Quantum transport through graphene and topological insulators

GUIMARAES COUTO, Nuno Jose

Abstract
In this thesis we experimentally study charge transport through nano-devices made of graphene and topological insulators. In both these materials the low energy electronic states can be described by the Dirac equation. From systematic transport investigations of graphene devices on top of different substrates we found that both the charge mobility and the amount of charge density fluctuations in high-quality graphene devices are limited by the same microscopic mechanism. The experiments suggest that this mechanism originates from the presence of random strain fluctuations in graphene. In topological insulator nano-devices, our experiments show that charge transport can be modulated from electron to holes through the application of a gate voltage. Once in the presence of a magnetic field we also observe the occurrence of quantum oscillations for both charge polarities. Our experimental investigations on topological insulators conclusively show that transport at the surface of these materials is mediated by Dirac fermions.

Reference


URN : urn:nbn:ch:unige-417591
DOI : 10.13097/archive-ouverte/unige:41759

Available at:
http://archive-ouverte.unige.ch/unige:41759

Disclaimer: layout of this document may differ from the published version.
Quantum transport through Graphene and Topological Insulators

THÈSE

présentée à la Faculté des sciences de l’Université de Genève pour obtenir le grade de Docteur ès sciences, mention physique

par

Nuno José Guimarães Couto

de
Pousada de Saramagos (Portugal)

Thèse N° 4709
Doctorat ès sciences
Mention physique

Thèse de Monsieur Nuno José GUIMARÃES COUTO

intitulée :

"Quantum Transport through Graphene and Topological Insulators"

La Faculté des sciences, sur le préavis de Monsieur A. MORPURGO, professeur ordinaire et directeur de thèse (Département de physique de la matière condensée et Groupe de Physique Appliquée), Monsieur A. B. KUZMENKO, docteur (Département de physique de la matière condensée) et Monsieur N. M. R. PERES, professeur (Universidade do Minho, Departamento de Fisica, Braga, Portugal), autorise l'impression de la présente thèse, sans exprimer d'opinion sur les propositions qui y sont énoncées.

Genève, le 10 septembre 2014

Thèse - 4709 -

Le Doyen

N.B. - La thèse doit porter la déclaration précédente et remplir les conditions énumérées dans les "Informations relatives aux thèses de doctorat à l'Université de Genève".
Acknowledgements

Doing a PhD in experimental solid state physics in the Quantum Electronics group of Prof. Alberto Morpurgo at the University of Geneva was a valuable and enriching experience. During these years I was lucky to be surrounded by brilliant scientists and fantastic friends, who were of great help into overcoming the daily challenges of scientific research.

First of all I would like to thank my supervisor Prof. Alberto Morpurgo with whom I witnessed how nowadays world-class scientific research is done. Alberto, your deep understanding and passion for physics together with your constant availability to discuss the results has deeply impressed me. I felt extremely lucky for being able to work with you and to use the excellent technical facilities of your research group, while at the same time I had the possibility to collaborate with other brilliant scientists. Also, I am indebted to Prof. Nuno Peres (Minho-Braga) and Prof. Alexey Kuzmenko (Geneva) for their role in discussing and evaluating this thesis as the members of the dissertation committee.

The opportunity of doing a PhD at the University of Geneva would have never been possible without the key contributions of Prof. José Carlos Gomes (Minho-Braga) and Prof. Nuno Peres (Minho-Braga), who supported my wish and motivation to perform scientific research, firstly by helping me on writing my first research project (the Gulbenkian Foundation project) and secondly by recommending me to do a PhD in Geneva. I am extremely grateful for all your support and kindness, and I wish you all the best.

During these years as a PhD student I was lucky to encounter exceptional friends who helped me all along this academic marathon. When I arrived to Geneva I was warmly received by Alberto’s research team at the time, which consisted of Benjamin Saceépé, Jeroen Oostinga (Dutchie), Hangxing Xie, Ignacio Gutierrez (Nacho) and Alexandre Ferreira. With the help of Benjamin and Dutchie, my first lab teachers, I learned the essential tools in order to survive in the lab. Benjamin thank you for your friendship and never ending availability to answer all my questions, as well as, for all your guidance and advice, I wish you the best for your scientific career. Dutchie, I always saw you as the “magic hands” of the lab, your advice and friendship touched me very deeply, our endless discussions played a very important role on the important
decisions that I had to make. Nacho you’re the man ;) thank you for always being there in the good and the less good moments, life in Geneva without you would’ve been less fun and enjoyable without friends like you. Hangxing thanks for introducing me to the lab and to the Chinese spice culture, I wish you best for you and your family. Alexandre, thank you for always being there whenever I needed a hand and for being a great friend. Thank for you for all the help you gave me in the french language and the swiss culture, assim como a ajuda que me deste em descobrir o carro – o Portie Mobile – e també em proteger as costas quando foi preciso ;).

I started the PhD practically as the same time as Nikolas Minder (a.k.a. the suissie). I must say that I didn’t know much what to expect about the PhD, but with you Niko (together with the usual gang), it was a pretty cool life experience. Thanks for always being there, whether it was about science or for beer time. Also in the first years of my PhD I was lucky to meet Shimpei Ono and Masaki Nakano from Japan where their rigour, knowledge and work hard/party hard philosophy suited us perfectly. I wish you both the best outcome for your scientific careers in Japan. I would like to thank Anya Grushina and Sandra Sopic for your never-ending kindness and discussions I wish you all the best for your PhD thesis writing. One very big thanks goes to Dong-Keun Ki, who never ceased to impress me with his deep knowledge of condensed matter physics, as well as his extraordinary lab skills. With you, Dong-Keun, I learned how to approach tricky technical problems as well as how to get a better feeling on to efficiently carry scientific experiments. Sanghyun Jo, I admire your work ethics and wish you the best for your upcoming research projects. In these last few years I was also lucky to have met Daniele Braga (the Dude), with whom I shared plenty of scientific and life discussions (besides drinking, hikking and other things), I admire your view of life and I wish you all the best for the future. I would also like to thank Master Davide Costanzo, the best master student that a PhD can get. Without your help Davide, I’m sure that our last paper would’ve not been possible, thanks for your hard work ethics. I would like to also thank Christophe Cailler for teaching me the basics of CVD graphene growth and also Seif Ben Khelil for valuable help in the lab and in conceiving new lab tools (wish you best for your EPFL ventures).

To the other members of the Quantum Electronics research group, Flavia, Fabio, Zhe, Lin, Young Woo, Evgeniy and Denise, I thank you all for the help whenever I needed it.

I was also blessed to meet other people outside the Quantum Electronics Group that played and important role during my PhD. A special thanks goes for Benedikt Ziegler, with whom I had several discussions, hikes and good adventures, I wish you all the best for these final stages of your PhD. I was
also lucky to be able to meet Pavlo, Marta and Alessia, real good friends with
whom I shared countless weekends in the lab and the institutionalized scientific
coffee breaks, thanks for being great lab mates. I would also like thank Esther
Schwarz, Raoul Scherwitzl, Alex Fete, Andrea Caviglia, Stefano Gariglio, Celine
Lichtensteiger, Stéphanie Fernandez, Marco Lopes (o meu outro camarada português),
Maria (a pessoa mais gentil do departamento), Claudia Cancellieri, the liquid
helium team (Daniel Chablaix, Spiros Zanos and Jerome Cadoret), Iaroslav Gaponenko
(the AFM master), Renan Villareal, Greg Manfrini, Daniel Mathey, Gaetan Giriat
(thank you with the french translations :)), Christoph Berthod (thank you for your fantastic
advanced solid state physics course), Carmine Senatore, Marco Bonura, Giorgio
Mondonico, Siony, Alberto de la Torre, Julien Levallois, Asa, Myriam, Susanna and
Elena who in one way or another helped me whenever I needed.

Finally, I would like to thank the people who are the closest to me. Um
muito obrigado aos meus pais, Rosa e Alberto, que sempre me motivaram e
apoiam todas as minhas decisões acadêmicas assim como as decisões mais
importantes da minha vida. Obrigado por todo o vosso amor, carinho, atenção
e disponibilidade, vocês são os melhores pais do mundo que um filho pode
desejar. Um muito obrigado também para o Hugo e o Daniel, os meus irmãos,
companheiros de brincadeiras e de filmes anedóticos, com quem tive o privilégio
de crescer e por vezes atasar... uups..(desculpa por qualquer coisa). Je
voudrais aussi remercier aussi toute l'attention, aide et accueil que j'ai reçu
de Christian, les parents de ma chérie. Pour finir je voudrais te
remercier Christelle, mon amour de ma vie, pour tout ton soutien, patience,
aide et beaucoup d’amour. Sans toi ma vie n’aurais pas le même sens ni valeur,
merci d’être toujours là pour moi, obrigado por tudo meu amor da minha vida.
Souvent dans le domaine de la physique de la matière condensée, la découverte de phénomènes physiques provient de l’étude de nouveaux matériaux. L’un des cas le plus remarquable est la découverte du graphène, un cristal bidimensionnel composé d’atomes de carbone ordonnés sous la forme de maille de nid d’abeille. La très haute qualité cristalline du graphène liée à ses propriétés électroniques uniques (e.g. les porteurs de charge ont une masse effective nulle) a conduit à l’observation de phénomènes quantiques inédits. L’étude des propriétés physiques du graphène a été tellement riche, qu’elle a stimulé des découvertes importantes dans différents domaines de recherche. Le cas le plus notable est la découverte d’une nouvelle classe de matériaux, appelés isolants topologiques. Ces matériaux sont des isolants à “l’intérieur” (i.e. ils ont une structure de bande de type isolant) mais en raison de la topologie de leurs bandes électroniques ils sont capables de conduire le courant électrique à leurs surfaces.

Les états électroniques responsables de la conduction du courant électrique à la surface des isolants topologiques et les états électroniques de basse énergie du graphène partagent une caractéristique commune: dans les deux systèmes, le caractère des électrons est décrit par l’équation de Dirac, une équation initialement développé pour expliquer le comportement des particules relativistes, connue sous le nom de fermions de Dirac. Ce travail de thèse, à travers l’étude des phénomènes de transport électronique dans des nano-dispositifs, vise à améliorer la compréhension des mécanismes fondamentaux liés au transport de charges électriques dans ces deux systèmes.

La première partie de cette thèse est consacrée à l’identification des mécanismes microscopiques qui limitent le transport du courant électrique dans des nano-dispositifs de graphène. Deux types de substrats (titanate de strontium (SrTiO3) et nitrure de bore (BN)) ont été utilisés. Nos mesures de transport sur plusieurs nano-dispositifs de graphène sur des substrats de SrTiO3 (matériau qui possède une constante diélectrique très élevée) montrent que la diffusion de porteurs de charge dans le graphène n’est pas dominée par la présence d’impuretés chargées. En effectuant diverses expériences sur plusieurs dispositifs de graphène sur des substrats de nitrure de bore (isomorphe cristallin du graphène isolant), nous avons obtenu un meilleur aperçu des mécanismes
microscopiques qui limitent le transport des porteurs de charge. L’analyse systématique de certaines propriétés électroniques (la mobilité et les fluctuations du niveau de Fermi) de plusieurs dispositifs ainsi qu’une analyse théorique, suggèrent que la déformation mécanique du cristal de graphène, est le principal facteur microscopique responsable de la dégradation des propriétés de transport.

La deuxième partie de cette thèse se réfère à des expériences de transport électronique à travers l’isolant topologique Bi$_2$Se$_3$. Nos expériences sur des nano-dispositifs de Bi$_2$Se$_3$ avec des électrodes supraconductrices montrent que l’application d’une tension sur une électrode de grille permet de régler la polarité des porteurs de charge. Selon la polarité et l’amplitude de la tension de l’électrode de grille le courant électrique peut être conduit soit par des électrons soit par des trous; un comportement typiquement associé à la présence des fermions de Dirac. Lorsqu’ils sont soumis à un champ magnétique perpendiculaire, ces dispositifs développent des oscillations quantiques de Shubnikov-de-Haas due à la formation des niveaux de Landau. A partir de l’analyse de ces oscillations quantiques, nous avons pu confirmer que des fermions de Dirac résident à la surface de Bi$_2$Se$_3$ et qu’ils jouent un rôle important dans la conduction du courant électrique à travers le cristal. De plus, lorsque les dispositifs sont refroidis au-dessous de la température critique des électrodes supraconductrices, nous avons également observé que les électrodes induisent un supracourant à travers le matériau Bi$_2$Se$_3$. L’application d’une tension sur l’électrode de grille permet aussi de régler l’intensité ainsi que la polarité de ce supracourant.

En résumé, nous visons à accréditer la compréhension des aspects fondamentaux liés au transport électronique dans le graphène et l’isolant topologique Bi$_2$Se$_3$, matériaux où les porteurs de charge responsables de la conduction électrique sont gouvernés par l’équation de Dirac. Dans le cas du graphène, nos mesures de transport réalisées sur plusieurs dispositifs, suggèrent que le transport de porteurs charge est limité par les déformations mécaniques du cristal induites par le substrat. Quant à l’isolant topologique Bi$_2$Se$_3$, un matériau isolant à l’intérieur mais qui peut transporter un courant électrique à sa surface, nos études de nano-dispositifs confirment que ce phénomène s’explique par la présence de fermions de Dirac.
## Contents

1 Introduction .................................................. 1
  1.1 Graphene .................................................. 2
  1.2 The discovery of Topological Insulators .................. 5
  1.3 This thesis ................................................. 8

2 Background .................................................. 11
  2.1 Electronic structure of graphene .......................... 11
    2.1.1 The tight binding model .............................. 11
    2.1.2 Low energy electronic states ......................... 14
  2.2 Basic aspects of graphene devices for transport experiments .... 16
    2.2.1 Gate modulated electronic transport .................. 16
  2.3 The effect of disorder ..................................... 18
    2.3.1 Long-range potentials ................................ 19
      2.3.1.1 Coulomb potentials ............................... 19
      2.3.1.2 Strain and mechanical deformation ................. 20
    2.3.2 Short-range potentials ................................ 21
    2.3.3 Graphene nanoribbons ................................ 22
  2.4 Low field electronic transport in graphene ................. 24
  2.5 High field transport in graphene .......................... 28
    2.5.1 From Landau levels to the Quantum Hall effect ....... 28
    2.5.2 Interactions in the Quantum Hall effect ................ 30
  2.6 Quantum Hall effect as a Topological Insulator ............. 32
    2.6.1 The Haldane model .................................... 33
    2.6.2 The connection with topology ........................ 35
  2.7 Spin-orbit topological insulators .......................... 38
    2.7.1 The spin-orbit interaction ............................ 38
    2.7.2 2D topological insulators ............................ 39
    2.7.3 3D topological insulators ............................ 42
      2.7.3.1 Connection with transport experiments ............. 43
  2.8 Electronic transport with superconducting contacts ........... 45
# Contents

2.8.1 Andreev Reflection ........................................... 46  
2.8.2 Proximity induced supercurrent ................................ 47  

3 Device fabrication ................................................. 49  
3.1 Graphene based electronic devices ................................ 49  
3.1.1 Graphene on top of Strontium Titanate substrates .......... 51  
3.1.2 Graphene on top of Boron Nitride substrates .............. 53  
3.2 Bi$_2$Se$_3$ based electronic devices ............................ 55  
3.3 Appendix .................................................................. 57  

4 Electronic transport through graphene on top of a high-$\epsilon$ substrate ................................................. 59  
4.1 Introduction ............................................................. 60  
4.2 Electronic transport at B=0T ....................................... 61  
4.3 Transport at high magnetic fields .................................. 63  
4.4 Graphene nanoribbons .............................................. 65  
4.5 Discussion and conclusions ......................................... 66  
4.6 Appendix .................................................................. 68  

5 Strain-limited transport in high-quality graphene devices .... 73  
5.1 Introduction ............................................................. 74  
5.2 High-quality graphene devices ...................................... 74  
5.3 Correlation between mobility and charge density inhomogeneities ................................................. 76  
5.4 Weak localization in high mobility devices ....................... 78  
5.5 The effect of strain on transport .................................... 79  
5.6 Conclusions ............................................................. 82  
5.7 Appendix .................................................................. 83  

6 Electronic transport through a topological insulator .......... 87  
6.1 Introduction ............................................................. 88  
6.2 Gate-tuned Shubnikov-de Haas oscillations of Dirac fermions 89  
6.3 Bulk contribution to the magnetoresistance .................... 93  
6.4 Landau levels for Dirac fermions ................................ 95  
6.5 Gate-tuned supercurrent through surface states .............. 97  
6.6 Discussion and Conclusions ....................................... 98  
6.7 Appendix .................................................................. 100  

References ..................................................................... 107
In condensed matter physics it often happens that the discovery of new physical phenomena originates from the study of new materials. One of the most recent and remarkable cases is graphene, a two-dimensional (2D) crystal made of carbon atoms, only one atom thick. The high crystal quality of graphene, together with its unique electronic properties, have triggered a large body of scientific work that has led to the observation of novel quantum phenomena. The study of the physical properties of graphene has been so rich, that it stimulated important discoveries in other research areas. The most notable case is the discovery of a new class of materials, in which the topology of the insulating bulk band structure is responsible for the existence of conducting states at the physical boundaries. These materials are called topological insulators and they can exist in all the three spatial dimensions. In fact, the electronic states responsible for surface conduction in 3D topological insulators and the low energy electronic states of graphene share a common feature: in both these systems the electrons are governed by the Dirac equation, an equation which was originally developed to describe the behaviour of relativistic particles.

