ground state configuration, in which each valley is occupied by an electron with a different spin orientation [96]; its canted phase (CAF) has been observed [95]. This type of broken symmetry induces
a staggered exchange potential without inducing an explicit charge or spin polarization. The top and the bottom layer acquire an exchange potential of the opposite sign, which acts in a similar fashion to the biasing potential described in Section 2.1.3 by adding an exchange term to the Hamiltonian and thus opens a gap.

Observation of both metallic and insulating samples has also lead to attempts to explain metallic and insulating bilayers using different interaction-based mechanisms, for example by a nematic phase emerging in a combination with modification of the electronic structure due to the trigonal warping [112, 116, 117]. The gapless phase, with properties corresponding to such description has been shown experimentally [24]: formation of additional Dirac cones results in a lower resistance at the CNP. Also, a scenario based on the single-particle picture has been proposed for thicker samples [118], which, however, fails to explain the experimental observations in thicker samples [30] (see the Section 5.4 for more detailed discussion).
Chapter 3

Fabrication and characterization of suspended graphene samples

The progress in graphene physics cannot be imagined without advances in sample fabrication. Despite of the fact that signature electronic properties of graphene (Dirac peak at charge neutrality, QHE) can be observed even in relatively low quality devices, ultra-high quality samples are essential to observe ballistic transport and phenomena which occur in the vicinity of the charge neutrality point, which are easily masked by charged impurities present in lower quality samples. This Chapter presents the sample fabrication and characterization methods used in this Thesis. Section 3.1 is dedicated to the fabrication and current annealing of high quality suspended devices of two types: with an additional bottom gate, which requires precise flake transfer, and four-terminal devices. Section 3.2 discusses methods to determine the thickness of graphene flakes. It outlines the basics of Raman spectroscopy of graphene and describes how to identify the number of layers in $N > 2$ Bernal stacks with help of magneto-phonon resonance, or magneto-Raman spectroscopy.

3.1 Fabrication of the high quality suspended graphene devices

Suspending graphene flakes exfoliated onto a polymer-covered substrate is a delicate process, involving few consecutive steps of electron beam lithography and gentle yet definitive removal of the substrate from under the flake. There are few methods which can be used to do this, and the acid-free approach
Quantum Transport in High Quality Suspended Graphene

Figure 3.1: Two types of suspended graphene devices fabricated for this Thesis. a, An optical microgram of a suspended two-terminal monolayer device with an additional bottom gate (seen in the darker orange shade between and under the contacts) to realize a $p_n$-junction, featured in the Chapter 4; b, SEM image of the suspended four-terminal bilayer graphene device like the ones discussed in the Chapter 5 and Refs. [37, 119].

developed by N. Tombros [31] has been chosen for the samples described in this Manuscript. This method has benefits as compared to etching out the SiO$_2$ from under the flake by the HF acid because, as it is less damaging for the contacts and avoids the critical point drying step and generally safer to use. Sample fabrication involves four consecutive electron beam lithography steps and demands overall very gentle handling. While bonding and mounting the sample on the measurement setup, one has to be careful to avoid electrostatic shocks. Once in the Heliox $^3$He fridge, the sample should be cooled down slowly to avoid strong thermal shock. Current annealing step is a bottleneck procedure, as generally reported yield of successfully annealed samples is about 20%.

Fabrication of a suspended device starts with the preparation of a substrate covered with the sacrificial resist: Polydimethylglutarimide (PMGI)-based lift-off resist (lift-off resist (LOR), MicroChem). After that, graphene flakes are exfoliated on top of it and covered by a resist for electron beam lithography (EBL), in our case Poly-meta-methyl Acrylate (PMMA) dissolved in Anisol. Metallic contacts are deposited on the developed pattern, and after the lift-off, the sacrificial resist is removed from the area under the device by EBL. In this thesis, two types of devices are discussed: suspended two-terminal devices with additional bottom gates (Fig. 3.1a) and suspended
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Figure 3.2: An optical image of typical mono- and few-layer graphene flakes after exfoliation on top of LOR-covered substrate; the bar corresponds to 10 µm. flakes of different thickness can be distinguished. Due to the high-contrast imaging regime and non-uniform thickness of underlying LOR, only intuitive thickness estimation can be done based on optical images.

Four-terminal devices (Fig. 3.1b).

3.1.1 Substrate with additional gating structure

External control of the charge carrier density in graphene is realized by using the highly p-doped Si (with 300 nm SiO$_2$ grown on top of it, the substrate of choice for making field effect graphene devices) as a gate. In case of suspended samples with additional bottom gate, the substrate has to be pre-patterned with extra gate electrodes by means of the EBL. For gates of $\approx$200 nm in width, only one layer of e-beam resist, 495 K PMMA, is used for the exposure, and a closer working distance of the e-beam is chosen to ensure that the structure is sharply defined and lift-off is good. Fabrication steps are similar to the patterning of the device contacts described below, with the difference being that no markers are necessary for the alignment and the gate electrodes are simply deposited in the center of the substrate and the lift-off process is done in hot Acetone. The external gate configuration of the successfully measured sample comprises a set of parallel gates 1-2 µm thick with 2-3 µm between them, the device schematic is shown on Fig. 3.3a, and
3.1.2 Graphene exfoliation

To prepare the samples described in Chapters 4 and 5, graphene was microcleaved on top of prepared substrates using the Magic 3M scotch tape following the same procedure as presented elsewhere. Some of the good flakes for fabrication are shown in Fig.3.2; they are large enough to incorporate several devices and there are no thick pieces of graphite adjacent to them, so they can be etched easily. Once all the flakes on the substrate have been identified and mapped, the sample is covered by the poly-methyl acrylate (PMMA) e-beam resist for the further fabrication of device electrodes. The substrate should be mapped before being covered with the resist: this approach allows the thickness of graphene flakes to be estimated more reliably (under PMMA they often look thicker or cannot be seen at all). Determination of flakes thickness is addressed in detail in Subsection 3.2.2.

3.1.3 High precision graphene flake transfer

For the flake transfer, graphene is exfoliated on large undoped Si/SiO₂ substrates (≈ 2 × 2 cm) covered with water-soluble polymer (a 9 wt.% Poly(4-Styrenesulfonic acid) solution in water, WSP) and a 950 K PMMA on top. A target substrate with pre-patterned gate structure (Fig.3.3a) covered with LOR, is placed under the microscope with a long working distance objective.

To facilitate handling of the PMMA film with graphene, a piece of flexible polyurethane (from a documents folder) with a hole in the middle is placed on top of the film in such a way that the flake selected for the transfer is in the center of the hole, and is held in place by patches of double-sided scotch tape. The substrate is then placed in a beaker with de-ionised water and, once the WSP is dissolved, is "fished out" by a rectangular support with a circular hole in the middle, surrounded by little patches of a double-sided scotch tape. Ideally, the flake would be located in the middle of the hole. The excess of water is dried by a corner of a paper tissue. In principle, the PMMA is mechanically robust enough to be supported by such frame but often (depending on the PMMA composition, which was a subject to variation) this is a bottleneck step as the film can be ruptured during fishing out or drying. A successfully "fished out" film on a frame is mounted on a micro-mechanical manipulator (see the Fig.3.3f) with the flake facing the target substrate (Fig.3.3b). The flake position is aligned with the gate structure and it is very gently brought down with continuous adjustment of...
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Figure 3.3: Schematic of steps of the fabrication process for suspended device with an additional bottom gate structure. 

a. A predefined additional bottom gate on Si/SiO₂ substrate covered with LOR; 
b. Precise transfer of a graphene flake supported by a PMMA membrane after it has been retrieved from the water; 
c. Sample with already defined source and drain 10 nm Ti/60 nm Au contacts is exposed to the e-beam to develop the LOR under the device; 
d. Graphene is suspended between metal contacts over an additional bottom gate structure; 
e. Optical picture of a set of suspended devices with additional bottom gates: the flake borders are outlined, lighter yellow metal stripes correspond to the source and drain contacts, darker shade – to the bottom gate, the purple color corresponds to the suspended region; 
f. Photograph of a micro-manipulator setup mounted on a microscope with a long working distance objective.

the X-Y position, until in contact with the target. Due to imperfections in lateral alignment between the frame and the target substrate sometimes the flake can not touch the target substrate or shifts with respect to the gate. In order to minimize the effect of misalignment few water drops of ∼1 μm can be deposited on top of the PMMA film by a micropipette around the flake to weight the PMMA around it down. In successful transfers, the aiming precision has reached ∼5 μm. After the transfer, once PMMA got stuck on the target substrate surface – which is evident from the cardinal change of color, the whole system is carefully moved onto a hot plate at ∼ 90°C to evaporate the water and improve the adhesion of the graphene to the sub-
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Figure 3.4: Fabrication steps for 4-terminal suspended graphene devices as the one shown in Fig. 3.1b. a, An optical image (here and in panels b-d) of contacts defined by the EBL, after the lift-off in hot Xylene; b, A developed etching pattern, to define the device geometry; c, Etched sample after the lift-off, patterned graphene devices can be seen in darker shade in the center; d, Developed suspension pattern, the purple color corresponds to the SiO₂; e, Sample mounted on a chip carrier and manually bonded with Indium wires.

strate. After that, the PMMA is lifted off and the sample is covered by the standard PMMA resist composite for the electron beam lithography.