Currently, the study of both graphene and topological insulators are very active fields of research. With this thesis we aim at contributing to the understanding of charge transport in both these new electronic systems, through the study of transport in nano-fabricated devices. Although graphene has already been the subject of numerous transport experiments, the origin of the microscopic mechanisms that limit charge transport are still under debate. With our experiments we aim at providing a deeper insight in these mechanisms. In
the field of topological insulators, more specifically the case of 3D topological insulators (3DTI), our experiments aim at probing the surface Dirac fermions by means of transport measurements.

1. Introduction

1.1 Graphene

Graphene is a sheet of carbon atoms arranged in a honeycomb lattice, a truly two dimensional crystal. In the family of carbon allotropes (see fig.1.1(a)), which contains diamond, graphite, carbon nanotubes and fullerenes, graphene was the last to be discovered despite the fact that it can be seen as the building block of all the other allotropes (except diamond). Indeed the electronic properties of graphene have been studied since the 1940s\cite{1}, at the time of the first calculations of the band structure of graphite, which can be viewed as a vertical stack of graphene layers bonded by Van der Waals force. However, for a long period of time, graphene was seen as a mere academic curiosity, because 2D crystals were thought to be thermodynamically unstable and therefore inexist-ent in nature. Surprisingly, in 2004 Andre Geim and Konstantin Novoselov, jointly with other co-workers at the University of Manchester, showed that graphene can be obtained by peeling off layers of natural graphite with an adhesive tape\cite{2,3}. It was found that through this simple method large area (with dimensions of hundreds of micrometers) crystals free of defects could be isolated, a finding that has important implications in several fields. Apart from the exfoliation of graphite (see fig.1.1(b)), currently graphene can also be obtained through the thermal decomposition of SiC wafers\cite{4} and by Chemical Vapour Deposition (CVD) methods\cite{5} (see fig.1.1(d)).

In terms of electronic bands, graphene is a zero-gap semiconductor in which the conduction and valence bands touch at specific points in the Brillouin zone, known as the Dirac points\cite{6}. The most fascinating aspects of the electronic properties of graphene are found in its low energy electronic states, which are described by the Dirac equation for massless relativistic particles. Electrons travelling in the graphene lattice are not relativistic (i.e. they travel at a speed much slower than the speed of light), but their interaction with the periodic potential of the lattice gives rise to states whose energy depends linearly on the momentum, resulting in an energy spectrum that mimics that of neutrinos. An additional peculiar feature of electrons in graphene is that, besides their spin, they also possess an extra degree of freedom known as the pseudospin, a property related to the existence of two sublattices in the graphene honeycomb structure. As a result, the electronic states in graphene are described by two-

\footnote{The isolation of graphene layers by chemical means was already shown before by Boehm\cite{2}, however it caught little attention from the scientific community at the time.}
1.1. Graphene

Figure 1.1: (a) The family of carbon allotropes. (b) Graphene crystals where initially isolated by cleaving larger graphite crystals with the use of an adhesive tape. (c) The number of scientific papers on graphene per year. A significant increase occurred after the first electronic transport measurements made in 2004 by Novoselov et al\cite{3}. (d) New methods for obtaining graphene through Chemical Vapour Deposition (CVD) allow the growth of large single layers of graphene on top of flexible substrates, suitable for future applications.

Component wavefunctions having the properties of conventional spinors. An important consequence of the pseudospin is that the electrons in graphene are chiral: the direction of the electron momentum is locked to that of the pseudospin, a feature which plays an important role in several physical phenomena. How the properties of these so-called Dirac fermions, determine the electronic transport through graphene devices will be discussed in detail in Chapter 2 of this thesis.

Early transport experiments showed that the polarity of the carriers in graphene can be tuned electrostatically, through the application of a voltage to a suitably designed gate electrode\cite{3}. The applied gate voltage results in the accumulation of charge in graphene, thereby tuning the position of the Fermi level in the valence or conduction band. Another remarkable feature of carriers in graphene is their high mobility. While the mobility reported in initial transport experiments was already reaching 10000 cm$^2$/Vs\cite{7}, nowadays with the improvements of device fabrication techniques, mobility values well above
100000 cm²/Vs, have been achieved at room temperature. As a result, electrons travelling through the graphene lattice can cover large distances (of the order of micrometers) without experiencing any scattering events. As it enables the realization of devices with very high mobility, graphene is attracting attention as a suitable material for microelectronic applications.

Devices made of graphene (both single and bilayer) provide a new platform for the observation of fascinating phenomena. These include new broken symmetry states originating from electron-electron interactions, the possibility to tune the material band structure electrostatically, or new regimes of the fractional quantum Hall effect. To access these phenomena experimentally it is increasingly important to realize devices in which the influence of disorder is minimal, which can be achieved by suspending graphene on top of a gate electrode. The fabrication of suspended devices of sufficiently high quality represents a considerable technical challenge. The yield of properly functioning devices is low and the requirements of having small dimensions imposes serious constraints on the device geometry. Recently, progress in the realization of high quality devices has resulted from the use of boron nitride (BN) as a substrate. The quality of devices based on graphene on BN substrates has been demonstrated through different measurements, including the observation of ballistic transport over large distances (e.g. by means of magnetic focusing). These devices also give access to new fascinating physics, largely due to the controlled influence that the substrate has on graphene. In particular, the BN lattice generates a periodic potential in graphene, such that the Dirac fermions effectively propagate in a superlattice. Among the experimental consequences, we mention the appearance of satellite Dirac mini-bands, and the occurrence of "Hofstadter butterfly physics" at high magnetic fields.

Despite the discovery of these recent physical phenomena, there are still several unanswered questions related to fundamental aspects of charge transport in graphene. In particular there is no consensus on which are the dominant mechanisms that are responsible for charge scattering and for the generation of charge inhomogeneity at low carrier densities in graphene devices. Finding an answer to these questions is important because: (1) charge scattering is responsible for limiting charge mobility, therefore preventing the achievement of ballistic-like transport in graphene; and (2) charge inhomogeneity prevents transport studies aiming to probe the states close to the charge neutrality (Dirac) point of graphene. So far several microscopic mechanisms, such as charged impurities, atomic defects, strain and crystal corrugations, have been put forward as responsible for affecting charge transport in graphene. Part of the experimental work done in this thesis consists in electronic transport
1.2 The discovery of Topological Insulators

Topological insulators are a recently discovered class of materials that have remarkable physical properties\cite{21-23}. These materials are bulk band insulators, i.e. there is a finite energy gap between the valence and the conduction bands in the material bulk, that have unconventional gapless states at their physical boundaries. The occurrence of the metallic states at the boundaries is intrinsically related to the non-trivial topology of the bulk bands, which is different from conventional insulators. Topological insulator materials have been found to exist in all three spatial dimensions. Here in this thesis, however, we will only discuss the case of 2D and 3D systems where the non-trivial topology is induced by strong electron spin-orbit coupling. It should be noted though, that despite the recent discovery of spin-orbit induced topological insulator materials, the effect of the non-trivial topology of the bulk electronic states has been known since the 1980s, and its relevance had already been appreciated in the analysis of the Quantum Hall effect (QHE)\cite{24}.

The Quantum Hall effect is a quantum phenomenon occurring in 2D materials at low temperatures and at high magnetic fields. It is defined by the observation of the quantization of the Hall conductivity ($\sigma_H$) in multiple integers ($N$) of the quantum of conductance $\sigma_H = N2e^2/h$. A 2D electronic system in the Quantum Hall regime is an insulator in the bulk, due to the formation of Landau Levels, but has gapless states at the edges through which current can flow without dissipation. It is the occurrence of these edge states that is responsible for the quantization of the Hall conductivity. Although the presence of edge states can be thought to originate from the Landau Levels in the bulk, Thouless et al\cite{25}, demonstrated that their existence has a more general and profound origin, which is related to the non-trivial topology of the electronic structure of the bulk insulating state. This topological aspect of the QHE was further explored in the late 1980s by a theoretical work of Haldane predicting that the QHE can be observed in a honeycomb lattice (similar to graphene) in the absence of Landau Levels, provided that time reversal symmetry and inversion symmetry are broken in an appropriate way. This model has important implications in the field of topological insulators, which will be discussed with greater detail in Chapter 2 of this thesis, together with its connection to topology.

Following the studies of the Quantum Hall effect, and despite the work of
1. Introduction

Figure 1.2: (a) Illustration of the bandstructure of an insulator where the conduction and valence bands are spin-degenerate. (b) In certain cases where the spin-orbit interaction is strong, the spin degeneracy is lifted and the bands can be inverted, meaning that states of the valence band have higher energy from those of the conduction band. This can be seen as a "twist" in the topology of the bands, that can lead to the generation of states that will close the bulk gap at the boundary of the crystal. (c) Depending on the spin-orbit interaction and the topological properties of the material, the topological twist can lead to boundary states that close the bulk gap several times\[26\]. (d) Energy as a function of momentum of the electronic surface states of Bi$_2$Se$_3$ obtained from ARPES experiments\[27\]. In this spectrum the existence of Dirac-like electronic states which are closing the gap between the conduction and the valence band of Bi$_2$Se$_3$ are clearly seen.

Thouless et al. and Haldane, it has long been believed that, in practice insulators with non-trivial topology could only be induced in practice, through the application of an external field to the system. However, recent theoretical work\[28, 29\] has shown that topological insulating states – with a gap in the bulk and conducting states at the edge – can also be found in more general systems in the absence of an applied magnetic field. These topological insulating states are induced by spin-orbit interaction, a relativistic effect where the electron spin is affected by its orbital motion. In crystals, one of the effects associated to the spin-orbit interaction is the inversion of electronic bands in solids. This means that the electronic states of the valence band have higher energy than the states of the conduction band (i.e. the order of the valence and the conduction band is swapped). In terms of topology, this effect of band inversion can be pictured as if the bands were subjected to a "twist"\[26\], as illustrated in fig.1.2(a)-(c). It is this topological band twist, which is responsible for the generation of conductive states with unique properties at the boundaries of the solid.

The field has started with the pioneering work of Kane and Mele\[28\], who predicted that spin-orbit interaction in graphene can induce an insulating state with a non-trivial topology. In this state, the bulk of graphene is insulating
and electrical current is only allowed to flow at the edges through so-called helical edge states. These helical edge states correspond to a pair of one-dimensional conduction channels with opposite spin direction propagating in opposite directions along the device edge. This effect is called the Quantum Spin Hall Effect (QSHE) and it can be seen as a two-copy version of the Quantum Hall Effect. Despite the important experimental advances made in the field of graphene research, the QSHE has not been observed in this material system, due to the small intrinsic spin-orbit coupling in carbon atoms\(^31,\,32\). However, quickly after Kane and Mele’s work, Bernevig, Hughes and Zhang\(^30\) predicted the occurrence of the QSHE in quantum wells of HgTe, a material with a much stronger spin-orbit interaction. This theoretical prediction was soon after confirmed through electronic transport measurements of HgTe quantum wells by the research group of Laurens Molenkamp at the University of Wuerzburg\(^33,\,34\).

Soon after the observation of the QSHE, the analogous spin-orbit induced topological state in 3D systems was found to exist\(^35,\,36\). In these systems the bulk is insulating and the surfaces of the material possess 2D gapless electronic states that are described by the Dirac equation. As in the case of 2D topological insulators, 3D topological insulators have helical surface states, consisting of the Dirac fermions residing at the material surface with their spin direction locked to the momentum. This property is responsible for the suppression of electron backscattering and for the generation of a non-trivial phase of \(\pi\), also known as Berry phase, whenever the electronic wavefunctions perform a closed path in momentum space. The 3D topological insulators are divided into two groups, depending on the number of Dirac cones (i.e. the number of gapless valleys that are described by the Dirac equation) that reside at the surface. Materials having an odd number of Dirac cones are referred to as strong topological insulators, while systems holding a even number of Dirac cones are called weak topological insulators. Since the experimental work done in this thesis focused on the study of the electronic properties of a strong topological insulator with a single Dirac cone at its surface states, we will not discuss the case of weak topological insulators.

The first strong 3D topological insulator to be theoretically predicted and experimentally confirmed was Bi\(_{1-x}\)Sb\(_x\)\(^37\). Experiments relied on Angle Resolved Photoemission Spectroscopy (ARPES), a technique that is able to probe the electronic states of crystal surfaces. Soon after, a second generation of materials including Bi\(_2\)Se\(_3\), Sb\(_2\)Te\(_3\) and Bi\(_2\)Te\(_3\), were predicted to be strong topological insulators. The prediction was again confirmed by ARPES measurements\(^38\). Among these topological insulators, Bi\(_2\)Se\(_3\), the material studied in this thesis has shown to be particularly interesting because of the
relatively large size of its band-gap. In principle this feature of Bi$_2$Se$_3$ allows the observation of its unique surface states in transport experiments even at room temperature. Moreover, despite the initial success in observing helical surface states through ARPES, the manifestation of these states through electronic transport measurements on nanodevices, has shown to be much less straightforward. This is because of the limited crystal quality of Bi$_2$Se$_3$ (as well as of all other 3D topological insulators that have been identified to date). Since the bulk of these materials is not a good insulator, an additional transport channel is present, which makes it difficult to isolate the contribution to transport given by the surface states. Currently transport experiments are still aiming at effectively probing and controlling the electronic states of the surface of 3D topological insulators, from where a large panoply of exciting new physical phenomena are expected to occur.

1.3 This thesis

This thesis is structured in the following way. In Chapter 2 we describe general theoretical concepts that are relevant to understand the work described in the later chapters. In particular we introduce the basic electronic properties of graphene and the main features observed from electronic transport measurements of graphene transistor devices at zero and finite magnetic fields. We also introduce the microscopic mechanisms that have been proposed to be the dominant sources of disorder in graphene. In the second part of this chapter, we briefly introduce the background concepts behind the development of the field of topological insulators. We focus in greater detail on the electronic properties of the 2D topological insulators which allow to discuss the basic concepts in a simpler way, and then argue by analogy to introduce the electronic properties of 3D topological insulators.

In Chapter 3 we provide an overview of the fabrication procedures and techniques employed for the production of the graphene and Bi$_2$Se$_3$ devices studied in this thesis.