3.1.4 Device patterning

Suspended graphene devices have to undergo a number of typical fabrication steps to define the metallic contacts and the device geometry and, finally, to remove the sacrificial resist from under the flake. The substrate with the flakes of choice is covered with a two layers resist consisting of 50K PMMA and 495K PMMA. Due to a smaller molecular weight of the bottom layer, the exposed structure has a larger undercut, which facilitates the subsequent lift-off. A set of markers around the flakes is exposed to the e-beam and developed: well-developed PMMA patterns can be easily identified by the electron microscope. This method allows to skip the time- and materials-consuming deposition of markers on the entire substrate. Once the device geometry has been designed, the pattern for electrodes is exposed. The contacts consisting of 10 nm Titanium and 50-70 nm Gold are deposited by electron beam evaporation. During the lift-off, the resist is dissolved and only the metal which covers the exposed pattern stays on the sample. PMMA lift-off is usually done in Acetone (cold or warm), but this is damaging for
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Figure 3.5: Current annealing of suspended graphene devices. a, Schematic of the circuit realized for the annealing; b, "Shorted" annealing configuration of four-terminal devices, a pair of probes adjacent to each side of the device is shorted together to achieve an effectively two-terminal configuration for the annealing; c, Typical current annealing curves from two annealing steps (1st annealing: blue curve, 2nd annealing: green curve) of the Sample 1 described in Chapter 5; jumps in sample resistance are evident at around 1 and 2.5 V; d, $R(V_{BG})$ gate dependence before annealing (black curve) and after each consecutive step (blue and green curve, correspondingly) from the panel b, showing the satisfactory resistance peak at charge neutrality after the second annealing; the inset shows a zoom into the data to show the resistance curve after the first annealing.

the LOR layer, so we use hot Xylene, which does not chemically react with LOR. For the etching step, necessary to remove unwanted flake fragments from suspended devices with a $p$-$n$-junction or to define the geometry of four-terminal devices, after lift-off, samples are covered with 495K PMMA and the etching pattern is defined by EBL. Oxygen or Argon plasma is used to etch off the exposed graphene (17 s or 30 s correspondingly). After the etching, the PMMA is lifted-off. To suspend the flake, LOR from under the device area is over-exposed by the electron beam. It is developed in Ethyl Lactate for 1 minute and then fixed in Hexane for 30 s, after which the sample is gently dried by $N_2$. The sample is fixed on a chip carrier using silver paste and then manually bonded with Indium wires, the result shown in Fig. 3.4e.
3.1.5 Current annealing

Ultra-high quality in suspended samples requires current annealing as the concluding step of the sample preparation in order to clean the impurities remaining after the fabrication exposure to the ambient conditions from the bulk of the sample. In general, this is a bottleneck step in sample preparation: only about 20% of the samples survive the annealing.

The schematic for the current annealing setup is shown in Fig.3.5a: a Keithley 2400 source-measure unit is used as a voltage bias source and to measure the current, and the voltage drop across the sample is measured by a digital multimeter (DMM). A low-pass filter is protecting devices from spurious voltage spikes. In this work, all current annealing has been done inside a Heliox $^3$He system at 4K in order to avoid condensation of remnant impurities present inside the fridge on the annealed sample surface during the cooling down.

This general annealing procedure is similar to the one presented elsewhere [33, 34, 36], and some intuition has to be developed regarding how to react to changes of sample properties during the annealing, which is an "anything can happen" kind of process. As the current density increases, a temperature gradient is established from the bulk of the sample to the contacts, with the temperature reaching an estimate value of $\approx 600^\circ$C [33]. As a consequence, the impurities diffuse towards the colder parts of the sample, leaving the middle part clean. The diffusion of adsorbates around the sample surface or sample structural changes lead to abrupt changes in sample resistance. The voltage across the sample is ramped in 5-10 mV steps until the voltage drop measured on the sample starts jumping. One of such jumps is evident in Fig.3.5c around 1 V. After each such jump the ramping is paused until the sample stops changing and then the rate is reduced until it reaches eventually about 0.1 mV step size. Normally, a successful annealing requires the voltage across the sample to reach at least 2 V. Depending on how many changes occur in a sample, the current annealing can be done in several steps: having reached a certain voltage (usually, beyond 1 V) the ramping is inverted, and the sample is let to cool down. Then the field effect is measured to assess the sample quality and if the peak at charge neutrality is not sharp enough or the sample is strongly doped the annealing step is repeated. Typically, best samples are obtained after 2-3 annealing steps. If more annealing steps are needed the sample can end up broken or reduced to a constriction with a high probability. In order to subject the sample to less thermal shock the current ramping can be inverted until the changes in the sample stop occurring, and then the annealing can be resumed.

It is challenging to current anneal samples with a Hall bar geometry
Contacts not used in the annealing invasively couple to the sample and affect the temperature gradient across the sample. This leads to an inhomogeneous distribution of impurities in the device, so the transport characteristics of the device depend on pair of contacts used to probe them. Our way around this issue is to etch constrictions connecting the contacts and the "bulk" of the sample, as shown in Fig.3.1b. To anneal such four-terminal device, two pairs of electrodes on each side of the device are shorted together, as shown in Fig.3.5b. In this "shorted" effectively two-terminal configurations, the sample can be annealed following the same procedure as previously outlined for actual two-terminal devices. Some impurities may accumulate on the constrictions which support the "bulk" of the sample and add to their resistance but the "bulk" of the sample is homogeneously annealed as will be demonstrated in Chapter 5. The added width of the constrictions should be not less then the total width of the device, otherwise they are subjected to higher current densities than the "bulk" of the sample and can be easily broken or reduced to a nanoribbon, so they become effectively insulating.

3.2 Raman spectroscopy for determination of graphene flakes thickness

3.2.1 Thickness determination in few-layer graphene

Optical contrast of graphene supported on Si/SiO₂ provides a robust tool to estimate graphene thickness [120], however it becomes insufficient for flakes exfoliated on top of polymers for further transfer or suspension, because polymer films do not have a uniform thickness so the relative contrast of graphene cannot be well quantified. One can develop an intuition to distinguish mono- and bilayer graphene by eye (see the Fig.3.2) and ultimately it can be confirmed during transport measurements – thickness-specific quantum Hall effect presents a straightforward way to determine the number of layers. However, when thicker samples are in question, neither intuition nor the QHE are sufficient to unambiguously identify the number of layers, especially in very clean samples, where a crossover to symmetry broken states occurs at relatively small magnetic fields.

Alternative methods to measure graphene thickness include atomic force microscopy (AFM) and Raman spectroscopy. AFM is a cumbersome and not reliable method to determine graphene thickness so we will focus on Raman spectroscopy.
**3.2.2 Raman spectroscopy for thickness determination**

Raman spectroscopy is based on the Stokes scattering of monochromatic light: a photon is absorbed and then inelastically re-emitted by a scatterer. The full Raman spectrum of graphene is rich and sensitive to many factors such as flake quality, thickness, coupling to the substrate, etc [121]. The \( E_{2g} \) phonon shown in Fig. 3.6a produces strongest Stokes scattering and results in the G-peak found around 1580 cm\(^{-1}\), see Fig. 3.6b, the exact height and position depending on the flake thickness. The D-peak at around 1310 cm\(^{-1}\) (not shown) is produced by the dangling bonds from the edges and impurities present on the flake. 2D-peak located around 2700 cm\(^{-1}\) corresponds to a photon-coupled recombination of an electron with a hole, once the former has been excited from the valence to the conduction band by a photon. Since it is closely related to the electronic structure, the shape and position of the 2D peak strongly depends on the number of layers and the stacking order, see the Fig. 3.6c. Samples with thickness \( N < 3 \) can be quite reliably identified by decomposing the 2D-peak in Lorenzians, but for thicker flakes it becomes tricky as the number of fitting curves increases. In order to compensate for numerous factors that have effect on Raman spectra in thicker flakes, one can collect a comprehensive set of spectra with different excitation wavelengths \( \lambda_{\text{exc}} \) – but this method, however reliable, is costly if there is no in-house Raman setup working with several \( \lambda_{\text{exc}} \).
3.2.3 Magneto-Raman spectroscopy

Looking at the evolution of Raman signal in a magnetic field can give a very precise information about the number of layers \[123\]. As discussed in Subsection 2.3.1, graphene energy spectrum splits into Landau levels, whose dispersion depends on the flake thickness. Charge carriers can be excited from an occupied level \(n_1\) to a higher energy unoccupied level \(n_2\), forming an excitonic pair. If such pair is formed between the LLs with \(|n_2 - n_1| = 1\), as shown in Fig.3.7, it can couple to the G-phonon of the Raman spectrum at certain values of magnetic field \(B\), producing magneto-phonon resonance (MPR) as shown in Fig.3.7. The energy necessary to induce such transitions is defined by the LL dispersion in the magnetic field, and therefore is thickness-specific \[123–125\].

The experimentally accessible signature of the MPR coupling is the change of the shape and position of G-peak of graphene Raman spectrum. Due to anticoupling character of the interaction, the peak first gains energy from the exciton and is blue-shifted, and then gives some of its energy to it, red-shifting and eventually returning to the non-interacting position \[124\]. As the
interaction takes place, the lifetime of the phonon becomes shorter, therefore widening the peak (as there is inverse proportion dependence of the peak width on the excitation lifetime). Therefore, the MPR can be observed by tracking the G-peak position and confirmed by the peak in the full width at half maximum (FWHM).