In Chapter 4 we present low temperature electronic transport measurements of graphene devices on SrTiO$_3$ substrates. SrTiO$_3$ is an insulator with a high dielectric constant, which increases with decreasing temperature. We found that the dielectric constant of the substrate does affect those transport phenomena in graphene that are influenced by long range potentials. In particular, at high magnetic fields we have monitored the resistance of the $N = 0$ Landau level in hall-bar devices and found that the resistance shows a metallic-like behaviour with decreasing temperature. This is opposite to what has been seen in other transport, where the resistance of the $N = 0$ Lan-
dau level increases exponentially at low temperatures because of an insulating state caused by the electron-electron interactions. We ascribe our observation to the substrate-induced screening of the electron-electron interactions responsible for the behaviour of the resistance of the $N = 0$ Landau level. Additionally, in graphene nanoribbons devices where transport close to the Dirac point is dominated by quantum dot physics, we find that the characteristic transport gap on SrTiO$_3$ substrates is at least one order of magnitude smaller than the one found in the same type of devices on top of other substrates. This observation is again consistent with the larger dielectric constant of the SrTiO$_3$ substrate, which effectively reduces the characteristic charging energy of the islands that contribute to transport. Despite the clear evidence of substrate screening, the dielectric constant of SrTiO$_3$ does not affect the charge mobility, nor the amount of charge density inhomogeneities occurring close to the Dirac point in graphene devices. This finding suggests that the presence of charged impurities, are not limiting charge transport in graphene because their effect would be strongly suppressed by the large $\epsilon$ of the substrate. This conclusion indicates that other microscopic mechanisms have a more predominant role in scattering charge carriers.

In Chapter 5 we present systematic transport measurements of several graphene devices on top of BN substrates, with mobility values ranging from 5000cm$^2$/Vs to 80000cm$^2$/Vs. In this large set of studied devices we found an unambiguous correlation between the charge density inhomogeneity close the Dirac point and the mobility. Higher mobility devices are systematically characterized by a lower charge density inhomogeneity. The correlation demonstrates that both quantities are limited by a same microscopic mechanism. Weak localization measurements in high mobility devices and other experimental observations, consistently point to the presence of random strain as the main microscopic mechanism limiting transport in graphene. We also show theoretically that strain can explain quantitatively the correlation between mobility and charge inhomogeneity. Our observations and theoretical analysis, therefore, strongly suggest that the presence of strain is the dominant microscopic mechanism limiting charge transport on high-quality graphene devices on top of substrates.

Finally in Chapter 6 we present electronic transport experiments through thin single crystal Bi$_2$Se$_3$ devices connected with superconducting leads. Bi$_2$Se$_3$ is a 3D topological insulator, whose surface states host a single Dirac cone. With the use of a gate voltage, we were able to observe ambipolar transport, where the polarity of carriers can be tuned from hole to electrons, as it would be expected for Dirac fermions residing at the surface of the crystal. In the presence of a perpendicular magnetic field, these devices develop Shubnikov-
de-Haas quantum oscillations for both carrier polarities, a consequence of the generation of Landau levels. From the analysis of these quantum oscillations, we were able to confirm the existence of Dirac fermions at the surface of Bi$_2$Se$_3$. In addition, when the devices are cooled below the critical temperature of the superconducting leads, we also observed an induced supercurrent at the surface of the Bi$_2$Se$_3$ devices that can be tuned with the gate voltage, and also exhibit an ambipolar behaviour. This observation indicates that Dirac states at the surface of a 3D topological insulator can mediate superconducting proximity effect.
2. Background

2.1 Electronic structure of graphene

The graphene crystal lattice consists of a two-dimensional array of carbon atoms organized in a honeycomb structure. In a single carbon atom the six electrons arrange themselves in a $1s^22s^22p^2$ orbital configuration. The inner electrons of the $1s^2$ shell are strongly bonded to the nucleus and do not play a role in the interatomic bonds. The four remaining electrons that occupy the $2s$ and the $2p$ orbitals are known as the valence electrons and are responsible for the electronic and chemical properties of carbon. The strong covalent bonds responsible for attaching the carbon atoms together result from the hybridization of these $s$ and $p$ orbitals, known as $sp^n$ hybridization states where $n = 1, 2, 3$. In graphite, carbon nanotubes and graphene itself the carbon atoms are bonded in the same $sp^2$ hybridization. This $sp^2$ hybridization results in three planar $\sigma$ bonds at low energy, responsible for holding the structure together, and one bond perpendicular to the $\sigma$ plane, known as the $\pi$ bond. The electrons of the $\pi$ bond – derived from the carbon $p_z$ orbitals – are not assigned to a specific atomic site, but are shared by all the atoms.

2.1.1 The tight binding model

The emergence of energy bands in solids is a direct consequence of the overlap between the individual atomic orbitals in the crystal. In the case of graphene the overlap of the $\pi$ electrons leads to the formation of $\pi$ and $\pi^*$ bands commonly known as the valence and conduction band, which can be calculated by using the tight binding method\cite{11, 12, 13, 14}.
First, one defines the primitive cell of graphene which can be seen as a
Bravais lattice consisting of two interpenetrating triangular sublattices, A and
B, each with one atom per unit cell (see fig. 2.1). The lattice vectors can be
given as

\[
\vec{a}_1 = \frac{a}{2}(3, \sqrt{3}) , \quad \vec{a}_2 = \frac{a}{2}(3, -\sqrt{3})
\] (2.1)

where \(a=1.42 \text{Å}\), is the distance between two neighbouring carbon atoms.

The reciprocal lattice vectors of this Bravais lattice are

\[
\vec{b}_1 = \frac{2\pi}{3a}(1, \sqrt{3}) , \quad \vec{b}_2 = \frac{2\pi}{3a}(1, -\sqrt{3})
\] (2.2)

The tight-binding Hamiltonian for the \(\pi\) electrons in graphene is then de-
 fined as

\[
H = -t \sum_n (|\phi_n^A\rangle \langle \phi_n^B| + h.c.)
\] (2.3)

where \(|\phi_n^{A,B}\rangle\), represent states of the p\(_z\) atomic orbital wavefunctions \(\langle \phi_n^{A,B}|\vec{r}\rangle = \phi(\vec{r} - \vec{R}_n^{A,B})\) in sublattices A, B and \(t \approx 2.8eV\) is the hopping integral.\(\text{[1]}\).
2.1. Electronic structure of graphene

Within this approximation we search for eigenfunctions, \( \Psi_k(\vec{r}) \), that are linear combinations of the atomic orbitals such as

\[
\Psi_k(\vec{r}) = c_A(\vec{k})\Psi_k^A(\vec{r}) + c_B(\vec{k})\Psi_k^B(\vec{r})
\]

(2.4)

\[
= \frac{1}{\sqrt{N}} \sum_n \left[ e^{i\vec{k} \cdot \vec{R}_n^A} c_A(\vec{k})\phi(\vec{r} - \vec{R}_n^A) + e^{i\vec{k} \cdot \vec{R}_n^B} c_B(\vec{k})\phi(\vec{r} - \vec{R}_n^B) \right]
\]

where \( N \) is the number of unit cells, \( c_{A,B} \) are the amplitude of the wavefunctions at sites \( A,B \) and \( \phi(\vec{r}) \) are the wavefunctions of the p\(_z\) orbitals. These wavefunctions satisfy the Bloch condition where the vector \( \vec{R} \in G \) \((\vec{R} = n\vec{a}_1 + m\vec{a}_2 \) and \( G \) denotes the set of all lattice vectors). Writing the Schrodinger equation, \( H|\Psi\rangle = E|\Psi\rangle \), and projecting on the different lattice sites we obtain

\[
\langle \phi_n^A | H | \Psi \rangle = E_k \langle \phi_n^A | \Psi \rangle \quad (2.5)
\]

\[
\langle \phi_n^B | H | \Psi \rangle = E_k \langle \phi_n^B | \Psi \rangle \quad (2.6)
\]

It is assumed that \( \langle \phi_n^A | \phi_n^A \rangle = \langle \phi_n^B | \phi_n^B \rangle = 1 \), and the overlap between the nearest neighbours is \( \langle \phi_n^A | \phi_n^B \rangle = \langle \phi_n^B | \phi_n^A \rangle = 0 \). The on-site energy is defined as \( E_0 = \langle \phi_n^A | H | \phi_n^A \rangle = \langle \phi_n^B | H | \phi_n^B \rangle = 0 \) and the transfer integral is \( \langle \phi_n^A | H | \phi_n^B \rangle = \langle \phi_n^B | H | \phi_n^A \rangle = t \). We then obtain

\[
E_k c_A = -t \left( e^{-i\vec{k} \cdot \vec{\delta}_1} + e^{-i\vec{k} \cdot \vec{\delta}_2} + e^{-i\vec{k} \cdot \vec{\delta}_3} \right) c_B \quad (2.7)
\]

\[
E_k c_B = -t \left( e^{i\vec{k} \cdot \vec{\delta}_1} + e^{i\vec{k} \cdot \vec{\delta}_2} + e^{i\vec{k} \cdot \vec{\delta}_3} \right) c_A \quad (2.8)
\]

which can be rewritten as the following matrix

\[
\begin{pmatrix}
0 \\
\left( e^{i\vec{k} \cdot \vec{\delta}_1} + e^{i\vec{k} \cdot \vec{\delta}_2} + e^{i\vec{k} \cdot \vec{\delta}_3} \right)
\end{pmatrix}
\begin{pmatrix}
c_A \\
c_B
\end{pmatrix} = E_k \begin{pmatrix}
c_A \\
c_B
\end{pmatrix} \quad (2.9)
\]

By determining the matrix eigenvalues we obtain the following dispersion relation

\[
E(k_x, k_y) = \pm t \sqrt{3 + 2 \cos(\sqrt{3}k_x a) + 4 \cos \left( \frac{\sqrt{3}k_x a}{2} \right) \cos \left( \frac{3k_x a}{2} \right)}, \quad (2.10)
\]
where the $\pm$ signs describe the valence (-) and the conduction (+) bands respectively. These two bands touch at two inequivalent points in the Brillouin zone, the $K = \left( \frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a} \right)$ and $K' = \left( \frac{2\pi}{3a}, -\frac{2\pi}{3\sqrt{3}a} \right)$ points or Dirac points (fig. 2.2), where $E(K) = E(K') = 0$.

2.1.2 Low energy electronic states

Important information on the graphene electronic properties can be inferred by looking at the low energy electronic states, i.e. the states close to the Dirac point where the conduction and the valence band touch. Looking at these states, close to $E = 0$ and momentum $\vec{k} = \vec{K} + \vec{q}$, where $|q| \ll K, K'$, one can expand the Hamiltonian from eq. (2.9), up to first order in $\vec{q}$ and obtain:

$$H_{K,K'} = \frac{3ta}{2} \begin{pmatrix} 0 & q_x \mp i q_y \\ q_x \pm i q_y & 0 \end{pmatrix} = \hbar v_F \begin{pmatrix} 0 & q_x \mp i q_y \\ q_x \pm i q_y & 0 \end{pmatrix}$$

(2.11)

This Hamiltonian gives rise to two symmetric conical bands, that yield a linear energy-momentum dispersion

$$E(\vec{q}) = \pm v_F \hbar |\vec{q}|$$

(2.12)

where $v_F = \frac{3at}{2\hbar} \approx 10^6 m/s$, is the electron Fermi velocity. The Hamiltonian
in eq.(2.11) around the $K$ point can be conveniently written as:

$$H = v_F \hbar \vec{\sigma} \cdot \vec{q} = -iv_F \hbar \vec{\sigma} \cdot \vec{\nabla}$$ (2.13)

where $\vec{\sigma}$ are the Pauli matrices and $\vec{\sigma} \cdot \vec{q} = \sigma_x q_x + \sigma_y q_y$. This low energy Hamiltonian of graphene is analogous to the relativistic Dirac Hamiltonian describing particles with zero mass and travelling at the speed of light. In the case of graphene the speed of light is replaced by the Fermi velocity of the electrons. The eigenfunctions of this Dirac Hamiltonian are represented as

$$\psi_{\pm, K}(\vec{q}) = \frac{e^{i\vec{q} \cdot \vec{r}}}{\sqrt{2}} \left( \frac{e^{-i\theta/2}}{\pm e^{i\theta/2}} \right)$$ (2.14)

$$\psi_{\pm, K'}(\vec{q}) = \frac{e^{i\vec{q} \cdot \vec{r}}}{\sqrt{2}} \left( \frac{e^{i\theta/2}}{\pm e^{-i\theta/2}} \right)$$ (2.15)

Here $\pm$ corresponds to energies $E(\vec{q}) = \pm v_F \hbar |\vec{q}|$ and $\theta = \arctan(q_x/q_y)$. The spinor part of these eigenfunctions does not represent the real electron spin, but a so-called pseudospin. The pseudospin expresses the probability amplitude of finding an electron on either the sublattice A, pseudospin pointing upwards $|\uparrow\rangle$, or sublattice B, pseudospin pointing downwards $|\downarrow\rangle$. In general the electron amplitude is shared by the two A and B atoms, therefore the pseudospin is a linear combination of these ‘up’ and ‘down’ states. Electrons in graphene also possess chirality, originating from the fact that the pseudospin direction is ‘pinned’ to the electronic momentum. The chirality of a state is defined by the eigenvalues of the helicity operator $\hat{\mathcal{h}} \equiv \vec{\sigma} \cdot \vec{q} |\vec{q}|$. When this operator is applied to the eigenfunctions, $\hat{\mathcal{h}} |\psi_{\pm, K}(\vec{q})\rangle = \pm |\psi_{\pm, K}(\vec{q})\rangle$, one finds two possible eigenvalues $\pm 1$, depending on whether the pseudospin is parallel or antiparallel to the momentum $\vec{q}$. In the $K$ valley, electrons have positive helicity and holes negative helicity, while in the $K'$ valley the opposite is true. An additional property is that the eigenfunctions change sign upon a $2\pi$ rotation of the pseudospin (as it is typical for spin$-1/2$ particles), revealing a phase shift of $\pi$ known as the Berry phase. The unique properties of these Dirac fermions have lead to the prediction of many new physical phenomena\[41, 42\]. Furthermore, well known mesoscopic phenomena such as Weak Localization and the Quantum Hall effect (which will be addressed in sections 2.4.1 and 2.5.1), manifest themselves rather differently in graphene when compared to previous observations of the same phenomena in other mesoscopic systems.
2. Background

![Figure 2.3: (a) Typical layout of a graphene transistor with a Hall bar shape. The graphene crystal is on top of an insulating layer which is itself in contact to a conductive back-gate. (b) The resistivity of graphene varies upon changing the back-gate voltage ($V_g$), which effectively can set the Fermi level of the graphene device in either the valence or conduction band. A maximum of resistivity is achieved at the charge neutrality point, here occurring at $V_g=0$V.](image)

2.2 Basic aspects of graphene devices for transport experiments

The intense experimental research on the physical properties of graphene, especially the electronic properties, started in 2004 through the development of the first graphene field-effect transistor. In the next sections I will present an overview of the basic properties of the graphene transistors and how the presence of disorder affects transport in these devices.

2.2.1 Gate modulated electronic transport

Many of the interesting electronic properties of graphene can be accessed through low-temperature transport experiments across graphene transistor devices, whose structure is sketched in fig. 2.3.(a). The graphene layer is obtained from the exfoliation of a graphite crystal and then deposited on top of an insulating substrate. In the initial stages of research on graphene, the substrate typically consisted of Si/SiO₂, where a 300nm thick layer of insulating SiO₂ lies on top of a heavily doped Si wafer. The metallic contacts on top of graphene are deposited in a Hall-bar geometry, in order to measure independently the longitudinal ($R_{xx}$) and the transverse ($R_{xy}$) resistances. The use of a back-gate voltage ($V_g$), allows the accumulation of charge carriers which shifts the Fermi level ($E_F$) in graphene into either the valence or the conduction bands. The
ability to shift the Fermi level in graphene with a gate voltage, allows transport of carriers of different polarity to occur. For instance when $V_g < 0$, the Fermi level lies in the valence band and electrical current is carried by holes while for $V_g > 0$ the Fermi level is located in the conduction band and transport occurs due to electrons (see fig. 3.3 (b)). When the Fermi level is located at the charge neutrality (or Dirac) point, which for the device on fig. 3.3 (b) is at $V_g \approx 0$, one finds that the device resistivity reaches its maximum. The charge carrier concentration ($n$) across the graphene transistor induced by the gate voltage can be estimated from a parallel plate capacitor model where $n = C_g V_g / e$ and $C_g$ is the gate capacitance, or it can be measured through the use of the Hall effect.

The initial transport measurements of graphene on Si/SiO$_2$ devices found that at higher carrier densities ($n$) away from the Dirac point, the conductivity shows a quasi-linear dependence on $n$ [3, 10, 13, 45], as seen in fig. 2.4 (a). At such carrier densities the mobility ($\mu = \sigma / ne$) of the carriers in graphene devices on Si/SiO$_2$ could reach values on the order of $\mu \approx 10-20 \times 10^3$ cm$^2$/Vs [13, 14, 15, 16]. When approaching the Dirac point at $n = 0$, the conductivity reaches its minimum and saturates at values around $\sigma_{min} = 3 - 8e^2 / h$ [3, 10, 13, 45], which deviates from the theoretical prediction of $\sigma_{min} = 4e^2 / \pi h$, where for a perfect graphene device without disorder transport is assumed to be mediated by evanescent states [48]. Experimentally when $E_F$ is close to the Dirac point one also finds that the conductivity is independent of the carrier density up
Background


to a density $n^*$ (see fig. 2.4(b)), which for devices on Si/SiO$_2$ substrates, is normally found to be in the $10^{11} \lesssim n^* \lesssim 10^{12}$ cm$^{-2}$ range [40, 45]. This $n$-independent conductivity region, results from the existence of charge density inhomogeneities, caused by the presence of random potentials that generate local electron or hole doped regions also known as "charge puddles" [6]. Currently one of the ongoing experimental challenges is to identify the origin of the disorder that limits the charge mobility and also establish the mechanisms that are responsible for the formation of charge puddles which prevent transport studies aiming to probe the states close Dirac point.

2.3 The effect of disorder

The systematic observation of a maximum carrier mobility of $\mu \approx 10 - 20 \times 10^3$ cm$^2$/Vs for graphene devices on Si/SiO$_2$ from different research groups, raised the question if such values correspond to the intrinsic limit in this system. This is not the case. The development of more sophisticated device fabrication techniques has led to a new generation of graphene devices, such as suspended graphene and graphene on top of Boron Nitride (BN) substrates, which are less disordered and exhibit much higher carrier mobility values.

In suspended graphene devices the underlying substrate is removed leaving the crystal hanging above the gate attached only by the metallic contacts. These devices show a significant reduction of the charge density inhomogeneity with $n^*$ as low as $10^8$cm$^{-2}$ and a record high mobility of $\mu_{sus} = 10^6$ cm$^2$/Vs [49]. Unfortunately however, suspended graphene devices are limited to dimensions of only a few micrometers and require very specific contact geometries [11, 12, 14]. Another path leading to improvements in device quality is to use particularly suitable substrates. It was found that the use of hexagonal BN [15] – which is an isomorph of graphene with a lattice mismatch of $\approx 1.6\%$, a bandgap of $\approx 6$eV and a very flat surface – can lead to mobility values higher (and sometimes much higher) than $\mu_{BN} = 10^5$ cm$^2$/Vs and $n^*_{BN} \sim 10^{10}$ cm$^{-2}$ or less [8, 13, 50, 51]. These values correspond to an improvement of one order of magnitude or more when compared to previous Si/SiO$_2$ devices.

Finding such significant improvements on the carrier mobility and the reduction of $n^*$ for graphene on BN substrates and suspended devices, indicates that the mechanisms that induce charge scattering and potential fluctuations in graphene are affected by the presence of the substrate. In conductivity measurements, while the presence of potential fluctuations is responsible for the charge inhomogeneities characterized by $n^*$ close to the Dirac point, the existence of scattering potentials are responsible for the elastic scattering rate.
2.3. The effect of disorder

1/τ, which determines the charge carrier mobility. One important question is whether the disorder potentials that determine \( n^* \) have the same microscopic origin as those limiting \( \tau \). Here \( \tau \) is the characteristic time between two collisions (the carrier mean free path is then \( \ell = v_F \tau \)) and can be estimated by using the Fermi golden rule

\[
\frac{1}{\tau} \propto N(E_F) \sum_{n'} |\langle nk|V|n'k'\rangle|^2
\]

(2.16)

where |\( nk \rangle\) and |\( n'k' \rangle\) are the incoming and outgoing states, \( V \), the scattering potential and the \( N(E_F) \) density of states at the Fermi energy. The net scattering rate due to the presence of several potentials of different microscopic origin, is the sum, \( \tau^{-1}_{\text{total}} = \sum_n \tau^{-1}_n \) of the individual scattering rates \( \tau^{-1}_n \). The determination of the scattering rate provides important information on which type of scattering potentials are affecting the conductivity of graphene at carrier densities far from the Dirac point.

In order to explain the experimental dependence of the conductivity at different carrier density regions, several types of potentials, which will be addressed in the next sections, have been proposed as the dominant scattering source determining the elastic scattering time in graphene.

2.3.1 Long-range potentials

Long range potentials in graphene are smooth potentials that do not vary appreciably over several lattice spacings \( a \) and induce a small electron momentum transfer upon scattering (small compared to the \( K - K' \) distance in momentum space). In the following sections I will address the effects on the electronic properties of Coulomb-like potentials and of potentials resulting from strain and deformations of the graphene crystal.

Coulomb potentials

The presence of charged impurities present at the surface of the material used as a gate insulator, has been proposed as the main source of Coulomb potentials in graphene\(^4\). The role of these potentials on the electronic transport properties of graphene has been extensively addressed in past work\([39, 40, 45–55]\] which aimed to explain the experimental dependence of the conductivity on the carrier density.

The existence of such charged impurities has been proposed as the main responsible for the constant conductivity region \( n^* \)\(^5\) [52] that occurs close to the

\(^1\)Coulomb potentials may also result from charged adsorbates or from dangling bonds at the substrate surface
Dirac point. Here the random distribution of charged impurities along the graphene device gives rise randomly distributed potentials that induce charge fluctuations. Scanning tunnelling microscopy (STM) measurements\cite{56,57} aiming to probe the states near the Dirac point, suggested that the observed charge density inhomogeneities could result from charged impurities that are predominantly located between the graphene crystal and the substrate.

The presence of Coulomb impurities has also been taken into account to explain the quasi-linear dependence of the conductivity at carrier densities away from the Dirac point. Theories developed assuming that Coulomb potentials are the main source of scattering\cite{52,53,55}, showed that the conductivity depends on the concentration of charged impurities, $n_{\text{imp}}$, as $\sigma_{\text{imp}} \propto \frac{n}{n_{\text{imp}}}$. Indeed, experiments performed by Chen et al.\cite{58}, found that the conductivity follows the $\sigma_{\text{imp}} \propto \frac{n}{n_{\text{imp}}}$ dependence upon varying the concentration of charged impurities which was achieved by the intentional deposition of potassium atoms.

Despite the observations of Chen et al.\cite{58}, theories accounting for the effect of charged impurities have also predicted that one should observe a significant improvement of the carrier mobility once the Coulomb potentials are screened. This can be achieved by modifying the dielectric constant ($\epsilon$) environment experienced by a graphene device. Transport studies on higher $\epsilon$ environments, where graphene devices were immersed in solvents\cite{59}, claimed that the mobility increase was either non-existent or too small to support the theoretical prediction of strong scattering originating from Coulomb impurities\cite{52,53,55}. Due to the freezing of the solvents these experiments had to be performed at relatively high temperatures, between 160-300 K, and therefore transport studies at low temperature were not possible. An alternative method to study the effect of the dielectric environment on graphene devices is to replace the low-$\epsilon$ substrate (SiO$_2$ and BN) with a high-$\epsilon$ substrate. For instance, a suitable candidate is SrTiO$_3$, a well known insulator which at room temperature has a $\epsilon \simeq 300$ and increases with lowering the temperature, reaching values as high as 10000 at 4 K\cite{60}. By using SrTiO$_3$ as a substrate it is possible to study the effect of a varying dielectric environment on the electronic transport properties of graphene devices. In chapter 4 the effect of the SrTiO$_3$ on the transport properties of graphene devices will be addressed.

\textit{Strain and mechanical deformation}

The presence of ripples, surface corrugations or other sources of strain (e.g., in-plane) in graphene are also an effective source of long ranged potentials. These ripples and corrugations can originate from out-of-plane fluctuations of
2.3. The effect of disorder

and also from the conformation of graphene to the topography of the underlying substrate. In fact, the existence of these ripples and surface corrugations generate strains that are able to affect the electronic properties of graphene. Additionally strain can originate from an in-plane displacement of the atoms (i.e. it does not require height fluctuations of graphene). These deformations which are responsible for the change of inter-atomic distances, couple to the electronic orbital degrees of freedom through both a scalar and a gauge potential.

The displacement of the carbon atoms from their equilibrium positions leads to the formation of regions with increased ionic charge density, that is responsible for the generation of a scalar potential. The deformation of graphene will also generate gauge potentials. Here the effect of strain is to induce variations on the nearest neighbour distances and correspondingly in the hopping amplitudes. These fluctuations in hopping integral enter the single valley Hamiltonian of electrons in graphene as a vector potential $\vec{A}$.

$$H = v_F \vec{\sigma} \cdot (\vec{p} - \vec{A})$$

Eq. (2.17), shows that the effect of strain is to generate an effective fictitious magnetic field. The main difference with a real magnetic field is that this effective fictitious field generated by strain, induces a vector potential $\vec{A}$ with opposite signs in the $K$ and $K'$ valleys, as it is needed to preserve time reversal symmetry.

Many articles have discussed how these gauge potentials can affect graphene electronic properties through the generation of so-called pseudo-magnetic fields. STM experiments on graphene nano-bubbles, for instance, have been interpreted by invoking the presence of strain-induced pseudo-magnetic fields as high as 300T. Regarding electronic transport experiments, the role of both gauge and scalar potentials has also been suggested to scatter electrons and cause charge density inhomogeneities. Katsnelson and Geim have predicted that the potentials generated by the ripples and corrugations might as well explain the quasi-linear behaviour of $\sigma$ at carrier densities away from the Dirac point, provided that the height profile of the graphene surface is known. In chapter 5, the effects of ripples and corrugations on graphene devices are taken into account to explain the behaviour of the transport properties of a large ensemble of devices.

2.3.2 Short-range potentials

A short range potential has the spatial extension corresponding approximately to the typical length of the lattice constant of graphene, which is much shorter
than the typical electron wavelength ($\lambda_F = 2\pi/k_F$) for all accessible electron densities. The presence of short ranged potentials in graphene can result from the existence of atomic defects, vacancies (missing carbon atoms), cracks and edges in the graphene crystal. Additionally, the presence of chemiabsorbed elements – resultant from the fabrication procedure – such as, monovalent impurities or -OH groups, that remove π orbitals from the hopping sites for transport, can also act as short range scattering potentials. When considering electronic transport experiments, the sole presence of short ranged potentials is unable to explain the behaviour of the constant conductivity region close to the Dirac point\[40,72,73\]. Moreover, when considering transport at higher carrier densities, these impurities affect the conductivity as follows

$$\sigma_s = \frac{2e^2}{\pi h} \frac{n}{n_i} \ln^2 \left( \sqrt{n\pi R} \right) \quad (2.18)$$

Here the $n_i$ and $R$ correspond to the concentration of impurities and the potential range respectively. Usually the fits from eq.(2.18) to the experimental data lead to values of $R \approx 0.3$ nm and $n_i$ of a few $10^{11}$ cm$^{-2}$, for devices on Si/SiO$_2$ substrates\[40,74,75\]. These values are physically meaningful and internally consistent e.g. ($R \approx a$) as they usually reproduce the data satisfactorily. It should be noted, however, that many different models give comparable functional dependences for the $\sigma(n)$ curve, making it difficult to discriminate the different models on the basis of this quantity.

In several works\[73–76\] the presence of short range scatterers has been argued to be the main mechanism that determines mobility, in spite of its inability to explain the existence of charge fluctuations close to the Dirac point. In principle, it is not a priori unreasonable to consider that the mobility is limited by short ranged potentials while the existence of charged puddles is determined by the presence of long ranged potentials. However, in chapter 5 our transport studies realized on several graphene-on-BN devices reveal that this assumption is not compatible with the experiments.

### 2.3.3 Graphene nanoribbons

The previous sections describing the effects of disorder in a graphene transistor focused on large devices having length and width in the micrometre scale or larger. However, once the size of a graphene device is confined to the nanometre scale – as in a nanoribbon – the effects of disorder play a much stronger role on the overall transport properties. A graphene nanoribbon consists of a quasi one-dimensional graphene crystal, which is fabricated by etching a larger graphene layer (see inset fig.2.5(a)). The typical sizes that characterize such
2.3. The effect of disorder

Figure 2.5: (a) Measurement of the differential conductance ($dI/dV$) as a function of $V_g$, of a graphene nanoribbon showing a region of suppressed conductance close to the charge neutrality point. (b) Measurement of $dI/dV$ for a smaller range in $V_g$ as a function of the voltage bias ($V_b$) between the contacts, showing that the blue area corresponds to a region where the measured current is heavily suppressed. (c) Relation between the measured $I$ (absolute $I$ is the green line) as function of the applied $V_b$ in the regime suppressed transport current (yellow dashed line in the (b)). The application of $\Delta V_b$ along nanoribbon is necessary in order to leave the regime of suppressed current, figure adapted from [77].

Ribbons range from few tenths to hundred nanometres in width, with a length of a few hundreds of nanometres to micrometres. The intense experimental work on graphene nanoribbons was triggered by the idea to use size quantization effects to open a band-gap in the electronic structure [78–80]. Electronic transport experiments in graphene nanoribbons on Si/SiO$_2$ substrates revealed that charge transport is heavily suppressed at gate voltages close to the charge neutrality point (see fig.2.5 (a)-(c)) [77, 81, 82]. Fig.2.5 (b) shows the differential conductance ($dI/dV$) measurement of a graphene nanoribbon as a function of the voltage bias ($V_b$) and gate voltage ($V_g$). The blue area of fig.2.5 (b) corresponds to an insulating region where $dI/dV$ is significantly suppressed due to the existence of a transport gap. The presence of such transport gap in nanoribbons leads to a non-linear relation between the applied $V_b$ and the measured current (black curve in fig.2.5 (c)), where the application of a certain $\Delta V_b$ is needed as in order to observe a steep increase in the measured current (green curve in fig.2.5 (c)). The transport gap is usually defined as $E_g = e\Delta V_b$. For nanoribbons on Si/SiO$_2$ substrates, it was been found that the energy of the transport gap ($E_g$) scales with the width ($W$) of the of the nanoribbon as $E_g \propto W^{-1}$ [77]. Typically for 1$\mu$m long ribbons with $W$ between 100nm and 30nm the size of this gap ranges from 40 to 100 meV [77, 82].

The suppression of conduction in graphene nanoribbon devices close to the Dirac point was indeed, found to be a consequence of the increased amount of
disorder. The physical reason is the proximity of the edges, that are much more disordered than the bulk. This leads to strongly suppressed electron mean free paths ($\ell$) and causes strong Anderson localization\cite{82}. As a consequence, electrons are localized in space, and the nanoribbon behaves as a random collection of islands which can be thought of as quantum dots\cite{81}. It is now widely accepted that the origin of the transport gap in graphene nanoribbons arises from the increased edge disorder, rather than from the opening of a band gap due to size quantization\cite{77,82}.

2.4 Low field electronic transport in graphene

When an electronic device is cooled down to few Kelvin the quantum mechanical wave properties of electrons manifest themselves through interference effects. Quantum interference occurs when electrons preserve their phase coherence while travelling through a diffusive conductor. In a diffusive conductor, electrons are subjected to many scattering events, which can be either elastic or inelastic. The presence of elastic scatterers are responsible for the randomization of the momentum direction of the electrons, and set the mean free path ($\ell$), the average distance between two elastic scattering events. Inelastic scattering events, caused by collisions with other electrons or with phonons, destroy information on the phase of the electrons and set a length scale, the phase coherence length ($\ell_{\phi}$), for the suppression of interference. The phase coherence length increases with lowering the temperature and at liquid He temperatures quantum interference effects become easily visible.