Graphene flakes of different thickness undergo MPR at different resonant magnetic fields, as shown on Fig.3.7. To estimate the expected resonance position for flakes of different thickness, it is convenient to use the effective sub-band model [27], in which the electronic structure of a few layer graphene is decomposed in mono- and bilayer-like bands, as discussed in Subsection 2.1.4. The energy of the G-peak crosses the spectrum of inter-LL excitations belonging to different sub-bands at different magnetic field values, and due to the parabolic dispersion, some of the excitation energies coincide with each other, see the Fig.3.7b,d. If such coincidence occurs near the energy of the G-peak then the photon coupling to the exciton is enhanced and we can observe a stronger anticrossing behavior, – even at the room temperature [38]. Resonant magnetic fields at which such crossings take place are unique for each graphene thickness, and therefore provide an unambiguous indication of the sample thickness. The benefit of measuring the enhanced coupling is that in already fabricated suspended samples, the resonance is strong enough to be observed despite of the parasitic signal coming from LOR and golden contacts.
Chapter 4

A ballistic pn junction in suspended graphene with split bottom gates

We have developed a process to fabricate suspended graphene devices with additional local bottom gates, and tested it by realizing electrostatically controlled pn junctions on a suspended graphene monolayer nearly 2 µm long. Transport measurements reveal that the conductance in the sample exhibits characteristic Fabry-Pérot oscillations in the cavities formed by the pn junction and each of the contacts, with transport occurring in the ballistic regime. An observed π-shift of the interference pattern in magnetic field is consistent with the Dirac nature of the charge carriers. Our results demonstrate the possibility to achieve a high degree of control on the local electronic properties of ultra-clean suspended graphene layers, which is a key aspect for the realization of new graphene nanostructures.

4.1 Introduction

Technical developments in device fabrication are essential to perform transport experiments revealing the intrinsic electronic properties of graphene. Suspended graphene devices [66, 75] and devices with hexagonal boron nitride (hBN) as supporting substrate [9, 127] provide clear examples. The same is true for double-gated devices, in which graphene is not in direct contact with any dielectric material [22, 57, 58]. In such devices, ballistic transport is manifested – e.g. through the negative resistance in multiterminal devices [24, 36]. Many-body interactions phenomena as the fractional

\footnote{The results presented in this Chapter are published in [126]}
quantum Hall effect can be observed in such systems [37, 69, 85, 87] as well as new interaction-induced symmetry broken states in bilayers, [22, 57]. Double-gating on suspended devices performed locally opens the possibility to realize high quality structures with interesting properties. In bilayer graphene, for instance, local double gating can result in a topological confinement [20, 58], and realization of fully electrostatically tunable pn junctions – of interest to generate or detect light at continuously tunable frequencies in the THz to mid-infrared range. Ballistic graphene devices with pn-junctions operating in magnetic field are an “optics for electrons” playground, as they allow electron guiding due to the snake states [12–16]. As an essential step towards the realization of these new structures, high quality suspended devices are necessary, with charge carriers being essentially ballistic on the scale of few µm. In Section 4.2, we describe the fabrication of high-quality suspended graphene devices with local bottom gates (see also Section 3.1) to achieve an electrostatically tunable ballistic pn junction in monolayer graphene. In Section 4.3, we discuss a Fabry-Pérot interference pattern emerging as the electrostatic field of the two gates is tuned independently, an indication of the ballistic character of charge carriers in the sample. Section 4.4 shows the Dirac nature of the charge carriers in our device: we observe a π-shift of the interference pattern in the magnetic field which illustrates that Klein tunnelling dominates the carriers transmission, as described in the Subsection 2.4.2. We also show energy scale of the interference pattern, which is in agreement with the rest of the data. Our observations are summarized in the Conclusions.

4.2 Fabrication of high quality suspended graphene device with an additional bottom gate

The fabrication process is illustrated schematically in Fig.4.1. As the first step, we prepare bottom gates of the desired configuration – in the present case, a simple single strip – on a doped silicon substrate covered with 300 nm SiO₂, by using conventional techniques (electron-beam lithography, Ti/Au evaporation, and lift-off), see Section 3.1. Next, a 450 nm-thick layer of Polydimethylglutarimide (PMGI)-based lift-off resist (LOR, MicroChem) is spun onto the substrate (Fig.4.1a). LOR resist is chosen because it is compatible with all subsequent micro-fabrication processes, and, importantly, it can also be exposed with an electron beam and developed away to suspend graphene at the end of the fabrication process [31, 119, 128].

For the high-precision flake transfer and further sample fabrication de-
A ballistic pn junction in suspended graphene with split bottom gates

Figure 4.1: Suspended graphene with an additional bottom gate. a, Optical microscope image of the device (the dashed lines indicate the edges of the graphene flake); the local bottom gate is visible under the right electrode (the bar is 2 µm long); b, Schematic top view denoting the regions 1 and 2 (coupled to the two different gate electrodes).

tails, see Subsection 3.1.3 and Fig. 3.3. The resulting device can be seen on the optical image presented of the Figures 3.3e and 4.1a. It features two-terminal monolayer graphene device 1.8 µm long contacted with Ti/Au electrodes (10/60 nm thick) with an additional bottom gate that overlaps with about half of the suspended length (see Fig. 4.1b). The split bottom gate defines two regions (1 and 2, see Fig. 4.1b), in which carrier density and type can be independently controlled by applying voltages to the doped silicon substrate ($V_1$) and to the local gate ($V_2$). Transport measurements as a function of $V_1$ and $V_2$ were performed in a Heliox $^3$He system (Oxford Instruments) with a base temperature of 250 mK to characterize the device at different magnetic field ($B$), bias ($V_{DC}$), and temperature ($T$). Prior to the measurements, the device was current annealed at 4.2 K following the procedure described in detail in Subsection 3.1.5.

4.3 Fabry-Pérot interference in a 1.8 µm-long suspended graphene p-n junction

Fig. 4.2a shows the resistance $R$ measured at $T = 0.25$ K as a function of $V_1$ and $V_2$. Four quadrants can be identified, roughly corresponding to $V_1$ and $V_2$ having the same or opposite sign. When the sign is the same, no pn junction
Figure 4.2: Fabry-Pérot oscillations in a $pn$ junctions in graphene. a, The color plot $R(V_1, V_2)$ shows four regions corresponding to different transport regimes: the upper left and lower right quadrants correspond to the regime where a $pn$ junction is formed, and feature two crossing ”checkerboard” interference patterns; the upper right and lower left quadrants correspond to the unipolar transport regime; inset: $R(n_1, n_2)$ corresponding to the area limited by dashed white lines on the panel a, recalculated taking the cross-talk between the gates into account; along the dashed white line, $n_1$ changes while $n_2$ is kept fixed at $2.82 \times 10^{10}$ cm$^{-2}$; b, Line-cut $R(n_1)$ corresponding to the white dashed line on the panel a shows resistance oscillations and higher average resistance in the region corresponding to a $pn$-junction formed in the device; c, Scatter plot for average oscillation period in the second cavity at different values of $n_1$, the broken line corresponds to a value $\Delta n_2 = 2\sqrt{n_2}/L_2$ with $L_2 = 800$ nm, estimated from a simple particle-in-a-box model.
A ballistic pn junction in suspended graphene with split bottom gates is present in the device: only charge carriers of one polarity are accumulated in regions 1 and 2. A pn junction is present between region 1 and 2 when \( V_1 \) and \( V_2 \) have opposite sign. The borders of different quadrants are not parallel to the \( V_1 \) and \( V_2 \) axis, because of the cross-talk between two gates: \( V_1 \) does not only change the density in region 1 \( (n_1) \) but also – to a lesser extent – the density in region 2 \( (n_2) \); similarly, \( V_2 \) also influences the density \( n_1 \). Obviously, the density is not spatially uniform in regions 1 and 2, for a pn junction is present, i.e. the carrier density vanishes at the interface between the two regions. However, accounting as much as possible for the effect of the cross-talk is useful to analyse the data. This can be done by looking at the gate and magnetic field dependence of quantized Hall conductance plateaus in the unipolar regime, where \( n_1 \approx n_2 \) (i.e., when the density non-uniformity is less pronounced). We find \( n_1 \left[10^{10} \text{cm}^{-2}\right] = 1.0 \times V_1 \left[V\right] + 0.35 \times V_2 \left[V\right] + 0.5 \) and \( n_2 \left[10^{10} \text{cm}^{-2}\right] = 0.2 \times V_1 \left[V\right] + 1.4 \times V_2 \left[V\right] - 0.4 \) (the constants account for the shift of charge neutrality point from \( V_{1/2} = 0 \text{ V} \); the proportionality terms between \( n_1/2 \) and \( V_{1/2} \) are in good agreement with the estimated geometrical capacitances). The resistance as a function of \( n_1 \) and \( n_2 \) defined in this way is shown in the inset of Fig.4.2a.

When \( V_1 \) and \( V_2 \) are biased with opposite polarity to create a pn junction, the resistance doubles as compared to when no pn junction is present (compare, e.g., the resistance for \( n_1 < 0 \) and \( n_1 > 0 \) in Fig.4.2b). In particular, the pn junction contribution is significantly larger as compared to previously studied pn and pnp junctions on SiO\(_2\) substrates [101, 103, 104, 129].

Fig.4.2a further shows that the resistance also oscillates as a function of \( V_1 \) and \( V_2 \) when a pn junction is formed, in a way resembling the behavior of graphene pnp junctions on a Si/SiO\(_2\) substrate [32, 107]. In that case, the oscillations were shown to originate from Fabry-Pérot interference of Dirac electrons moving ballistically within the \( (\approx 100 \text{ nm long}) \) cavity defined by the pnp region [32, 106, 107]. In our device, Fabry-Pérot oscillations occur in cavities formed by the pn junction and each of the two interfaces with the metal contacts, where carriers are also backscattered [130, 131]. Our device therefore consists of two Fabry-Pérot cavities connected in series, and the “checkerboard” pattern visible in Fig.4.2a is a manifestation of interference in both cavities. The clear visibility of the oscillations directly in the resistance (Figs.4.2a and 4.2b), without the need of plotting the derivative of the conductance, is indicative of the high quality of the suspended pn junction [32, 107].