One of the most relevant consequences of quantum interference in diffusive systems is the enhanced probability that electrons have to backscatter. This can be understood by considering the interference of an electron with itself when following different trajectories\cite{84,85}. In fig. 2.6 (a), two possible trajectories are sketched between points $A$ and $B$ in a diffusive system. The probability $P(A, B, t)$ of motion from position $A$ to $B$ in a definite time $t$, is given by

$$P(A, B, t) = \sum_i |a_i|^2 = \sum_i |a_i|^2 + \sum_{i \neq j} a_i a_j^*$$

(2.19)

Where $a_i$ are the probability amplitudes for each trajectory $i$. The first term on the right-hand side in eq.(2.19) corresponds to the classical diffusion probability, while the second term accounts for the quantum interference between different paths. Generally the contribution of different uncorrelated
Figure 2.6: (a) In a 2D diffusive system carriers leaving point A to B can perform several different paths. (b) A pair of counter-propagating trajectories performing the same closed path contributes to the enhancement of backscattering and therefore weak localization. (c) For the case of graphene electrons on the $K$ or $K'$ valleys are not allowed to scatter in the backwards direction (upper part) because electrons can’t reverse their pseudospin direction whereas scattering on other directions is allowed (lower part). Figure adapted from ref[83].

paths averages out, when summing over all possible trajectories. However in the case of backscattered trajectories the probability amplitudes are identical in the presence of time reversal symmetry, giving a non-zero quantum contribution to the backscattering probability.

Fig. 2.6 (b), illustrates electron trajectories performing a closed path where the starting and finishing point is the same. When time reversal symmetry is preserved, the probability amplitudes of $a^+$ and $a^-$ corresponding to clockwise and counter-clockwise trajectories are the same ($a^+ = a^- \equiv a$), leading to a coherent backscattering probability of $|a^+ + a^-|^2 = 4a^2$, twice the classical result. This enhanced backscattering behaviour of electrons is known as weak localization, due to the “tendency” of electrons to localize which leads to a decrease of the conductivity. The typical correction to the conductivity due to weak localization is $\delta \sigma \sim (e^2/h)$.

The weak localization effect can be suppressed through the application of a magnetic field which breaks time reversal symmetry. Under the effect of a magnetic field, the probability amplitudes $a^+$ and $a^-$ develop a phase difference even if the displacement due to the Lorentz force is negligible. This phase, known as the Aharonov-Bohm phase, results from the fact that the electron momentum, $\vec{p} = m\vec{v} - e\vec{A}$, in a magnetic field contains the vector potential $\vec{A}$. The acquired phase over a closed loop of clockwise (+) and counter-clockwise (-) paths is
\[ \phi = \frac{1}{\hbar} \oint_{+} \vec{p}\, d\vec{r} - \frac{1}{\hbar} \oint_{-} \vec{p}\, d\vec{r} = \frac{2e}{\hbar} \int (\vec{\nabla} \times \vec{A}) \cdot d\vec{S} = \frac{2eBS}{\hbar} \equiv \frac{4\pi \Phi}{\Phi_0}, \quad (2.20) \]

where \( \Phi_0 \equiv \hbar/e \) is the magnetic flux quantum and \( \Phi = BS \) the magnetic flux through the area \( S \) enclosed by the trajectories. Since all closed trajectories have different areas \( S \), this phase difference randomizes the phase of the probability amplitudes and averages out the interference effects of the counter-propagating paths, leading to the suppression of weak localization at higher fields. Through this mechanism weak localization is strongly suppressed on a magnetic field scale of \( B \gtrsim h/(2e\ell^2) \) \[85\].

### 2.4.1 Weak localization effect of Dirac fermions

Since graphene has two valleys at the \( K \) and \( K' \) points of the Brillouin zone, besides the observation of weak localization it is also possible to observe weak anti-localization, where the interference between counter-propagating electron paths is destructive instead of constructive. Weak anti-localization occurs in graphene if the electrons travelling in a single valley do not break the effective time reversal symmetry between the electronic states \( k \) and \( -k \) inside that valley. The operator defining this symmetry is \( A = \sigma_y \hat{K} \), where \( \hat{K} \) is the complex conjugation and has the following property when acting on the single valley Hamiltonian \( (H_K(\vec{k})) \) of graphene

\[ AH_K(\vec{k}) A^\dagger = H_K(\vec{k}) \quad (2.21) \]

This effective time reversal symmetry is not the real time reversal symmetry of the graphene Hamiltonian, which connects the electronic states between the \( K \) and \( K' \) valleys. The real time reversal symmetry is broken by the presence of a magnetic field, while the effective time reversal symmetry is also broken by lattices distortions, curvatures (ripples and corrugations) and trigonal warping \[86\]. The characteristic time-scale for breaking this effective time reversal symmetry is denoted by \( \tau_* \). Besides the preservation of the effective time reversal symmetry, the observation of weak anti-localization requires that scattering between the two valleys does not occur. In the absence of scattering between valleys when considering an electron in a single valley performing a closed path, (fig. 2.6.(b)), a phase difference of \( \pi \) between the time-reversed paths is developed, due to the Berry phase associated to the rotation of the...
2.4. Low field electronic transport in graphene

pseudospin. This is because the propagation along a closed path in real space requires a complete rotation in momentum space encircling the $K$ point (again under the assumption that inter-valley scattering is not present). This leads to a destructive interference and therefore a zero probability to backscatter\[87\], resulting in an increase in conductivity known as weak anti-localization.

In order to observe weak localization in graphene, electron scattering between the $K$ and $K'$ valleys must occur, because the time reversed state in one valley is in the opposite valley\[86\],\[88\],\[89\]. In graphene, such inter-valley scattering events can result from the presence of short-ranged potentials. The characteristic time of inter-valley scattering processes is defined by $\tau_i$.

The overall effect of the elastic scattering times $\tau_\ast$, $\tau_i$, $\tau$ and the phase coherent time ($\tau_\phi$) on weak (anti-)localization in graphene, leads to the following conductivity correction \[88\],\[89\]:

\[
\Delta \sigma(B) = \frac{e^2}{\pi \hbar} \left( F \left( \frac{\tau_B^{-1}}{\tau_\phi} \right) - F \left( \frac{\tau_B^{-1}}{\tau_\phi^{-1} + 2\tau_i^{-1}} \right) - 2F \left( \frac{\tau_B^{-1}}{\tau_\phi^{-1} + \tau_i^{-1} + \tau_\ast^{-1}} \right) \right)
\]

where $F(z) = \ln z + \psi(0.5 + z^{-1})$ and $\psi(x)$ is the digamma function, $\tau_B^{-1} = 4eDB/\hbar$, the diffusion constant is $D = v_F\tau/2$ and $\tau = \mu h k_F/ev_F$ is the transport time. At low temperatures, where $\tau_\phi$ greatly exceeds $\tau_\ast$ and $\tau_i$, weak localization is generally observed \[90\]–\[92\]. In the work of Thikonenko et al\[93\], weak antilocalization in graphene was observed by increasing the temperature (resulting in a reduction of $\tau_\phi$) and reducing carrier density (which increases $\tau_i$). The shorter phase coherent paths contributed to prevent inter-valley scattering, bringing to evidence the interference effects in the same valley that gave rise to a positive magnetoresistance.

Weak localization measurements, as they enable the determination of characteristic scattering times such as $\tau_\ast$ and $\tau_i$, can provide important information on the microscopic mechanisms that affect electronic transport in graphene. For instance, comparing the inter-valley scattering time $\tau_i$ with the transport time $\tau$ provides a method to establish which type of potentials dominate transport. If short-ranged potentials are dominating transport one expects that $\tau_i \ll \tau$, while the opposite case of $\tau_i \gg \tau$ indicates that intra-valley scattering and therefore long-ranged potentials are limiting transport in graphene. In chapter 5, we take into account the hierarchy of the scattering times in order to determine the dominant source of scattering in high-mobility graphene


2.5 High field transport in graphene

When a high mobility graphene device is subjected to a strong perpendicular magnetic field, the cyclotron motion of the electrons leads to the observation of plateaus in the Hall Resistance \( R_{xy} \), that are integer multiples of \( \frac{h}{e^2} \) \cite{10, 17}. This phenomena is known as the Quantum Hall effect and it was initially discovered in the two dimensional electron gas (2DEG) of a MOSFET device in 1980 by von Klitzing et al.\cite{24}. Since then it has been observed in several different 2DEG systems and the quantization of \( R_{xy} \) has been verified with an impressive accuracy \cite{94}. When compared to other 2DEG systems the quantization of \( R_{xy} \) in graphene, occurs at a different sequence of integer multiples of \( \frac{h}{e^2} \). The observation of this new sequence of plateaus is a direct manifestation of the unique properties of non-interacting Dirac fermions under the effect of a magnetic field. It has been the observation of this characteristic quantization that has originally led to the conclusion that non-interacting electrons in graphene are well described by the massless Dirac Hamiltonian. Subsequent magneto-transport experiments on less disordered graphene devices and at higher magnetic fields also revealed the effect of interactions, which led to the observation of additional integer \cite{9, 95–97} and fractional \cite{11–13} plateaus of \( \frac{h}{e^2} \) in the Hall resistance.

2.5.1 From Landau levels to the Quantum Hall effect

An important concept for the understanding of the quantum Hall effect is the existence of Landau levels (LL) that occur once a magnetic field is present. In the case of graphene, the Hamiltonian describing the electrons under the effect of a magnetic field is

\[
H = \pm v_F \left( \Pi_x \sigma_x + \Pi_y \sigma_y \right). \tag{2.23}
\]

where \( \vec{p} \rightarrow \vec{\Pi} = \vec{p} + e\vec{A} \) and for the vector potential we choose \( \vec{A} = B(0, x, 0) \). Similarly to the case of a harmonic oscillator, it is possible to define creation \((\hat{a}^\dagger)\) and annihilation \((\hat{a})\) operators, which are linear combinations of the \( \Pi_x \) and \( \Pi_y \), such that \([\hat{a}, \hat{a}^\dagger] = 1\). These operators are defined as

\footnote{These fractional plateaus of the Hall resistance will not be addressed in this thesis but the interested readers can follow ref.\cite{18} containing a review of the Fractional Quantum Hall effect in graphene.}
2.5. High field transport in graphene

Figure 2.7: (a) Scheme of the low energy linear dispersion of graphene in the absence of a magnetic field ($\mathbf{B}$), which will develop (b) discrete LL once $\mathbf{B}$ is turned on. (c) Observation of the Quantum Hall effect in graphene, where $\rho_{xx} = R_{xx}W/L = 0$ for each observed plateau in $\sigma_{xy} = R_{xy}^2 + \rho_{xx}^2$, occurring at $\sigma_{xy} = 4(N + 1/2)e^2/h$ characteristic of non-interacting Dirac fermions. This figure was adapted from ref. 46 and ref. 99.

$\hat{a}^\dagger = \frac{\ell_B}{\sqrt{2h}} (\Pi_x + i\Pi_y)$ and $\hat{a} = \frac{\ell_B}{\sqrt{2h}} (\Pi_x - i\Pi_y)$, where $\ell_B = \sqrt{\frac{\hbar}{eB}}$ corresponds to the magnetic length. The Hamiltonian from eq. (2.23) then reads

$$H = \pm v_F \sqrt{2e\hbar B} \begin{pmatrix} 0 & \hat{a} \\ \hat{a}^\dagger & 0 \end{pmatrix}. \quad (2.24)$$

The corresponding eigenvalues of this Hamiltonian are found to be

$$E = \pm v_F \sqrt{2e\hbar B N}. \quad (2.25)$$

This expression was first derived by McClure[100] and describes the energy of the LL in graphene. Here the $\pm$ correspond to states in the conduction (+) and valence (-) bands and $N$ is the LL index. An interesting feature of the LL in graphene is the existence of a zero-energy Landau level ($N = 0$), which separates hole states from electron states[1], as seen in fig. 2.7(a). Besides the existence of a $N = 0$ Landau level, there are other striking differences between graphene and other 2DEG systems. In graphene the LL energy, as well as, the energy difference between two consecutive levels depends on $E \propto \sqrt{BN}$, while in conventional systems with a quadratic energy-momentum dispersion relation, the LL energies $E_N = \hbar \omega_c (N + 1/2) = \hbar eB/m(N + 1/2)$, depend linearly on $B$.

The existence of LL in two-dimensional systems gives rise to rather unique electronic states at the edges of the device. When the Fermi level is between
two LL there are no available bulk states that contribute to conduction, electronic transport then occurs via edges states that are one-dimensional conducting channels existing at the physical edge of the device. For any finite energy in these states, the electrons at one edge propagate in one direction ($+\vec{k}$ states), while electrons at the other edge propagate in the opposite direction ($-\vec{k}$ states). As a consequence, backscattering in these edge states is not allowed, because in order to reverse the electron momentum from $\vec{k} \rightarrow -\vec{k}$, the electrons would have to traverse the insulating bulk to reach the other edge. When considering four-terminal resistance measurements, this absence of backscattering leads to a vanishing longitudinal resistance ($R_{xx} = 0$). At the same time, the Hall resistance develops quantized plateaus of $R_{xy} = \frac{h}{\nu e}$, where $\nu$ is the so-called filling factor, corresponding to the ratio between the electronic density ($n$) and the magnetic flux density ($n_B$), i.e. $\nu = \frac{n}{n_B} = \frac{h n}{e B}$.

In 2005 the Quantum Hall effect was observed for the first time in graphene\[46, 47\], revealing marked differences from the same observed phenomena in other 2DEG systems (see fig. 2.7(c)). In graphene the sequence of quantized plateaus in $R_{xy}$ occurs at different filling factors of $\nu = 4(N + 1/2)$, where $4 = g_s \times g_v$ accounts for the degeneracy of the valleys ($g_v = 2$) and spins ($g_s = 2$), while $N$ corresponds to the LL index. The presence of the term $1/2$ is a consequence of the existence of a zero energy $N = 0$ LL, which is equally shared by electron and hole states in graphene and therefore shifts the sequence of all the other plateaus. This new distinct quantization sequence of $R_{xy}$ is unique to graphene and is commonly used to confirm the existence of single layer of graphene crystals.

### 2.5.2 Interactions in the Quantum Hall effect

After the initial observation of the Quantum Hall Effect (QHE) in graphene, further experiments at higher magnetic fields led to the observation of new plateaus in $R_{xy}$ outside the original QHE sequence (fig. 2.8(a)). These plateaus in $R_{xy}$ (and also $\sigma_{xy}$) at filling factors $\nu = \pm 1, \pm 4$ (corresponding to LL $N = 0$ and 1) were initially observed in graphene devices on Si/SiO$_2$ substrates at magnetic fields above $B = 20T$\[95\]. The observation of these new plateaus is a manifestation of the lifting of the degeneracy associated to the spin and valley quantum numbers of graphene.

Among the initially observed degeneracy lifted Quantum Hall plateaus, new distinct features at the half filling of the $N = 0$ LL corresponding to $\nu = 0$ where also observed, as shown in fig. 2.8(a)). At $\nu = 0$ there is no well defined plateau in $R_{xy}$ (neither in $\sigma_{xy}$) nor a minimum on $R_{xx}$ which is characteristic of the QHE plateaus \[63, 71, 101, 103\]. Additionally, further
2.5. High field transport in graphene

Figure 2.8: (a) $\sigma_{xy}$ as function of $V_g$ for several magnetic fields between 9T and 45T for a graphene on Si/SiO$_2$ device. At high fields the observed plateaus at $\nu = 1, 4$ (also features at $\nu = 0$) result from the full and partial degeneracy lifting of the $N = 0$ and $N = 1$ LL, respectively (figure adapted from ref. [95]). (b) Measurement of $R_{xx}$ and $R_{xy}$ on a high-mobility graphene device on a BN substrate, as a function of the filling factor ($\nu$) at $B = 12T$ for several temperatures between 2K and 10K. At the lowest temperature all the integer $\nu$ between 2 and 14 are observed. These observations shown by Young et al. [9] are an indication of the complete degeneracy lifting of the LL corresponding to $N = 1, 2, 3$.

experiments addressing the behaviour of the Quantum Hall state at $\nu = 0$ on both graphene on Si/SiO$_2$ substrates [97, 103] and suspended devices [11, 12], found a pronounced divergent behaviour of $R_{xx}$ when decreasing the temperature and increasing the magnetic field, an effect associated to emergent electron-electron interactions.