An estimate of the oscillation period \( \Delta n \) – the distance in density between two nearest resistance peaks or dips – is obtained by considering that the dynamical phase acquired by an electron wave propagating back and forth in the cavity is equal to \( 2\pi \), i.e. \( \Delta(2k_{F,i}L_i) = 2\pi \) (the subscript \( i = 1,2 \) labels the
As \( k_{Fi} = \sqrt{\pi n_i} \), we obtain \( \Delta n_i = 2\sqrt{\pi n_i}/L_i \). Note that several previous references reported an incorrect expression, \( \Delta n_i = 4\sqrt{\pi n_i}/L_i \), differing by a factor of 2 from ours \[32, 107, 132\]. The dotted line in Fig. 4.2c represents the values of \( \Delta n_2 \) estimated using this formula for region 2 \((L_2 = 800 \text{ nm})\), and the open squares are the experimental values extracted from the most pronounced oscillations measured upon changing \( n_2 \) (a similar result is obtained for region 1). The order of magnitude and the trend in the data are well captured by this simple estimation. The experimental values, however, are somewhat larger than expected, because the carrier density in the region close to the \( pn \) junction is lower than the calculated value \( n_2 \). The lower density causes a smaller value of \( k_F \), and therefore a smaller phase shift and an additional increase in carrier density is needed to compensate for this effect.

### 4.4 Interference pattern dependence on magnetic field \( B \) and bias voltage \( V_B \)

The evolution of the oscillation phase upon increasing magnetic field \( B \) (see Fig. 4.3) provides further evidence for the Fabry-Pérot nature of the interference \[32, 106, 107\]. Fig. 4.3a shows the \( B \)-dependence of the oscillations upon changing \( n_1 \) at fixed \( n_2 = 2.82 \times 10^{10} \text{ cm}^{-2} \) (i.e., by changing \( V_1 \) and \( V_2 \) along the dashed line depicted in Fig. 4.2a), which exhibits a \( \pi \) phase shift at \( B \equiv B^* \approx 20-30 \text{ mT} \) (varying \( n_2 \) at fixed \( n_1 \) gives comparable results). Fig. 4.3b shows the same effect in the derivative of the conductance \( (G = 1/R) \) with respect to \( n_1 \), and panel c illustrates the occurrence of the phase shift, with three individual slices of the color plot shown in the panel a, taken at \( B = 0, 30, \) and \( 50 \text{ mT} \): maxima of \( R(n_1) \) in the absence of magnetic field coincide with \( R(n_1) \) minima at 30 and 50 mT.

As discussed for \( pnp \) junctions \[32, 106, 107\], the phase shift originates from the unique properties of Dirac electrons, namely the angular dependence of the reflection probability at a \( pn \) junction \[4, 5\], and the accumulation of a \( \pi \) Berry phase along momentum-space trajectories that enclose the origin \[4, 5\]. For a given position of the Fermi energy, the electrons contributing predominantly to the Fabry-Pérot resistance oscillations are those incident on the \( pn \) junction with a certain transverse momentum \( (k_{y0}; \text{the specific value depends on the density profile across the junction}) \[32, 106\]. Upon increasing the perpendicular magnetic field, the electron trajectories in the Fabry-Pérot cavity are bent, and they eventually enclose the \( K \) or \( K' \)-point in the momentum space \[32, 106\]. When this happens, an additional Berry’s phase \( \pi \) is acquired, causing the phase shift in the resistance oscillations. For
A ballistic pn junction in suspended graphene with split bottom gates

Figure 4.3: Magnetic field dependence of $R(n_1)$ measured at $T = 0.25$ K, at fixed $n_2$, along the dashed line shown in Fig.4.2a. a, Plot of $R(n_1, B)$, showing characteristic $\pi$-shift at $B = B^* \approx 20-30$ mT; the broken lines indicate the values of $B$ ($B = 0, 30, 50$ mT) at which the data in panel c are measured; b, Plot of $dG/dn_1$, as a function of $n_1$ and $B$, shown for comparison with similar data reported in the literature; c, Line-cuts $R(n_1)$ at different values of magnetic field $B$.

$\simeq 100$ nm long $pnp$ junctions on substrate, the shift was found to occur at $B^* \approx 2h\kappa_0/eL \approx 250-500$ mT [32, 107]. Assuming a comparable value of $\kappa_0$ (within a factor of 2-3), this is consistent with our observations: the phase shift occurs at an order of magnitude smaller $B^* \approx 20-30$ mT, corresponding to an order of magnitude longer cavity.

Finally, we discuss the characteristic energy scale of the resistance oscillations. Fig.4.4a shows the differential resistance measured as a function of bias $V_{DC}$ and density $n_1$. Systematically, the position of the resistance peaks shifts linearly upon increasing $V_{DC}$, as expected for Fabry-Pérot interference [130, 131]. The shift is also illustrated by Fig.4.4b, which compares measurements taken at $V_{DC} = 0$ and 5.2 mV. From both Figs.4.4a and 4.4b, the bias needed to shift a maximum of differential resistance into a minimum is approximately 5 meV. We have also studied the energy dependence of the oscillation by changing temperature, and found that the oscillations are washed out at about 40 K ($\approx 3.5$ meV). Since, owing to the non-uniform charge density, the level spacing in the cavity is somewhat larger than the
Figure 4.4: Energy dependence of the Fabry-Pérot interference. a, Resistance $R$ measured at $T = 0.25$ K as a function of bias $V_{DC}$ and $n_1$ (at fixed $n_2$ along a dashed line in Fig.4.2a); the yellow dashed lines are guides to the eye; b, Two representative curves of $R(n_1)$ measured at $V_{DC} = 0$ and 5.2 mV, showing a $\pi$ shift in the oscillation phase; c, $T$-dependence of $R(n_1)$ measured at $V_{DC} = 0$ mV. All data in this figure were taken at $B = 40$ mT.

particle-in-a-box value $\hbar v_F/2L \approx 2.5$ meV (with $L \approx 1$ µm and $v_F = 10^6$ ms$^{-1}$), the energy scale found in the experiments is consistent with the simplest theoretical estimation.

Conclusion

We have developed a high-precision transfer technique for graphene flakes and used it to fabricate a suspended high quality graphene device with predefined additional bottom gate structure. We have found that the behavior of our device is consistent with the presence of a $pn$ junction, and electronic transport occurs in ballistic regime over a length comparable to the device size (1.8 µm). The measurements therefore confirm that the LOR-based fabrication technique indeed enables the realization of suspended graphene devices with local bottom gates preserving the high quality of the material. As compared to the previously measured devices, the ones produced by this technique show one order of magnitude longer ballistic transport.
Chapter 5

Insulating state in tetralayers reveals an even-odd interaction effect in multilayer graphene

Close to charge neutrality, the electronic properties of graphene and its multilayers are sensitive to electron-electron interactions. In bilayers, for instance, interactions are predicted to open a gap between valence and conduction bands, turning the system into an insulator [18, 60, 65, 108, 109, 112]. In mono and (Bernal-stacked) trilayers, which remain conducting at low temperature [17, 30], interactions do not have equally drastic consequences. It is expected that interaction effects become weaker for thicker multilayers, whose behaviour should converge to that of graphite. Here we show that this expectation does not correspond to reality by revealing the occurrence of an insulating state close to charge neutrality in Bernal-stacked tetralayer graphene. This phenomenology – incompatible with the behaviour expected from the single-particle band structure – resembles that observed in bilayers [21, 23, 57], but the insulating state in tetralayers is visible at higher temperature. We explain our findings, and the systematic even-odd effect of interactions in Bernal-stacked layers of different thickness that emerges from experiments, in terms of a generalization of the interaction-driven, broken symmetry states proposed for bilayers.

Introduction

In the absence of magnetic field, close to charge neutrality (i.e. at small charge carrier density), in graphene systems, such as mono- and bilayers,

\footnote{The results presented in this Chapter are published in [38]}

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effects of electron-electron interactions have been observed. As has been discussed in the Subsection 2.5.1, suspended graphene of high quality is the optimal system for observing such effects, for the substrate does not screen the interactions. In monolayer graphene, the Fermi velocity near the CNP is renormalised [17], and in bilayers, they cause a spontaneous symmetry breaking which results in an insulating state [21, 23, 57], whereas suspended Bernal-stacked trilayer high quality graphene devices remain conducting [30].

Here, we focus on the insulating behavior of high quality suspended multiterminal tetralayer graphene close to the charge neutrality. The samples are fabricated and current annealed following the procedure described in Section 5.1. Section 5.2 describes evaluation of the sample quality and thickness determination by magneto-Raman spectroscopy (see the Subsection 3.2.3 on the method). Section 5.3 is dedicated to the characterization of the insulating state at charge neutrality at $B = 0$ and comparison with the insulating behavior of a high quality bilayer graphene fabricated by the same method. Section 5.4 shows the broken symmetry states away from the charge neutrality in high magnetic field. Based on these observations, in the Section 5.5 we discuss a possible mechanism for gap opening by generalizing the staggered exchange potential approach developed for bilayers to the case of the tetralayer. In Section 5.6 we discuss an even-odd effect of interactions close to the charge neutrality in high quality suspended samples. The findings of this work are summarized in the Conclusions.

### 5.1 Methods

Four-terminal samples for this study have been fabricated using Polydimethylglutarimide (PMGI) based lift-off resist (LOR, MicroChem) as a sacrificial layer [31], following the procedure described in the Section 3.1 and Ref. [36]. Suspended and mounted on a chip carrier, the devices are cooled down in a Heliox $^3$He system to $T = 4.2$ K (Oxford Instruments; base temperature of 250 mK) and current annealed in a two-terminal configuration as discussed in detail in the Subsection 3.1.5 and Ref. [36]), by using shorted adjacent pairs of contacts (1 and 2) and (3 and 4) as a source and drain, see the inset in Fig. 5.1, for the labelling convention.