Several mechanisms have been proposed to be responsible for the degeneracy lifted states at $\nu = 0, \pm 1$ of the $N = 0$ LL. The Zeeman effect has been considered as a mechanism that is able to lift the spin degeneracy of the LL, though it can not by itself explain the observation of all the degeneracy lifted states [104, 105]. For the lifting of the valley degeneracy, the proposed mechanisms rely on the generation of a mass gap which breaks the inversion symmetry between the graphene sublattices $A \leftrightarrow B$. This broken inversion symmetry can be seen as electrons in sublattices $A$ and $B$ having different on-site energies. It has been proposed that the effect of electron-phonon coupling could generate a Peierls-like instability in graphene, which can effectively break the inversion symmetry of graphene [106]. Another proposed mechanism known as magnetic catalysis, predicts that the inversion symmetry can also
be broken due to the effect of electron-electron interactions at high magnetic fields\cite{22,28,29}. An alternative proposal to explain these broken symmetry states relies on the occurrence of Quantum Hall Ferromagnetism (QHF).

With the improvement of fabrication techniques, graphene devices on BN substrates with increased mobility have been realized\cite{31}. In fig.\ref{fig:2.8} (b), the measurements of $R_{xx}$ and $R_{xy}$ of these high quality devices, as function of filling factor at $B=12T$, show the occurrence of plateaus in $R_{xy}$, for all integer filling factors between $\nu = 2$ and $\nu = 14$\cite{32}. The observation of these plateaus outside normal QHE sequence, results from the complete lifting of both the spin and valley degeneracy of the $N = 1, 2, 3$ LL. Without going into details these observations strongly support the theoretical proposal of the existence of SU(4) QHF in graphene at high magnetic fields\cite{33,31,22,29}.

2.6 Quantum Hall effect as a Topological Insulator

The topics discussed in the previous sections were related to the electronic properties of graphene relevant for the work carried out in this thesis. In the following sections of this chapter, we will discuss the electronic properties of a new class of materials known as Topological Insulators, which are important for the discussion of the experimental results of Chapter 6.

The description of the electronic properties of crystalline solids in terms of bands is one of the early successes of quantum mechanics. Until very recently, most of the materials could be grouped into two large classes, metals and insulators, depending on their band structure and on the position of the Fermi level. In metals, electrical current is allowed to flow upon the application of a small electric field due to the existence of partially filled bands. In insulators, the application of an equally small electric field does not generate current, because all bands are completely filled and separated from empty bands by an energy gap. In terms of the position of the Fermi level ($E_F$), this means that in metals $E_F$ lies in a partially filled band, whereas in an insulator $E_F$ is located inside the band-gap.

Recent studies have found a new class of materials having electronic properties different from those of metals and insulators. These materials in their bulk are band insulators but at their boundaries they can carry current due to the existence of robust (and unconventional) metallic states. Materials having these electronic properties are called Topological Insulators, because the existence of such robust metallic boundary states were found to be a consequence of the (non-trivial) topology of the insulating state. Topological insulator materials were recently confirmed to exist in all the three spatial dimensions.
Already in the 1980s it was known that the topology of the electronic states of the bulk played an important role on the manifestation of certain physical phenomena. One of the most emblematic cases was the Quantum Hall Effect (QHE) occurring in 2DEG systems. The QHE manifests itself through the quantization of the Hall resistance in units of $R_{xy} = \frac{h}{N e^2}$, which happens when at low temperatures a 2D metal is submitted to a large perpendicular magnetic field. In fact, a system in the QHE regime can be described as 2D topological insulator. In this regime the bulk of the system is seen as band insulator due to the formation of Landau levels, but at the edges of the material, current can flow without dissipation through the existence of gapless states known as edge states. These edge states, which are responsible for the quantization of $R_{xy}$, in a work of Thouless et al.\[25\] were formally shown to be a manifestation of the non-trivial topology of the insulating state. The details and implications of this finding will be discussed in section 2.6.2.

While in the particular case of the QHE the non-trivial insulating state is generated by the application of a magnetic field, recent works have shown that topological insulating states can also exist in the absence of a magnetic field. This effect is due to the spin-orbit interaction and it can occur in 2D and 3D systems\[21, 22, 38, 108\]. In this thesis (Chapter 6) we investigated the electronic properties of a spin-orbit induced 3D topological insulator, which has unique metallic surface states that are characterized by Dirac fermions.

Since many of the theoretical aspects of these systems are rather sophisticated and mathematically advanced, we will try to introduce the key concepts by discussing 2D topological insulators in the simplest case and discuss the 3D by analogy. To this end we will by first consider a model proposed by Haldane which we will use to establish the connection with topology. The Haldane model predicts that in a honeycomb lattice QHE can occur in the absence of Landau Levels in the bulk, provided that the time reversal symmetry (TRS) and parity are broken, in order to generate a new insulating state with different topology. In the the subsequent sections we will then discuss topological insulators with preserved TRS where the topological state is induced by the spin-orbit interaction. First, we will introduce the Kane and Mele model describing 2D topological insulators, which can in the simplest case be understood in terms of the Haldane model. We will then argue by analogy to introduce the electronic properties of 3D topological insulators.

2.6.1 The Haldane model

The discovery of the QHE triggered considerable theoretical work which has resulted in several impressively deep ideas in condensed matter physics. One of these ideas was put forward by Thouless et al.\[25\] who were the first to realize
the connection between the Hall conductivity and topology that we introduce here. The results of Thouless and co-workers stimulated other work, among which of Haldane\cite{Haldane1988}, who proposed a model predicting that the Quantum Hall Effect could be generated in absence of Landau levels. Haldane’s model considered a two dimensional (2D) crystal with a honeycomb lattice, as in the case of graphene, under the effect of a periodic magnetic field, normal to the 2D plane, having the full symmetry of the lattice but with zero total flux in the unit cell. The presence of this magnetic field does not generate Landau levels but breaks TRS in the system. Another important ingredient of Haldane’s model is the breaking of the inversion symmetry through the presence of a staggered sublattice potential, such that the A and B atoms of the honeycomb lattice have different on-site energies. It is by breaking both the time reversal and inversion symmetry of the honeycomb lattice – which opens a gap in the bandstructure at the $K$ and $K'$ momentum points – that Haldane could show how, in certain conditions it is possible to observe a Hall conductivity of $\sigma_{xy} = \pm e^2/h$.

The Hamiltonian introduced by Haldane has the following form

\begin{equation}
H = t_1 \sum_{\langle i,j \rangle} c_i^\dagger c_j + t_2 \sum_{\langle\langle i,j \rangle\rangle} e^{i\mu_{ij}\phi} c_i^\dagger c_j + M \sum_{\langle i \rangle} \epsilon_i c_i^\dagger c_i. \tag{2.26}
\end{equation}

Here $t_1$ and $t_2$, correspond to the hopping terms between the nearest-neighbours and the next-nearest-neighbours, respectively. The second term of the Hamiltonian takes into account the phase acquired from the periodic vector potential, $\phi = e/h \int A \, dr$ where the integral is along the hopping path.
The phase $\phi$ is acquired when considering next-nearest-neighbours hopping $\langle\langle i,j \rangle\rangle$, while the first-neighbour hops are unaffected by this phase because they perform a closed path along the unit cell ($\nu_{ij} = \pm 1$ depending on whether the hopping direction if positive or negative) as illustrated in fig. 2.9. The third term of eq. (2.26), refers to the presence of a staggered sublattice potential where the term $\epsilon_i = \pm 1$ defines an on-site energy of $+M$ and $-M$ for sublattice atoms A and B, respectively.

For states with momentum $\vec{k}$, the Haldane Hamiltonian eq. (2.26) can be expressed in a compact form as $h(\vec{k}) = \vec{d}_n(\vec{k})\vec{\sigma} + \epsilon(\vec{k})$, where $n = 1, 2, 3$ and the $\sigma_1, \sigma_2, \sigma_3$ are the $\sigma_x, \sigma_y, \sigma_z$ Pauli matrices. The components of $\vec{d}_n(\vec{k})$ and $\epsilon(\vec{k})$ read:

$$
\epsilon(\vec{k}) = 2t_2 \cos(\phi) \left[ \cos(\vec{k} \cdot \vec{a}_1) + \cos(\vec{k} \cdot \vec{a}_2) + \cos(\vec{k} \cdot (\vec{a}_1 - \vec{a}_2)) \right] \quad (2.27)
$$

$$
d_1(\vec{k}) = t_1 \left[ \cos(\vec{k} \cdot \vec{a}_1) + \cos(\vec{k} \cdot \vec{a}_2) + 1 \right]
$$

$$
d_2(\vec{k}) = t_1 \left[ \sin(\vec{k} \cdot \vec{a}_1) + \sin(\vec{k} \cdot \vec{a}_2) \right]
$$

$$
d_3(\vec{k}) = M + 2t_2 \sin(\phi) \left[ \sin(\vec{k} \cdot \vec{a}_1) - \sin(\vec{k} \cdot \vec{a}_2) - \sin(\vec{k} \cdot (\vec{a}_1 - \vec{a}_2)) \right]
$$

where $\vec{a}_1$ and $\vec{a}_2$ correspond to the Bravais vectors of the honeycomb lattice. The specific form of the Hamiltonian in eq. (2.27) will be useful for the discussion of the topological properties of the insulating state predicted by Haldane, which we will do in the following section.

2.6.2 The connection with topology

So far we have mentioned the existence of 2D insulating materials whose non-trivial topology of the bulk electronic states is responsible for the appearance of robust conductive states at their edge. We will now discuss the link between the topology of the bulk states and the existence of these so-called edge states.

The concept of topology in insulating systems that we discuss here is associated to a so-called topological number of the electronic band structure. This topology-defining number is an invariant, i.e. it is insensible to continuous deformations of the bulk electronic band structure – provided that the band gap remains finite – and can be used to predict the existence (or not) of robust metallic states at the edges of the insulator. In order to calculate this invariant we start from the compact form of the Haldane Hamiltonian $h(\vec{k}) = \vec{d}_n(\vec{k})\vec{\sigma} + \epsilon(\vec{k})$ in eq. (2.27) and define a unit vector $\hat{h}(\vec{k}) = \vec{d}(\vec{k})/|\vec{d}(\vec{k})|$, with the momentum $\vec{k}$ spanning over the Brillouin zone. As $\vec{k}$ “moves” across the
Figure 2.10: Representation of the mapping of the unit vector $\hat{h}(\vec{k})$, along the Brillouin zone on the unit sphere. The complete or incomplete wrapping of the sphere characterizes the topology of the Hamiltonian $h(\vec{k}) = \bar{d}_n(\vec{k})\vec{\sigma}_n + \epsilon(\vec{k})$, which is defined by the winding number $\mathcal{N}$.

entire Brillouin zone (which is a torus in 2D), the unit vector $\hat{h}(\vec{k})$ evolves along a unit sphere, as shown in fig. 2.10. It is the mapping of $\vec{k} \rightarrow \hat{h}(\vec{k})$ along on the unit sphere that captures the topology of the Hamiltonian $h(\vec{k})$. These mappings can be trivial or non-trivial depending on the number of times the unit sphere is covered when $\vec{k}$ moves through the Brillouin zone. The quantity that describes how many times the unit sphere is covered is a topological invariant known as the winding number ($\mathcal{N}$) and can be calculated in the following way

$$\mathcal{N} = \frac{1}{4\pi} \int dk_x \int dk_y \hat{h}(\vec{k}) \left( \frac{\partial \hat{h}(\vec{k})}{\partial k_x} \times \frac{\partial \hat{h}(\vec{k})}{\partial k_y} \right). \quad (2.28)$$

It is the winding number $\mathcal{N}$ that determines the topological properties of the insulating phases. This is precisely the result of Thouless et al. (TKNN) that we referred to at the beginning of this section. When analysing the Hall conductivity of a 2DEG in the Quantum Hall regime, TKNN found that $\sigma_{xy}$ (in units of $e^2/h$) is also given by precisely the same integral eq. (2.28). This means that if the unit vector $\hat{h}(\vec{k})$ covers the unit sphere once, the system will have a Hall conductivity of $\sigma_{xy} = e^2/h$ (or $\sigma_{xy} = -e^2/h$, depending on which direction $\hat{h}(\vec{k})$ takes to covers the sphere) and correspondingly one edge state whose direction of propagation is determined by $\mathcal{N}$ is also present. If $\hat{h}(\vec{k})$
Figure 2.11: Phase diagram of the transition from normal insulator with \( \nu = 0 \) to a non-trivial insulator \( \nu = \pm 1 \). The quantum Hall effect occurs \( (\sigma_{xy} = \nu e^2/h) \) at a net zero magnetic field for values of \(| M/t_2 | < 3\sqrt{3}\sin(\phi)\). This figure was adapted from ref. [109].

If the Brillouin zone does not cover the sphere, then a non-zero topological invariant cannot be associated to the bulk Hamiltonian which then describes a trivial band insulator, with \( \sigma_{xy} = 0 \). It is this finding of TKKN, which connects the topology of the insulator bulk bands to the value of the Hall conductivity which also linked to the the existence (or absence) of conducting states at the edges. A concept referred to as the bulk-edge correspondence. The winding number is also commonly named the TKNN or the Chern number.

By calculating \( \mathcal{N} \), one can predict in which cases the insulating phase of the Haldane model has a non-trivial topology. For instance, if only inversion symmetry of the honeycomb lattice is broken, \( \mathcal{N} = 0 \) and the system is a topologically trivial insulator with \( \sigma_{xy} = 0 \) and no edge states. However, once time reversal symmetry is also broken by the magnetic field with unit cell periodicity, \( \hat{h}(\hat{k}) \) covers the unit sphere (with \( \mathcal{N} = \pm 1 \)) upon letting \( \hat{k} \) run through the Brillouin zone, resulting in an insulating state with non-trivial topology. In the Haldane model the non-trivial insulating state hosts one edge state and leads to Hall conductivity of \( \sigma_{xy} = \pm e^2/h \), whenever the relation \(| M/t_2 | < 3\sqrt{3}\sin(\phi) \) is satisfied (see fig. 2.11). The most important aspect of this is that it shows that the existence of Landau levels is not a prerequisite for the existence of quantized Hall conductivity. Despite the experimental inability to generate the required periodic magnetic fields, the Haldane model has played an important role in the understanding of topological insulators because, as it turns out, it is closely related to what happens to graphene in the presence of spin-orbit interaction.
2.7 Spin-orbit topological insulators
Both the QHE and the Haldane model are examples of topological insulators where the spin of electrons does not play a role in the generation of the non-trivial topological state. Recent theory has shown that in certain materials an insulating state with non-trivial topology can also be induced by the spin-orbit interaction. These spin-orbit topological insulators are bulk insulators possessing conductive states with unique physical properties at the boundaries of the material. In the following sections, the fundamental concepts of 2D and 3D spin-orbit topological insulators will be introduced.

2.7.1 The spin-orbit interaction
The spin-orbit interaction is a relativistic effect that describes how the electron spin interacts with its orbital motion. The origin of this interaction can be understood by considering an electron moving in an electric field and analysing the motion from the rest frame of the electron. Because of special relativity, in the rest frame of the electron, the electric field ($\vec{E}$) is also seen as an effective magnetic field ($\vec{B}'$). The effective magnetic field couples to the magnetic dipole moment of the electron, i.e. to the spin via Zeeman interaction, and contributes to the Hamiltonian through the form

$$H_{SO} = -\frac{g}{2}\mu_B \vec{B}' \vec{S}$$

(2.29)

$$= -\frac{g}{2}\mu_B \frac{1}{c^2} (\vec{v} \times \vec{E}) \vec{S}.$$

(2.30)

In this equation $\mu_B = |e|\hbar/2m$ is the Bohr’s magneton, $g = 2.0023$ and $\vec{S} = \frac{\hbar}{2}\vec{\sigma}$ where the components of $\sigma$ are the Pauli matrices. In certain cases the spin-orbit interaction can be conveniently combined with the kinetic energy of the electron to give a complete Hamiltonian of the type

$$H = -\frac{1}{2m} \left[ \vec{p} - \frac{g\mu_B}{2c^2} \left( \vec{E} \times \vec{S} \right) \right]^2.$$

(2.31)

From this Hamiltonian the spin-orbit interaction of the electron can be interpreted as if a magnetic field, whose orientation depends on the spin direction of the electron, is being applied to the system. The strength of the spin-orbit interaction depends on the electric field that the electrons feel, and the effect is therefore stronger in materials having larger atomic numbers.