### 5.2 Sample characterization

Before discussing the detailed characterization of the thickness and the layers stacking order in our devices, we present the experimental indications of the
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Figure 5.1: Very high resistance at charge neutrality in high-quality suspended tetralayer graphene devices. a, \( V_G \)-dependence of the two-terminal resistance \( R_{2-4} \) of two devices (S1 and S2) at 4.2 K shows a resistance peak \( \approx 0.3 \) M\( \Omega \) at the CNP. Left inset: optical micrograph of a device under a PMMA mask for etching (see the Subsection 3.1.4) shows contact labels, the scale bar is 2\( \mu \)m. Right inset: crystal structure of Bernal-stacked 4LG; b, Conductance \( G_{2-4} = 1/R_{2-4} \) as the function of \( n \) in a double-logarithmic scale, the arrow shows the level of charge inhomogeneity (\( n^* = 2 - 3 \times 10^9 \) cm\(^{-2} \)); c, Fully developed QHE at \( B = 0.45 \) T, with vanishing longitudinal resistance \( R_{xx} = R_{1-4,2-3} \) (black curve) and quantized transverse resistance \( R_{xy} = R_{1-3,4-2} = 1/\nu \times h/e^2 \) (red curve) at \( \nu = 8, 12, \) and 16 at 250 mK; \( R_{\alpha-\beta,\gamma-\delta} \) corresponds to the ratio of the voltage drop between contacts \( \gamma \) and \( \delta \), and the current flowing from contact \( \alpha \) to \( \beta \).

high device quality and of the unusual highly resistive state at the charge neutrality point (CNP), which can be appreciated already from the most basic transport measurements. Fig 5.1a shows the gate voltage (\( V_G \)) dependence of the two-terminal resistance (\( R_{2-4} \)) of two different devices measured at 4.2 K. In both samples, a very high and narrow peak is observed around the CNP, approximately 50 times higher than that observed in suspended monolayer and Bernal-stacked bi/trilayer graphene at the same temperature [17, 21, 22, 30, 66, 75]. The resistance in both devices reaches \( \approx 0.3 \) M\( \Omega \) as compared to 4 – 8 k\( \Omega \) in high quality suspended bilayers (see Fig 5.6a). The two devices exhibit identical behavior and in the rest of the manuscript we show the data from one of them.
Quantum Transport in High Quality Suspended Graphene

Figure 5.2: Magneto-Raman spectroscopy and four-probe quantum Hall transport in suspended tetralayer graphene. a, Position of the Raman G-band peak as a function of $B$ measured at room temperature on one of our suspended devices, exhibiting characteristic magneto-Raman oscillations (the inset shows the 2D Raman peak at zero $B$). b, Full width at half maximum (FWHM) shows a resonant G-peak widening. The empty circles denote the position at which the anti-crossings occur, which coincide at values of $B$ for which the FWHM peaks. The red, blue and green circles between panels a and b correspond to the values of $B$ at which the anti-crossings are expected for tri-, tetra-, and pentalayer Bernal-stacked graphene respectively (see the main text for details): this comparison unambiguously identifies our flake as Bernal-stacked 4LG.
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The peak width is extracted from the log-log plot of the conductance $G_{2-4} = 1/R_{2-4}$ versus carrier density $n$, as illustrated in Fig. 5.1b. $n$ is calculated from the applied $V_G$, with the gate capacitance obtained from the analysis of the quantum Hall effect: the charge carrier density is given by $n = \alpha (V_G - V_{CNP})$, with $\alpha = 4.66 \times 10^9$ cm$^{-2}$V$^{-1}$ determined from the analysis of QHE (see Fig. 5.3b). The range in which the conductance is not affected by increasing $n$ – a measure of the carrier density fluctuations [66, 75] – extends only up to $n^* \approx 2 - 3 \times 10^9$ cm$^{-2}$, comparable to the best values reported in the literature for suspended graphene of any thickness [17, 21, 23, 30, 36, 37, 57, 66, 75]. Finally, the multiterminal configuration allows magneto-transport to be measured in both longitudinal and transverse configurations [36, 37]. Already at moderately low $B \sim 0.45$ T, a fully developed integer quantum Hall effect (IQHE) is observed (see Fig. 5.1c), with integer conductance plateaus (in units of $e^2/h$) in the transverse resistance ($R_{xy}$) and concomitant vanishing of the longitudinal resistance ($R_{xx}$).

The thickness and stacking order of our samples are determined by magneto-Raman spectroscopy (see Subsection 3.2.3). The 2D Raman peak, occurring around 2710 cm$^{-1}$ at $B = 0$ when measured with an excitation at $\lambda_{exc} = 514$ nm, exhibits the contribution of two components (see inset of Fig. 5.2a), as expected for 4LG with Bernal stacking [121, 122, 133]. This observation, however, is not sufficient to exclude tri- and pentalayer graphene unambiguously. To gain conclusive evidence, Raman spectra were collected in the regime of Landau quantization, by applying a finite $B$ to split the single-particle energy spectrum into discrete Landau levels (LLs). In this regime, the G Raman peak exhibits characteristic anti-crossings upon increasing $B$ – an oscillatory shift of the peak position with a concomitant broadening (see Figs. 5.2a-b) – when the energy of the $E_{2g}$ phonon matches that of specific inter-LL transitions (see [123] and Subsection 3.2.3 for details).

In few layer graphene, whose electronic spectrum consists of several bands [26, 43, 55, 59, 60, 134], the effect of coupling is enhanced in the presence of nearly degenerate transitions (i.e., when inter-LL transitions from different bands occur at nearly the same energy) [28], and become measurable even at room temperature (RT). For non-degenerate transitions, the effect of coupling is too weak to be detected at RT, at least in the available samples. In the simplest approximation – we will refer to it as the effective bilayer model – the single-particle band structure of 4LG consists of two independent bilayer-like bands with different effective masses (See the Subsection 2.1.4 and [26, 28, 43, 55, 59, 134, 135], and predicts pairs of nearly degenerate inter-LL transitions to match the phonon energy at $B \approx 5.8$ T, 7.8 T, and 12 T as marked by the blue circles between Figs. 5.2a-b [28]. As indicated by the blue dashed lines in Figs. 5.2a-b, the observed features are in virtu-
Figure 5.3: Quantum Hall effect in tetralayer graphene. a, $R_{xx}$ plotted as a function of $B$ and $n$. Clear Shubnikov-de Haas oscillations are visible starting from $B = 0.1$ T, and fully developed quantum Hall states from $B = 0.3$ T. The arrows indicate the local $R_{xx}$ minima at $\nu = 4, 8, 12, 16$ (the $\nu = 8$ state is the first to develop fully at $B \approx 0.3$ T; white dashed line). At low $n$, below $2.5 \times 10^{10}$ cm$^{-2}$, the device becomes highly insulating (see Fig.5.4), preventing multi-terminal measurements; b-c, Traces of the longitudinal and transverse conductivities, $\sigma_{xx} = \rho_{xx}/(\rho_{xx}^2 + \rho_{xy}^2)$ and $\sigma_{xy} = \rho_{xy}/(\rho_{xx}^2 + \rho_{xy}^2)$, as a function of $\nu$, measured for $B$ between 0.475 T and 0.8 T ($\rho_{xx} = R_{xx}W/L$ and $\rho_{xy} = R_{xy}$ with the device aspect ratio $W/L = 0.87$). The filling factor $\nu = nh/eB$ is calculated from $B$ and $n = \alpha(V_G - V_{CNP})$ with $\alpha = 4.66 \times 10^9$ cm$^{-2}$V$^{-1}$ determined by imposing scaling of all the measured curves in this magnetic field-range. The good scaling enables averaging of the magnetoconductivity curves to suppress noise, as shown in panel c.

ally perfect agreement with these predictions, whereas they do not match the expectations for tri- and pentalayer graphene (respectively, green and red circles between Figs.5.2a-b). Magneto-Raman spectroscopy therefore unambiguously identifies our devices as made of Bernal-stacked tetralayer graphene. Additionally, by showing the persistence of Landau quantization at room temperature, these observation provide another indication of the high quality of our devices.

To characterize the device quality in more detail, and to gain additional understanding of the low-energy electronic properties, we have investigated
Insulating state in tetralayers reveals an even-odd interaction effect in multilayer graphene

transport in the quantum Hall regime by taking advantage of the multi-terminal geometry that enables the independent access to both $R_{xx}$ and $R_{xy}$ to be measured [36, 37]. Fig. 5.3a shows a color plot of $R_{xx}(V_G, B)$, exhibiting clear features originating from the QHE, with Shubnikov-de Haas (SdH) oscillations becoming visible from $B \approx 0.1$ T. Through the condition for their visibility ($\mu B >> 1$), we estimate the carrier mobility $\mu$ to be larger than 100,000 cm$^2$V$^{-1}$s$^{-1}$ [66, 75]. The oscillations evolve into fully developed IQHE states – with plateaus in $R_{xy}$ and vanishing $R_{xx}$ starting from $B \approx 0.3$ T at filling factor $\nu = nh/eB = 8$ (see the white dashed line in Fig.5.3a), and subsequently at $\nu = 12$ and 16 (starting from $B \approx 0.4 – 0.5$ T). These states are clearly apparent in Fig.5.3b, which shows the longitudinal ($\sigma_{xx}$) and transverse ($\sigma_{xy}$) conductivity, measured as a function of $V_G$ for $B$ in the range 0.475 – 0.8 T and plotted as a function of $\nu$. To convert from longitudinal and transversal resistivity to the corresponding conductivity values. For rectangular samples of width $W$ and length $L$, longitudinal and transversal resistivity can be defined as $\rho_{xx} = R_{xx}W/L$ and $\rho_{xy} = R_{xy}$, so the corresponding conductivity tensors are:

$$
\sigma_{xx} = \frac{\rho_{xx}}{\rho_{xx}^2 + \rho_{xy}^2} \quad \text{and} \quad \sigma_{xy} = \frac{\rho_{xy}}{\rho_{xx}^2 + \rho_{xy}^2}.
$$