3In this situation for simplicity we are only considering the case of intrinsic spin-orbit re-
An important feature of the spin-orbit coupling is that it preserves time reversal symmetry (TRS). Indeed upon the application of the time reversal symmetry operator ($T$), $T\vec{p}T^{-1} = -\vec{p}$ and $T\vec{\sigma}T^{-1} = -\vec{\sigma}$, so that the spin-orbit coupling which depends on the product of $\vec{p}$ and $\vec{\sigma}$ is invariant upon time reversal symmetry. In systems where the time reversal symmetry is preserved there is a theorem, known as the Kramers degeneracy, stating that the energy eigenstates of the system have to be doubly degenerate. This implies that for each energy eigenstate there is always a corresponding time reversed state with the same energy. For instance, if we consider a system where spin-orbit interaction responsible for lifting the spin degeneracy, e.g. into spin-$\uparrow$ and spin-$\downarrow$, the Kramers theorem leads to the following relation

$$E(\vec{k}, \uparrow) = E(-\vec{k}, \downarrow).$$

(2.32)

This relation shows that for crystals with spin-orbit interaction there is always a pair states at finite energies – the Kramers doublets – having opposite spin and momentum. In the specific case of spin-orbit topological insulator materials, the Kramers theorem has profound consequences on the low energy electronic properties. For instance the metallic states that reside at the boundaries of topological insulators, correspond to Kramers doublets whose properties are responsible for the unique features (e.g. absence of electron backscattering) associated to topological insulators with time reversal symmetry.

### 2.7.2 2D topological insulators

The experimental discovery of the new class of 2D topological insulators with preserved time reversal symmetry (TRS) \[33\], was preceded by the theoretical work of Kane and Mele\[28\] and also Bernevig et al.,\[30\], that considered a strong spin-orbit interaction in graphene and quantum wells of HgTe respectively. Here in order to introduce these unique properties of topological insulators we only consider the model developed by Kane and Mele, which is convenient for drawing a parallel with the previously discussed Haldane model.

The Kane-Mele model predicts that in graphene one can find an insulating state with non-trivial topology, if the spin-orbit interaction is strong enough to open a band-gap in the material. In the simplest case, which is when the intrinsic spin effect of graphene is the only source of spin-orbit interaction (i.e. resulting from the interaction with the atomic nucleus. However in crystals with broken inversion symmetry other spin-orbit effects such as Dresselhaus and Rashba effect might also occur\[112\].
the Rashba effect ($\lambda_R$) due to the presence of the substrate is negligible), this model can be seen as two copies of the Haldane model: the strange periodic magnetic field used by Haldane corresponds to the spin-orbit interaction acting on only one of the spin directions. Consequently in the insulating state of the Kane-Mele model, one finds pairs of edge states where electrons of opposite spin propagate in opposite directions, instead of a single spinless edge state as in Haldane’s model.

The Hamiltonian developed by Kane and Mele which describes the spin-orbit interaction in graphene reads as

$$ H = t_1 \sum_{\langle i,j \rangle} c^\dagger_j c_i + i \lambda_{SO} \sum_{\langle\langle i,j \rangle\rangle} \nu_{i,j} c^\dagger_i s_z c_j. \quad (2.33) $$

The first term of the Hamiltonian corresponds to the nearest-neighbour hopping where $c^\dagger_i$ is defined as $c^\dagger_i = \left( c^\dagger_{i\uparrow}, c^\dagger_{i\downarrow} \right)$, for electrons with spin directions $\uparrow$ and $\downarrow$. The second term defines the spin-orbit interaction ($\lambda_{SO}$) of the next-nearest-neighbours hopping and assumes that spin along the $z$-direction ($s_z$) is a conserved quantity. Here $\nu_{i,j} = -\nu_{j,i} = \pm 1$ depending on the orientation of the two nearest-neighbour bonds the electron will traverse in going from site $i$ to site $j$.

The Hamiltonian eq. (2.33) leads to the formation of four bulk energy bands that are separated by an energy gap at the $K$ and $K'$ points of the Brillouin zone. However at the edges of the crystal, a pair of gapless states connecting
the $K$ and $K'$ points are present, as it is shown in fig. (a). These gapless states correspond to a pair of "spin-polarized" (either spin $\uparrow$ or spin $\downarrow$) states where electrons with opposite spin propagate in opposite directions at the same edge. Edge states with these properties are referred to as "helical edge states" and their occurrence is a manifestation of the so-called Quantum Spin Hall effect.

Although our discussion is based on a specific case (e.g. with conserved $z$ component of spin) Kane and Mele have analysed the problem much more in general and found that these helical edge states were predicted to be robust against disorder, provided that time reversal symmetry of the system is preserved. In this situation, backscattering at the edge states is not allowed, because in order to backscatter, the electron would have to reverse its spin and therefore break time reversal symmetry. This robustness is the reason why the quantum spin Hall effect can be considered as a characteristic manifestation of a new state of matter (fig. (b)).

It should also be noted that, in the simplest version of the Kane-Mele model that we discuss here, the $z$ component of the electron spin $s_z$ is a conserved quantity. This means that we can think separately about the spin-up and spin-down component, i.e., the Hamiltonian can be separated into a part describing spin-up electrons and a part describing spin-down electrons. The two parts are through Kramers theorem the time reversed one of other. Therefore if one considers only one spin direction, the corresponding part of the Hamiltonian does not satisfy time reversal symmetry. Indeed for a fixed spin direction, the Kane-Mele model with conserved $s_z$ corresponds to the Haldane model with spin-orbit interaction generating the periodic phase that in the Haldane model is generated by the periodic magnetic field. Since, the two spin orientations can be treated separately, also the topological properties can be described separately for each spin orientation. This means that one can define two Chern numbers $N_\uparrow$ and $N_\downarrow$, and it is found that $N_\uparrow = 1 = -N_\downarrow$. This implies that there are two gapless edge states with opposite spins propagating in opposite directions (since $N_\uparrow = -N_\downarrow$). The existence of such helical edge states, is the hallmark of the Quantum Spin Hall effect (QSHE) in two dimensions.

Although we will not discuss this in detail it is important to realize that in general $s_z$ is not a conserved quantity and therefore the two spin orientations cannot be treated separately. In that case the spin dependent Chern number cannot be defined. It is one of the important findings of Kane and Mele that, even when $s_z$ is not conserved, a topological invariant can be defined. This topological invariant can only take 0 and 1 as values and is therefore referred as a $\mathbb{Z}_2$ topological invariant. When its value is 0, the system is trivial and no edge states are expected. When the value is 1, the system is not trivial.
and a pair of helical gapless modes (or an odd number of pairs of helical modes) is present at the edges. This result is important because if the existence of the Quantum Spin Hall effect would require \( s_z \) to be conserved such states would be very easily destroyed in real physical systems. The existence of the \( Z_2 \) invariant, therefore implies that the QSH effect is a robust state of matter.

When considering electronic transport experiments in the QSH regime, transport along the helical edge states can in fact be understood within the Landauer-Buttiker formalism, as in the case of the QHE. For devices with a 2-terminal geometry, the charge conductance along this channel is \( G = 2e^2/h \) as it would be expected for ballistic-like transport along the edge states. Despite the intense experimental research on the transport properties of graphene, so far the QSH effect has not been found \(^4\) at experimental accessible temperatures due to the fact that the spin-orbit interaction in graphene is extremely weak \([31, 32]\). However this effect has been successfully observed in carefully engineered quantum wells of HgTe \([33]\) where the effects spin-orbit coupling are much stronger.

### 2.7.3 3D topological insulators

In the previous section we discussed the specific case of topological insulators in two dimensions. In those systems the bulk of the material is insulating and electrical current is allowed to flow at the physical edge of the device through 1D conduction channels known as helical edge states. However when considering topological insulators in three dimensions, while the bulk still remains an insulator, the boundaries of the material are now surfaces instead of edges. By analogy it is expected that in such materials the current is carried by 2D gapless states residing at the surface of the material. In 3D topological insulators, the 2D surface states analogous to the 1D helical edge states of the QSH correspond to helical massless Dirac fermions whose spin direction is pinned to their momentum. These surface states which are predicted to exist at all surfaces of the crystal, are responsible for closing the bulk band gap. In short 3D topological insulators are bulk band insulators, which have gapless surface states described by Dirac fermions (see fig. 2.13 \([35, 115]\)).

Three dimensional topological insulators are divided in two groups known as weak and strong topological insulators \([21–23, 38, 108]\). This classification depends on the properties of their surface states, more specifically on the number of Dirac cones (the number of valleys defined by the Dirac equation) that reside in those surfaces. Topological insulators where the surface states

---

\(^4\)In fact the occurrence of the QSH in the absence of the magnetic field has not been observed but recent experimental works have claimed to have observed a QSH-like behaviour in graphene at the \( N = 0 \) Landau Level at high magnetic fields \([114]\).
have an even number Dirac cones are referred to as weak topological insulators because the presence of disorder can destroy the topological state. The strong topological insulators instead, have an odd number of Dirac cones at their surfaces and are robust against disorder, provided that the time reversal symmetry of the system is not broken. These two types of 3D topological insulators can also be defined by a 3D topological invariant analogous of the $\mathbb{Z}_2$ invariant that is used to identify 2D topological insulators. In the most general and simplest case, strong topological insulators are defined by a $\mathbb{Z}_2 = 1$ while weak topological insulators are defined by a $\mathbb{Z}_2 = 0$. In this thesis due to our experimental investigations of the electronic properties of Bi$_2$Se$_3$ – strong topological insulator with a single Dirac cone – we will not cover the case of weak 3D topological insulators.

**Connection with transport experiments**

In order to establish a connection between the properties of a 3D topological insulator and experiments we will now discuss the electronic properties of the recently discovered topological insulator Bi$_2$Se$_3$. The crystal structure of the 3D strong topological insulator Bi$_2$Se$_3$, shown in fig. 2.14, consists of covalently bonded quintuple layers of Se-Bi-Se-Bi-Se that are vertically stacked through van der Waals forces. Fig. 2.14(c) shows the bulk band structure of Bi$_2$Se$_3$.
2. Background

Figure 2.14: (a) Scheme of the crystal structure of Bi$_2$Se$_3$, where each quintuple layer of Bi$_2$Se$_3$ is Van der Walls stacked. (b) Illustration of the Brillouin zone of the Bi$_2$Se$_3$ crystal. (c) Numerical calculations of the band structure of Bi$_2$Se$_3$ where in the band-gap at the Γ point, helical surface states hosting Dirac fermions are predicted to occur. Figure adapted from [27].

where a band gap of 0.3eV is present at the Γ point of the Brillouin zone. It is around the Γ point in momentum space where the single Dirac cone of the helical surface states is located.

The fact that the surface states of strong topological insulators consist of massless Dirac fermions, allows comparisons with the case of Dirac fermions in graphene. The Hamiltonian ($H_{SS}$) describing the Dirac surface states reads

$$H_{SS} = v_F \hbar \tilde{\sigma} \cdot \vec{k},$$  \hspace{1cm} (2.34)

where $\vec{k}$ is the electron wavevector and $\tilde{\sigma}$ corresponds to the real electron spin, this is different from graphene where the $\sigma$ in the Dirac Hamiltonian denotes the pseudospin degree of freedom. Additionally, graphene has both spin and valley degeneracy (at the $K$ and $K'$ points), while the Dirac fermions in 3D topological insulators are non-degenerate. Similarly to the case of graphene in these helical Dirac surface states one finds a non-trivial Berry phase of $\pi$ whenever the electrons perform a closed loop in momentum space, and that backscattering from a $\vec{k}$ state to $-\vec{k}$ state is forbidden. This forbidden electron backscattering is responsible for the absence of electron localization in these helical surface states.

Once a magnetic field is applied, Dirac fermions develop Landau Levels which have the following energy

$$E = \pm v_F \sqrt{2e\hbar BN}.$$  \hspace{1cm} (2.35)
The energy of these Landau levels ($N$) have similar features as those in the case of Dirac fermions in graphene when subjected to a magnetic field. There is also a zero energy $N = 0$ Landau level that is equally shared by electron and hole states. Despite the similarities with the Landau Levels with graphene, since the Dirac cone of the helical surface states is non-degenerate, there are no additional valley or spin degeneracies, a unique feature of 3D topological states with a single Dirac cone.

One of the goals in the field of topological insulators is to use electronic devices to control and probe the surface Dirac fermions in transport experiments. However in most cases the observation of the Dirac surface states in transport has proven to be difficult because of the limited quality of the materials available. In principle through transport measurements it is also possible to confirm the existence of Dirac fermions in 3D topological insulators. Electronic transport signatures of these surface states would be, the observation of graphene-like ambipolar transport behaviour, where the application of a gate voltage allows conduction to occur either by electron or hole states. In particular, under the effect of the magnetic field, the observation of ambipolar Landau levels and their indexing can also confirm (or not) the existence of Dirac fermions at the surface of a 3D topological insulator. However if the bulk is not a good insulator, which regularly happens if the material contains a large amount of defects or impurities, the measured conductivity is determined by both the contributions of the surface and the bulk states. This makes it difficult to distinguish the effect of Dirac fermions in transport.

2.8 Electronic transport with superconducting contacts

While in the previous sections the main electronic properties of graphene and topological insulators were introduced, we will now briefly discuss transport phenomena occurring in mesoscopic devices once superconducting contacts are used to perform electronic transport measurements. The following concepts are particularly relevant for the discussion of the experiments carried out in Chapter 6, where we contacted the 3D topological insulator Bi$_2$Se$_3$ with superconducting leads.

Among the metallic elements of the periodic table, many of them turn into superconductors once the temperature is decreased below a specific critical value ($T_C$) that is material dependent. Once below $T_C$, the electrons close to the Fermi level ($E_F$) form Cooper pairs\[116\], which are pairs of electrons of opposite momentum and spin. These Cooper pairs have the tendency to “condense” into the same ground state, leading to the appearance of an energy
2. Background

Figure 2.15: Illustration of the process of Andreev reflection at a metal-superconductor interface. Due to the formation of a Cooper pair in the superconductor, the incident electron will be reflected as a hole.

gap ($\Delta$) where the normal density of states of the metal vanishes. This gap occurs at energies close to $E_F$ within the range of $[E_F - \Delta, E_F + \Delta]$, where $\Delta$ is typically of the order of 1 meV or smaller, for conventional superconductors. Importantly the electric current carried by Cooper pairs is dissipationless, leading to the measurement of a vanishing resistance of the superconductor once the temperature is below $T_C$.

In this section we will introduce a special type of electron reflection that occurs at the interface between a superconductor and a metal, known as Andreev reflection (AR). We will also consider the case of a metal which is connected by two closely spaced superconductors where in certain cases a dissipationless current can pass through the normal metal due to the so-called Josephson effect.

2.8.1 Andreev Reflection

Electronic transport across a junction between a metal and a superconductor is rather unique, due to the fact that a metal has a continuous density of states near the Fermi energy ($E_F$), while a superconductor has an energy gap. When an electron is travelling through the metal with energy $E_F + \epsilon$, it will experience the superconducting gap ($\Delta$) at the interface with the superconductor as a "barrier" if $\epsilon < \Delta$. In order to enter the superconductor, the electron needs to form a Cooper pair with another electron of opposite momentum and spin, which can be extracted from the metal. Due to charge conservation, this process leaves a hole in the metal (see fig 2.15). This process where an incoming
2.8. Electronic transport with superconducting contacts

Figure 2.16: Illustration of the mechanism behind the Josephson effect that leads to the generation of a supercurrent. It is due to multiple Andreev reflections at the metal-superconductor interface which yield bound states in the metal, where Cooper pairs can be transferred from the left to right superconducting lead. Figure adapted from [218].

electron is reflected as a hole in the metal is known as Andreev reflection[117]. At the Fermi energy ($\epsilon = 0$) an incoming electron with wavevector $\vec{k}_e$ can form a Cooper pair with a second electron having an opposite wavevector $\vec{k}^{II}_e = -\vec{k}_e$, leaving a hole with the same wavevector of the first electron $\vec{k}_h = \vec{k}_e$. The wavevectors of the incident electron and the reflected hole are identical but the hole propagates with opposite velocity and retraces the path of the initial electron, a phenomena called retroreflection.