(5.1)

The gate capacitance is determined by enforcing the scaling of all curves; the good scaling also allows us to reduce noise by averaging [37] as shown in Fig.5.3c. These fully developed states at low $B$ follow the sequence expected from the simplest description of the electronic structure of 4LG in terms of two decoupled bilayer-like bands, for which a 16-fold degenerate LL at zero energy needs to be completely filled before electrons occupy (four-fold degenerate) LLs at higher energy, as discussed in the Subsection 2.1.4 and 2.3.1 [135]. The appearance of the $\nu = 4$ state, which starts from $B = 0.8$ T, indicates that at higher fields, the 16-fold degeneracy of the zero energy LLs starts to break. Possible mechanisms responsible for breaking this degeneracy are the effect of next-nearest-layer hopping [29] (that is not considered in the effective bilayer model) or electron-electron interactions, for which an analysis of the behavior at larger $B$ provides additional evidence (Fig.5.8). Irrespective of these details, the observation of the 16-fold degenerate zero-energy LL provides useful information about the low-energy electronic properties of suspended tetralayer graphene.
Figure 5.4: Insulating state at charge neutrality and $B = 0$ in tetralayer graphene. a, $\log(G)$ versus $V_G$, measured in several different two-terminal configurations, as indicated in the legend (refer to the inset in Fig. 5.1a for the contact labelling convention). The same behavior – a pronounced suppression of $G$ in a very narrow range of gate voltages $|V_G - V_{CNP}| < 5$ V, corresponding to $|n| < 2 \times 10^{10}$ cm$^{-2}$ – is observed irrespective of the contacts used, which is indicative of the high device homogeneity; b, $T$-dependence of $\log(G)$-versus-$V_G$ measured in a two terminal configuration. Upon increasing $T$, the minimum conductance $G_{\text{min}}$ at the CNP increases by more than four orders of magnitude, exhibiting a thermally activated behavior for $T > 1$ K, as shown in panel c ($G_{\text{min}} = \exp(-E_A/2k_B T)$ with $E_A \approx 14.6$ K).

5.3 Insulating state at the charge neutrality in tetralayer graphene and its comparison with the case of bilayer graphene

With the device structure and quality well characterized, we focus on the high resistance peak found close to the charge neutrality (Fig. 5.1a). At the base temperature ($T = 250$ mK), the conductance $G$ becomes immeasurably small (the resistance is larger than 100 M$\Omega$), as shown in Fig. 5.1a. Different curves in the figure correspond to 2-terminal measurements done using different pairs of contacts as indicated in the legend (for the highly resistive behavior of the device, four-terminal measurements cannot be done reliably), and show that the strong suppression always occurs in a same narrow range of carrier density $|n| < 2 - 3 \times 10^{10}$ cm$^{-2}$, irrespective of the measurement configuration. This observation indicates very high device homogeneity – checking it directly is an advantage of working with multi-terminal devices [36, 37]. Fig. 5.4b.
Insulating state in tetralayers reveals an even-odd interaction effect in multilayer graphene

**Figure 5.5:** Insulating state at the charge neutrality and \( B = 0 \) T in tetralayer graphene.  
(a) Colorplot of the differential conductance \( G = dI/dV \) (in log scale) as a function of source-drain \( (V_B) \) and gate voltage \( (V_G) \), measured at 250 mK. The insulating state corresponds to the dark blue region close to the CNP and \( V_B = 0 \) V;  
(b) Line-cut, \( dI/dV(V_B) \), corresponding to the white dashed line in the color plot shown in panel a, taken at \( V_G = 1.6 \) V. Below \( V_B \approx 1.5 \) mV (indicated by the arrow), the conductance vanishes within the accuracy of the measurement.

shows the temperature dependence of \( G(V_G) \) measured in one of the two-terminal configurations (other configurations give identical results), which exhibits a pronounced insulating behavior upon lowering \( T \). Above 1 K, the minimum conductance is thermally activated \( G_{\text{min}} = \exp(-E_A/2k_B T) \) with an activation energy \( E_A \approx 15 \) K (see Fig.5.4c), indicating the presence of an energy gap at the CNP.

We have also probed the dependence of the insulating behavior on the bias voltage. The gap closes very rapidly when the device is gate-biased away from the CNP, as it can be seen in the measurement of the differential conductance \( (dI/dV) \) as a function of \( V_G \) and applied bias voltage \( V_B \) (Fig.5.5a). Fig[5.5b] further shows that at low bias, the \( dI/dV \) vanishes, within the accuracy of the measurements, for all bias voltages \( V_B \) below a threshold (≈ 1.5 mV, corresponding approximately to the activation energy extracted from the \( T \)-dependent measurements), above which it increases sharply. In the case of bilayer graphene (BLG), a qualitatively similar behaviour has been observed and interpreted in spectroscopic terms, with the applied bias taken to be a direct measure of the energy of the injected electrons \([21, 22] \). It cannot be excluded, however, that the dominant effect of the applied bias is the
electrostatic accumulation of charges on the suspended 4LG flake. Indeed, since the gap closes very rapidly upon increasing the charge density away from the CNP, the accumulation of even a very small amount of charges can result in a drastic suppression of the gap, leading to a large and sharp conductance increase.

Here we also present the data obtained from a high-quality multiterminal suspended bilayer device (for details see Refs. [36] and [37]), which shows an insulating behavior as in Refs. [21, 22] and discuss some differences with the case of tetralayer. As can be seen from Fig.5.6a, at the CNP at 4.2 K, the resistance of the bilayer is $\sim 8 \, \text{k}\Omega$, much smaller than that of 4LG in our study (Fig.5.1a). Fig.5.6b illustrates the high quality of the sample – the density of charge inhomogeneity is extremely low (as pointed to by the arrow, $n^* = 3 \times 10^9 \, \text{cm}^{-2}$). The $G_{\text{min}}$ corresponding to the insulating state seen in Fig.5.6 is three orders of magnitude smaller than the one measured in the tetralayers (Fig.5.6a) and exhibits thermally activated behavior for $T$ larger than few Kelvin degrees (Fig.5.6d). The activation energy – approximately 13 K – provides an estimate of the energy gap in the system, which is comparable to that found in 4LG. In the bias voltage dependence of the insulating state ($G(V_G, V_B)$ which is shown in Fig.5.6e) we find that the insulating state only occurs very close to the CNP, and that a small bias is sufficient to induce transport (independent of the configuration of the measurement, i.e. of which leads are used). Contrary to the case of 4LG, however, the detailed low-bias behavior of the differential conductance in bilayers depends on the specific pair of contacts used in the measurement (see two curves in Fig.5.6f). Additionally, in all cases, low-bias suppression of the conductance in bilayers is not as pronounced as in 4LG (for it allows 4-terminal measurements) and two energy scales can be distinguished and the transition from high to low differential resistance upon increasing $V_B$ is less sharp then in 4LG.
Insulating state in tetralayers reveals an even-odd interaction effect in multilayer graphene.

Figure 5.6: Insulating behavior of multi-terminal high quality suspended bi-layer graphene. a, Four-terminal resistance $R(V_G)$ measured at 4.2 K; b, Four-terminal conductance $G(n)$ in a double logarithmic scale. The arrow indicates the density of charge inhomogeneities, $n^* = 3 \times 10^9$ cm$^{-2}$; c, Temperature dependence of $G(V_G)$ in a 2-terminal configuration; d, Minimal conductance $\log(G_{\text{min}})$ as a function of $1/T$, shows thermally activated behavior of $G_{\text{min}}$ above 2 K, with an activation energy of $\sim 13$ K; e, Colorplot of $\log(dI/dV)$ as a function of $V_G$ and $V_B$, in a 2-terminal configuration; f, The blue line corresponds to $G(V_B)$ extracted from the data shown in panel e at $V_G = 3.8$ V. The cyan line shows the same measurement using a different pair of contacts. Note the difference in low-energy $dI/dV$ suppression.
Figure 5.7: Strong electron-electron interactions at high magnetic field. a, \( V_G \)-dependence of the longitudinal (\( \sigma_{xx} \)) and the transverse (\( \sigma_{xy} \)) conductivity at \( B = 2.3 \) T, showing fully developed broken symmetry states at \( \nu = 1, 2, \) and 3 with zeros in \( \sigma_{xx} \) and plateaus in \( \sigma_{xy} \); b, Fan-diagram of the derivative of the conductance \( dG/dB(B,n) \), illustrating the evolution of the quantum Hall states at \( \nu = 1, 2, 3, \) and 4 (indicated by arrows) as a function of \( B \) and \( n \): these states survive down to \( \approx 1 \) T (the vertical features visible at \( B \) around 1.8 and 2.8 T are likely to appear due to the crossing in energy between the different symmetry broken Landau levels); c, Upon the application of perpendicular magnetic field, the insulating state extends through a much broader range of carrier density, similarly to what happens in mono- and bilayer graphene; d, If the magnetic field is applied in the plane, no change is seen in the range of \( B \) accessible in our laboratory (15 T). All measurements shown in this figure have been taken at \( T = 250 \) mK.
5.4 Electron-electron interactions in 4LG at high magnetic field

The occurrence of an insulating state at the CNP in tetralayer graphene is unexpected and it cannot be accounted for in terms of the gapless single-particle band structure of 4LG [26, 43, 55, 59, 134, 135]. Before discussing the behavior of our samples at high magnetic fields, we consider if the insulating behavior in 4LG can be explained by an alternative scenario based on the presence of macroscopic defects such as AB-BA stacking faults – which has been proposed for bilayers to explain why high quality suspended devices sometimes remain conducting at low $T$ [136]. We find that this explanation is incompatible with our data, and with different observations reported in the literature. Homogeneous transport in our devices (Fig.5.4a) suggests that stacking faults are not strongly affecting transport (we find it unlikely that stacking faults could affect each pair of contacts in the device in such similar manner). The energy scale of the gapped state due to a stacking fault is estimated to be an order of magnitude smaller than what it observed (Fig.5.4c, Fig.5.5b). Extending the argument of AB-BA stacking faults to the case of trilayer graphene, one would expect that there should not be considerable difference between ABA- and ABC-stacked flakes, for the stacking faults would convert one stacking order into another [137], which is in contrast with experimental observations [30].

To this point, observations suggest that the insulating state at charge neutrality can be a result of electron-electron interactions. We have studied the behavior of the system at high magnetic field $B$ and shown that, indeed, electron-electron interactions play an important role for the transport in our devices. The appearance of fully developed QHE at $B = 2.3$ T with plateaus in $\sigma_{xy}$ at 1, 2, and $3e^2/h$ and vanishing $\sigma_{xx}$ (Fig.5.7b) demonstrates that interactions are strong enough to completely lift the degeneracy of the zero-energy LL already at low $B$. Plotting $dG/dB$ as a function of $B$ and $n$ shows that these symmetry broken states start developing from $B \approx 1$ T (Fig.5.7b). This value corresponds to the magnetic field at which the $\nu = 4$ state becomes visible, suggesting that this state appears due to interactions, too. Note that, in the fractional quantum Hall effect (likely to be within experimental reach at higher $B$ with devices of the quality shown here), the 16-fold degeneracy of the zero-energy Landau level is expected to lead to new unexplored regimes, occurring when states belonging to different LLs are mixed by interactions [24, 118, 138]. The first manifestations of these new regimes – the appearance of an even-denominator fractional state at $\nu = -1/2$ [37] and of electron-hole asymmetry [139, 140] – have just been
reported in BLG; with its larger degeneracy, 4LG should lead to an even
ericher spectrum of new phenomena. Finally, additional evidence for the
relevance of the interactions in 4LG is provided by the enhancement of the
insulating state around charge neutrality, which at higher magnetic field ex-
tends throughout a larger density range (Fig. 5.7c). This behavior is identical
to that observed in mono- and bilayer graphene, where it has been shown
to originate from a canted anti-ferromagnetic state due to interactions (see
Refs. [25, 96, 141] and Subsection 2.3.2). A similar explanation may be valid
for 4LG: Fig. 5.7f, shows that the insulating state is not affected by a parallel
magnetic field $B$ up to 15 T, which indicates that the electron spin is not a
good quantum number for the insulating state. Finding that the enhance-
ment starts already at low $B$ (Fig. 5.7a), and that the insulating state at finite
field evolves continuously into the $B = 0$ insulating state upon reducing $B$,
suggests a related origin of both states.

5.5 Staggered interlayer exchange potential
as a mechanism to open the gap

Here, we extend the general staggered exchange potential approach developed
for bilayer graphene to the case of Bernal-stacked tetralayers, as a compre-
hensive analysis of electron-electron interactions in such system goes beyond
the scope of this work. Our observation that the magneto-Raman measure-
ments and the IQHE at low $B$ are in surprisingly good agreement with the
behavior expected from the effective bilayer model suggests that treating
4LG by analogy with the case of graphene bilayers is a good starting point.
The mean-field treatment can be generalized to the case of 4LG in a natural
way, by describing the low-energy electronic properties in terms of a $4 \times 4$
matrix Hamiltonian of the type

$$H_{i,j}^{4LG} = K_{i,j} + (-1)^i \Delta \delta_{ij}$$

(5.2)

where the indices $i, j$ identify the layer ($i, j = 1, \ldots, 4$; see [134]). The first
term is the kinetic energy of electrons (see the Subsection 2.1.4, equation
(2.26)) and the second one is the order parameter originating from interactions.
$\Delta$ has an effect of a potential difference between the ”upper” (the first
and second) and ”lower” (the third and fourth) layers of this effective bilayer
because the ”upper” (”lower”) wave bases are actually localized on the 1st,
3rd, \ldots (2nd, 4th, \ldots) layers (see the Subsection 2.1.4 and the Supplemen-
tary of the Ref. [38]), so that a staggered potential gives effectively the same
effect as the top-bottom potential asymmetry in bilayer graphene.
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Figure 5.8: Even-odd effect of the staggered interlayer potential $\Delta$ on the band structures of few layer graphene. 

(a), Band structure of few layer graphene with an even number of layers ($N = 2$ on the left and $N = 4$ on the right) in the absence (upper part) and presence (lower part) of a staggered interlayer potential $\Delta$ (calculations are based on the tight-binding approximation, including only nearest neighbour hopping in the plane and perpendicular to the plane). The opening of a gap at the charge neutrality point at finite is apparent; 

(b), No gap is opened by a staggered potential $\Delta$ in the case of few layer graphene with an odd $N$, as shown for the case of trilayer graphene ($N = 3$), because of the presence of a monolayer-like band.

In bilayers, different ground states emerge, depending on how the sign of the order parameter $\Delta$ changes upon switching valley or spin [22, 109], but in all cases, the bulk of BLG is gapped (see Fig. 5.8a) as the term $\Delta$ in the Hamiltonian has an opposite sign in opposite layers for any fixed spin and valley configuration. In the case of tetralayers, following our generalized approach, the staggered potential $V_i = (-1)^{i+1} \Delta$ ($i = 1, \ldots, 4$ is the layer index) changes its sign between the neighbouring layers. More specifically, the Hamiltonian of the 4LG is decomposed into blocks describing two effective graphene bilayers using a unitary transformation, and the staggered potential then works as the $\Delta \sigma_z$ term for each bilayer (see the Subsection 2.5.2). It is straightforward to show by direct diagonalization of the 4LG Hamiltonian.
that, within the effective bilayer model, the staggered potential $\Delta$ opens a gap at the CNP in 4LG (see Fig. 5a; Fig.5.8a, in analogy to the BLG, ground states with different properties shown in the Fig.5.9 originate from the way in which $\Delta$ changes upon switching valley or spin).

While the above discussion based on the analogy with BLG certainly cannot substitute a complete theoretical analysis, it has the benefit of showing explicitly a realistic scenario based on electron-electron interactions, which leads to the opening of a gap at the CNP and naturally explains why the gap size in 4LG is comparable to that observed in BLG (since within the current approximation, the electronic structure of 4LG is equivalent to that of two decoupled BLG, even in the presence of a staggered potential).

The analogy with the case of graphene bilayers which has been studied already in quite some detail \[60, 96, 108, 111, 116, 142, 143\] allow several broken-symmetry states to be suggested, as shown in Fig.5.9 depending on how the sign of the staggered potential changes upon switching spin and valley. In each panel, the spin and valley polarization of each layer is indicated by arrows with different directions and colors. The quantum anomalous Hall states (QAH), the quantum spin Hall states (QSH), and the quantum valley Hall (QVH) states have finite Hall, spin Hall, and valley Hall conductivity, respectively \[83\]. The layer antiferromagnetic state (LAF) does not have any kind of Hall conductivity, but possesses a net magnetic moment on each layer. Among these candidates, the QVH is the only state which has a interlayer

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**Figure 5.9**: Systematic representation of the spin and valley ordering of possible broken symmetry states in 4LG, based on the analogy with graphene bilayers. **a**, Quantum anomalous Hall (QAH); **b**, Quantum spin Hall (QSH); **c**, Layer antiferromagnet (LAF); **d**, Quantum valley Hall (QVH)
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charge density modulation, and thus it is energetically unfavorable in terms of the cost of Hartree energy. The remaining three states, QAH, QSH and LAF, have a uniform charge distribution, and the ground state energy is lowered by the exchange. In the continuum approximation, the exchange interaction works only between electrons with the same spin and valley \[109\], so that the total energy is equal among those three states. Which of the three states is the actual ground state may depend on details, in complete analogy to what has been discussed for graphene bilayers.

5.6 Even-odd effect of interactions close to CNP in few layer graphene

Interestingly, the proposed staggered exchange potential scenario also captures the systematic behavior of charge neutral Bernal multilayers, which emerges experimentally with our finding of an interaction-driven insulating state in 4LG graphene. Specifically, as it has been reported in previous experiments, ”odd” \(i.e.\) mono- and tri-) layers remain conducting at low temperature \[17, 30, 66, 75\], whereas, as we can conclude from this work, ”even” \(i.e.\) bi- \[21–23, 57\] and tetra-) layers exhibit a gap and become insulating. This phenomenon cannot simply be explained in terms of an enhanced susceptibility to interactions due to a larger low-energy density of states, since Bernal-stacked trilayers, for instance, have a larger density of states than bilayers, and yet they remain conducting at low temperature. On the contrary, describing the effect of interactions in terms of a staggered mean-field potential at the level of approximation of Eqs. \(2.53\) and \(5.2\) leads precisely to the experimentally observed even-odd effect. In fact, at the same level of approximation used to discuss tetralayer graphene, the electronic structure of even multilayers generally decouples into bilayer-like bands \[26, 43, 55, 59, 134, 135\], and since each band opens a gap in the presence of a staggered potential, the electronic state of a generic even multilayer is gapped (see Fig.5.8a). When performing the same analysis for odd multilayers, additionally to the bilayer-like bands, there emerges a linearly dispersing monolayer-like band which remains ungapped – as it is only shifted in energy in the presence of a staggered potential (see Fig.5.8b). As a result, odd multilayers remain metallic without opening a gap. It remains to be understood why the simple approximation used in this study to describe Bernal multilayers (which neglects, for instance, next-layer hopping processes, described by \(\gamma_2\) and \(\gamma_5\) parameters in the tight-binding description of graphite) correctly captures the basic aspects of the electron-electron interactions. It
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is likely that the robustness of the even-odd effect is rooted in the symmetry of these systems, which is different in the two cases: even multilayers are inversion symmetric whereas odd ones possess reflection symmetry [134] (for thickness larger than the monolayer). It therefore seems reasonable that the appearance of a staggered potential – which breaks inversion and preserves reflection symmetry – can account for a drastic modification of the behavior of even multilayers, and lack of it in the odd ones.

An implication of the robustness of the even-odd interaction effect, and of the experimental findings reported here, is that electron-electron interactions can be expected to determine also the properties of thick multilayers that are normally considered as bulk graphite. Indeed, finding an insulating state in 4LG already clearly visible well above 4.2 K, i.e. much more pronounced than in BLG (where it becomes visible only below 1 K; see Section [5.3]), shows that the role of interactions becomes stronger, and not weaker, upon increasing layer thickness. This finding and the theoretical considerations made above, therefore, indicate that the commonly held notion that bulk graphite can be well understood within a single particle model is unlikely to be entirely correct, and that at sufficiently low-energy the effects of electron-electron interactions become important. These effects can easily be eclipsed in experiments on samples of microscopic size, which unavoidably contain structural defects, but when probing well-characterized, small multilayers – which can be made defect free – they become fully apparent.

Conclusions

In this work, we have fabricated high quality suspended multiterminal Bernal-stacked tetralayer graphene devices. The thickness was identified by means of magneto-Raman spectroscopy and confirmed by quantum Hall sequence expected within effective bilayer approach, which essentially takes into account only nearest neighbor hoping. Surprisingly, both MPR and QHE show that this approximation is sufficiently accurate and correctly describes the data obtained from ultra-high quality devices. The quality is confirmed by an early onset of the QHE and appearance of broken symmetry states. At the charge neutrality at \( B = 0 \), the samples show highly insulating behavior in a narrow range of charge carrier density with \( G_{\text{min}} \) approaching the instrumental limit at 250 mK. Temperature dependence of the \( G_{\text{min}} \) shows a thermally activated behavior of the insulating state. Activation energy is of the same order of magnitude as the insulating state energy scale estimated from voltage bias dependence and resembles the one of suspended bilayer graphene of high quality, also shown here. As the effective bilayer approach
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fits very well with our experimental observations, we adopt the mechanism suggested to explain the insulating behavior of bilayers. The fact that the staggered exchange potential based on simplified nearest-neighbor hopping outlines the mechanism for the gap opening even in high quality flakes, where the effect of near-nearest neighbor hopping should be non-negligible (in fact, $\gamma_2$ and $\gamma_5$ are of the same order of magnitude as the activation energy $E_A$) is unexpected. Moreover, this approach explains why a gap cannot be observed in Bernal-stacked trilayer graphene, therefore revealing an even-odd effect: high quality suspended graphene with even number of layers undergo a spontaneous gap opening around charge neutrality at low temperature at $B = 0$, whereas graphene with odd number of layers remain conducting even at low temperature. Together, these two observations suggest a high importance of the symmetry of the system for electron interactions, independently of precise details of electronic structure and allow the properties of thicker Bernal graphene stacks to be estimated based on the parity of the number of layers.
Résumé

Le graphène est une couche d’atomes de carbone arrangés en maille de nid d’abeille. Les propriétés électroniques de graphène se distinguent des autres systèmes bidimensionelles. Au cœur de ses propriétés du graphène se trouve le fait que les porteurs de charge forment un gaz des électrons à 2 dimensions (2DEG) avec une structure de bande électronique semi-conducteur de gap nul et une dispersion linéaire entre son énergie et sa quantité de mouvement autour du point de neutralité de charge (là où les bandes de valence et de conduction se touchent) et les porteurs sont essentiellement relativiste: sans masse et chiraux. Cette structure électronique mène à un effet Hall quantique unique (QHE) lié au fait que les fermions prennent une phase de Berry supplémentaire. Une autre conséquence intéressante de la chiralité et du comportement relativiste des porteurs est Klein tunneling - un électron d’incidence normale ne va pas rétrodiffuser et sa probabilité de transmission ne va pas baisser exponentiellement avec la largeur de la barrière de potentiel, mais il va traverser la barrière comme son antiparticule. Car densité d’états disparaît au point de neutralité de charge, les interactions entre électrons peuvent modifier la structure de la bande autour de ce point par les rémodelage de la dispersion d’énergie-moment.

Dans les couches de graphène, la structure électronique est modifiée: le graphène bicouche a une dispersion d’énergie-moment parabolique. Une propriété importante et unique de la structure de bande bicouche est qu’un champ électrostatique perpendiculaire peut ouvrir une gap entre la valence et bande de conduction. Piles plus épaisses peuvent être formés suivant différents ordres d’empilage dont Bernal empilage est la plus stable thermodynamiquement. Dans ce manuscrit, tri- et tetracouches de Bernal sera discutés. La structure électronique de ces empilements peut être considéré comme une combinaison des bandes linéaires et paraboliques respectivement. Les piles de graphène donnent origine à plus d’espèces de l’effet Hall quantique et sont tous soumis à des interactions entre électrons proches de la neutralité de charge. Ils peuvent produire un état isolant spontanément (i.e. en l’absence de champ magnétique): un potentiel d’échange avec le signe
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différent sur chaque couche a un effet similaire à un champ électrostatique perpendiculaire.

Le travail présenté dans ce manuscrit a été axé sur la fabrication et la caractérisation des échantillons de graphène suspendu de haute qualité. Le clé de cette thèse sont les deux conséquences du fait que les flocons du graphène suspendu sont découplés du substrat. Grâce à la technique recent de fabrication, les dispositifs en suspension peuvent être nettoyés pour atteindre de qualité très haute; deuxièmement, les échantillons de graphène suspendu très propres permettent de prober expérimentalement la physique proche de la neutralité de charge - où les interactions entre les électrons modifient la structure électronique du graphène.

Principalement, nous avons développé une technique de transfer de haute précision pour les flocons de graphène, qui a permis la fabrication d’un échantillon de graphène de haute qualité en suspension avec une grille inférieure supplémentaire prédéfinie. Nous avons trouvé que le comportement de notre échantillon est compatible avec la présence d’un jonction, et que le transport se produit dans le régime balistique sur une longueur comparable à la taille de l’appareil (1-2 µm). Les mesures confirment donc que la technique de fabrication à base de LOR permet en effet la réalisation des échantillons de graphène suspendu avec les grilles locales et assure une haute qualité des appareils. Par rapport aux échantillons mesurés précédemment, ceux produits par cette technique présentent transport balistique sur une échelle d’un ordre de magnitude plus grande.

Cette approche peut être appliquée afin de produire de nouveaux dispositifs de graphène avec la possibilité de contrôler le potentiel électrostatique localement, comme les nano-structures nécessaires pour réalisation des lentilles de Veselago et le confinement topologique, et ainsi que des collimateurs les porteurs de charge, grâce à l’angle spécifique de transmission à travers d’une jonction pn dans le graphène monocouche.

Dans la deuxième partie, nous nous concentrons sur la physique proche du point de la neutralité de charge dans les échantillons de graphène en suspension à plusieurs couches. Nous avons fabriqué des échantillons suspendus de graphène de haute qualité, qui à tetracouche, Bernal-empilé et qui ont 4 électrodes. L’épaisseur a été identifié par les moyens de spectroscopie Raman magnétique (MPR) et confirmée par la séquence de l’effet Hall quantique expectée dans l’approche au sein de l’approche à la structure électronique qui utilise les bicouches effectives, et qui prend en compte seulement le hopping entre les voisins les plus proches. Étonnamment, les deux méthodes montrent que cette approximation est suffisamment précise et décrit les données obtenues des dispositifs de ultra-haute qualité correctement. La haute qualité est confirmée par une apparition précoce de l’effet.
Hall quantique et l’apparence des états de symétrie brisée. Au point de la neutralité de charge à $B = 0$, les échantillons présentent un comportement hautement isolant où la conduction minimale $G_{\text{min}}$ approche la limite instrumentale de 250 mK. Un changement de la température montre un comportement thérmiquement activé de l’état isolant. L’énergie d’activation est du même ordre de grandeur que celle du de graphène bicouche de haute qualité, également représenté ici. Comme l’approche de la bicouche effective cadre très bien avec nos observations expérimentales, nous adoptons le mécanisme proposé pour expliquer le comportement isolant des de bicouches. Cette approche explique pourquoi un gap ne peut pas être observé en graphène Bernal-empilé à trois couche, révélant donc un effet pair-impair: haute qualité du graphène suspendu de haute qualité avec un nombre pair des couches subissent une ouverture spontanée d’un gap autour du point de la neutralité de charge à basse température et $B = 0$, tandis que graphène avec un nombre impair des couches reste conducteur même à basse température.

Ces résultats contribuent au progrès dans la fabrication des échantillons de haute qualité en suspension et dans la compréhension plus profonde du transport électronique à basse énergie dans les échantillons de graphène de haute qualité. Nos résultats fournissent un aperçu sur le rôle des interactions entre électrons sur le transport quantique du graphène à plusieurs couches, ce qui à son tour est très important pour compréhension fondamentale et la recherche appliquée dans cette domaine.
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