2.8.2 Proximity induced supercurrent

A normal metal when closely contacted by two superconductors can also conduct electrical current without dissipation. These metal-superconductor junctions are called Josephson junctions and the observation of the proximity induced supercurrent occurring in the absence of a driving voltage is called the Josephson effect[118]. In order to observe supercurrent (i.e. a current with zero applied voltage, $V = 0$) the current ($I$) must be smaller than the critical current ($I_C$), but once $I > I_C$, a dissipating current (i.e. $V \neq 0$) will flow through the metal. The experimental observation of supercurrents for $I < I_C$, can be understood as the occurrence of multiple coherent Andreev reflections (MAR) at the metal-superconductor interfaces.

The occurrence of MAR in Josephson junctions can be depicted by considering that an electron in the metal with energy $E_F + \epsilon$ is travelling to the superconductor at the right side of junction (see fig. 2.10). At the interface, due to AR the electron enters the superconductor and a hole with energy $E_F - \epsilon$ is reflected. Once the hole arrives to the superconducting interface on the left
side of the junction, it can enter the superconductor returning an Andreev reflected electron having the same energy as the initial electron. It is apparent that the net effect of cycle of this process, is to transfer a Cooper pair from the left to the right superconductor. This current can flow at zero applied voltage and is at the origin of the Josephson supercurrent. However, it needs to be realized that also the time reversed process can occur – an electron arriving towards the left generating an Andreev reflected hole propagating towards the right – which gives a contribution to the supercurrent in the opposite direction. In practice, when the phase difference between the order parameter of the two superconductors is zero, the contribution to the supercurrent are equal and opposite and the total supercurrent vanishes. When a finite phase difference is present, no perfect cancellation occurs and a supercurrent flows. The supercurrent therefore depends on the phase difference ($\Delta \phi$) as $I_S = I_C \sin \Delta \phi$. In the simplest case the $I_c = N e \Delta / \hbar$ is the critical current of the junction, i.e. the maximum supercurrent that the junction can sustain.

The induced supercurrent can also manifest itself when a finite voltage bias ($V$) is applied to the junction. In this situation sharp features are observed in the measurement of the differential resistance ($dV/dI$) as a function of $V$. These features (corresponding to minima) in $dV/dI$ occur whenever the applied voltage across the junction passes through $V_n = 2 \Delta / ne$. At these $V_n$ voltages, the occurrence of $n$ Andreev reflections at the interface of the superconductor are responsible for changing the resistance of junction and leads to observed features in the $dV/dI$-vs-$V$ curve[120, 121].
Device fabrication

The experimental work carried out on this thesis relied in electronic transport measurements performed on nano-devices made of either graphene or topological insulators. Several aspects of these devices are non-conventional and have required the development and optimization of targeted nano-fabrication processes. In this chapter we briefly discuss the most relevant aspects of the fabrication procedure of our devices.

3.1 Graphene based electronic devices

The initial stages of graphene research have heavily relied on the use of nano-fabricated devices and transport experiments to probe its electronic properties. For instance, the first demonstration that electrons in graphene behave as massless particles has come from the measurement of the characteristic half-integer Quantum Hall effect, whose observation requires the investigation of transport through Hall-bar shaped graphene devices. Initially, device fabrication relied on graphene obtained from the exfoliation of a graphite crystal with an adhesive tape to obtain atomically thin flakes, which are then deposited on top of doped Si substrates (acting as a gate electrode) covered with an insulating layer of SiO$_2$. Devices of this type, readily allow the realization of transistor structures in which carrier mobility values of approximately 10000cm$^2$/Vs can be reached. Improving the devices, adding functionalities, or establishing fabrication protocols that can be scaled to much larger areas/number of structures realized simultaneously requires the development of new techniques for
the synthesis of graphene, to control the interaction between graphene and the substrate, and to gain access to larger area graphene.

As for the production of graphene, several different new processes have been developed that can lead to large-area high quality materials\(^1\). Examples are the synthesis of graphene by means of chemical vapor deposition (CVD), or the epitaxial growth of graphene by heating SiC wafers in ultra-high vacuum\(^2\). Both processes are now enabling the production of large area graphene with very high electronic quality. In particular, CVD graphene monolayers can now be synthesized over square meters, exhibiting mobility values that are comparable to those measured in exfoliated graphite\(^3\). These developments are truly impressive, but – since the related technologies have not been employed in the work done in this thesis – they will not be discussed in further detail.

An aspect that has also witnessed truly impressive progress – next to the synthesis of graphene – is the development of new fabrication processes for the assembly of higher quality devices. Two examples are the development of suspended graphene devices, in which a graphene layer "floats" on top of a gate electrode, held by the metal contacts, and the development of graphene on Boron Nitride (hBN) substrates. Suspended devices enable the minimization of disorder experienced by charge carrier down to a level that cannot be matched by any other graphene structure. Indeed, it is now clear that considerable disorder in graphene is generated by the contact with any substrate material (although there is no consensus about the precise microscopic nature of this disorder, as we will discuss in much more detail in Chapters 4 and 5 of this thesis), which is why suspended devices have superior quality. These devices, however, are difficult to fabricate controllably, mainly because it is very difficult to eliminate all adsorbates attached to graphene, after the graphene layer has been suspended. Additionally, suspended devices can only have rather small dimensions (otherwise they bend, and touch the gate electrode) and only very recently a successful strategy to realize multi-terminal structure has been demonstrated\(^4\). However, since suspended devices have not been used in the course of the work done in this thesis, we will not go into any more details here.

In this thesis we have investigated – next to conventional graphene devices on Si/SiO\(_2\) – devices on top of two different substrate materials, which were chosen for specific reasons. These are SrTiO\(_3\), which was chosen because of its extremely large dielectric constant, and hexagonal Boron Nitride (hBN), which was selected because previous work\(^5\), \(^6\), \(^7\), \(^8\), \(^9\) had shown that this material enables the realization of graphene devices of very high quality. The realization

\(^1\)The ref.\(^1\) provides a review on several methods used for the growth of graphene
of graphene devices on these substrates poses new challenges that have to be addressed. SrTiO$_3$ consists of a thick (500 $\mu$m), insulating single crystals on which the graphene layers have very limited optical contrast, which makes its identification difficult. Additionally, when performing electron-beam (e-beam) lithography, the thick insulating substrate leads to a build-up of charge, which affects the lithography process itself. As for hBN, a major difficulty comes from the fact that the material consists of rather small crystalline grains. To realize hBN substrates, it is necessary to exfoliate these grains – just like it is done to extract graphene from graphite – and transfer the resulting crystalline flakes on a supporting substrate. Since the hBN flakes produced in this way have typical dimensions of several tens of microns at the most, it is necessary to develop a strategy to controllably transfer a graphene layer onto a hBN flake with sufficient precision, in order to realize graphene/hBN structures.

The nano-fabrication processes that have been employed to realize graphene on SrTiO$_3$ and on hBN substrates are presented in the following subsections. Although of rather technical nature, the work described in this chapter is part of a rapidly developing area of research that focuses on the control and understanding of new structures based on the stacking of layers of atomic thickness. Indeed, next to graphene and hBN, several new materials are now being used in this type of activities, and the field is broadening rapidly.

### 3.1.1 Graphene on top of Strontium Titanate substrates

The fabrication of graphene devices on top of SrTiO$_3$ substrates is based on the well established exfoliation technique of graphite crystals with adhesive tape. Graphene crystals are obtained by peeling layers of graphite with an adhesive tape and then depositing them on top of a SrTiO$_3$ substrate, which is a single crystal slab with a thickness of 500$\mu$m and area of $5 \times 5$ mm$^2$ (crystals were purchased from Crystec$^2$). The SrTiO$_3$ substrates are oriented along the [001] crystal axis, they have an atomically flat surface, and are optically transparent. Typically the graphite crystals found on top of SrTiO$_3$ show a white color under the optical microscope, which then becomes progressively transparent for thinner graphite crystals, making the identification of single- and multi-layers of graphene through color contrast a very difficult task. In order to overcome this problem we coupled a CCD camera to the optical microscope and enhanced the image contrast with the image acquisition software. Only then single and few layer graphene crystals become visible, allowing their characterization through the measurement of their relative "white contrast" with respect to the SrTiO$_3$ substrate. We found that, micrometer sized single layer,

$^2$www.crystec.de
bilayer and trilayer graphene crystals have relative contrast values of 1.25%, 2.5% and 3.75% respectively (the correct identification of mono and bilayers of graphene was confirmed by subsequent Quantum Hall measurements).

**Contacting graphene on top of SrTiO$_3$ substrates**

As for devices on Si/SiO$_2$ substrates, the metallic contacts to graphene devices on top of SrTiO$_3$ substrates, are defined by e-beam lithography techniques, followed by metal evaporation and lift-off. However, SrTiO$_3$ substrates pose a problem for the proper use of e-beam lithography, due to inevitable surface charging effects that affect the e-beam lithography process itself. This problem is solved with the evaporation of a thin layer (7 nm) of Cu on top of the sample before its exposure to the e-beam to define the contact pattern. This thin film of Cu provides a conductive path to discharge the electrons coming from the electron beam, therefore suppressing surface charging effects and allowing the proper exposure of the pattern design. The Cu layer is then chemically etched (e.g in a solution FeCl) in order to allow the development of the contact
pattern. The electrodes are then defined by the evaporation of Ti/Au (10/50 nm) followed by lift-off. As a gate electrode, we evaporated a metallic film consisting of Ti/Au with thickness 10/20 nm on the back-side of the SrTiO$_3$ substrate.

We have also fabricated nanoribbon devices, consisting of 1 μm long and 50-70 nm wide graphene strips, on top of SrTiO$_3$ substrates. As compared to the fabrication of the Hall-bar devices that we just described these nanoribbon devices require an additional e-beam lithography step, in order to define the nanoribbon shape through an etching process. After the e-beam lithography patterning and subsequent development of the etch mask, the nanoribbon is made by etching the graphene crystal with an Argon gun with a driving voltage of 500V for 20s.

3.1.2 Graphene on top of Boron Nitride substrates
As we mentioned earlier, the hBN substrate consist of crystalline flakes obtained from the exfoliation of small crystallites of irregular shape, subsequently transferred onto a supporting material (typically a conventional Si/SiO$_2$ wafer, with the highly doped Si acting as a gate electrode). The key difficulty, as compared to the use of other substrates, is that graphene layers need to be precisely positioned on top of a hBN flake, which typically has dimensions of only a few tens of microns. In practice this requires the development of a technique to manipulate graphene layers and move them around in a controlled manner\cite{8, 15, 51, 124}. As we describe in more detail below, this is done by exfoliating graphene onto a thin polymeric layer, which is subsequently detached (without breaking) from the supporting substrate and mounted on a micro-manipulator under an optical microscope.

The hBN exfoliated flakes that we have used have been obtained from crystals provided by T. Taniguchi and K. Watanabe at the National Institute for Materials Science in Japan\cite{125}. After transferring these flakes on a Si/SiO$_2$ substrate, the quality of their surface is assessed by inspection with an atomic force microscope (AFM). It is important to select flakes that are sufficiently large – since otherwise the procedure to align the graphene layer becomes too complex – and that are homogeneous and flat over their entire surface (to achieve the highest quality, it is important to avoid substrates with terraces). The AFM measurements also allow us to determine the thickness of the hBN flake, which is useful to estimate the capacitance of the gate in the final device.

Graphene is then isolated (using the conventional adhesive tape technique and optical microscope inspection) on a polymeric support which is used to controllably transfer a selected layer onto hBN. To prepare this polymer support we followed the method developed by Dean et al\cite{13}, where on top of a
Device fabrication

We spin-coat a water soluble polymer and PMMA (polymethyl methacrylate), as shown in fig. 3.2(a). The water soluble polymer will act as a sacrificial layer once it is exposed to water and allow the detachment of the PMMA film from the substrate. This PMMA film that hosts the graphene crystals, is then used as a support for targeted transfers onto hBN crystals.

Transferring graphene onto the hBN crystals and defining the electrodes

After identifying suitable graphene crystals for the fabrication of devices, we proceed to the detachment of the polymer support from the Si wafer, leaving the Si wafer floating on top of deionized water. We gently press the corners of the wafer so that water can contact the polymers, while at the same time we ensure that the regions of the polymer film where graphene is located, remain dry. Few minutes after, the water soluble polymer underneath the PMMA is completely dissolved and the PMMA film is detached from the Si wafer. Typically, this PMMA film floats on top of the water surface, while the Si wafer sinks. The PMMA film is then scooped with a plastic holder having a 1 cm diameter hole (see fig. 3.2(b)) that is subsequently fixed on a micro-manipulator that is coupled to an optical microscope. The use of the micro-manipulator allows the positioning of the film, so that graphene can be properly aligned to the target hBN crystals, which are on top Si/SiO$_2$ substrates. By using this micro-manipulator, graphene can be transferred onto the hBN crystal with a precision of the order of 1 µm (see fig. 3.2(c)-(d)).

Immediately after positioning and transferring graphene onto hBN (see fig. 3.2(e)), we heat the Si/SiO$_2$ substrate up to 90°C for 5-10 minutes using a hot plate, in the attempt to improve the adhesion between graphene and hBN. The PMMA film used for the transfer is then removed in a hot acetone bath, leaving (most of the times) the transferred graphene crystal on top of hBN unaffected. Usually after these transfers it is common to find "bubbles" – rounded features with the height of several nanometres, whose origin is still not well understood – on the graphene crystals. The occurrence of these "bubbles", which have been extensively reported by other research groups[8, 10, 50, 51, 126], are known to affect the quality of the graphene devices. We therefore design the structure of our devices in regions of graphene that are "bubbles"-free. The metallic contacts are then defined by standard nano-fabrication techniques: e-beam lithography was used to generate the contact pattern, and e-beam evaporation followed by lift-off was used to define the Ti/Au (10/75 nm) electrodes. In most graphene on hBN devices, a final graphene etching step is required in order to properly define the geometry. The etching mask is defined by a second e-beam lithography step and the graphene crystal is then etched in an oxygen plasma generated at 250V for 30s.
3.2. **Bi$_2$Se$_3$ based electronic devices**

The 3D topological insulator nano-devices on which we carried out the transport experiments discussed in Chapter 6 were made out of Bi$_2$Se$_3$ single crystals grown in the laboratory of the Quantum Materials group of the University of Geneva\(^3\). Since Bi$_2$Se$_3$ is a layered material consisting of the stacking of quintuple layers (of Se-Bi-Se-Bi-Se) that are van der Waals bonded, thin Bi$_2$Se$_3$ crystals can also be easily cleaved from a large crystal (see fig. 3.3(a)). For the devices used in our experiments we focused on the isolation of Bi$_2$Se$_3$ crystals with the thickness of few quintuple layers, i.e. these crystals have an approximate thickness of few nanometres. Using thin flakes is important to minimize the bulk contribution to transport that is inevitably present present due to defects in the material. The thin layers of Bi$_2$Se$_3$ were obtained by exfoliation of

---

\(^3\)A detailed description of the growth method can be found in the Appendix of this chapter.
single crystals using an adhesive tape, while monitoring the process under an optical microscope, similarly to what is carried out to extract graphene from graphite. The layers were transferred onto a degenerately doped Si substrate (functioning as a gate electrode) covered with a 300-nm layer of thermally grown SiO$_2$ (gate insulator), simply by pressing the adhesive tape onto the substrate. Most layers produced in this way appeared to be shiny when observed under the microscope, corresponding to a large thickness (several tens of nanometres or more). In few cases, however, thinner layers (characterized by a darker colour – see fig. 3.3 (b)) were also found (the thinnest layer that we observed had a thickness of approximately 4 nm). These thinner layers were selected for the fabrication of devices. Compared to graphene, the production of very thin Bi$_2$Se$_3$ layers is considerably more difficult because Bi$_2$Se$_3$ is more brittle than graphite, and the material tends to easily break into very small pieces during the exfoliation process. Devices were fabricated by conventional nano-fabrication techniques: electron-beam lithography was used to generate the contact pattern, and electron-beam evaporation followed by lift-off was used to define the Al/Ti (75/5 nm) electrodes (fig. 3.3 (c)).
3.3 Appendix

The following section provides a description of the growth technique used to produce the Bi$_2$Se$_3$ crystals, from which we fabricated our electronic nanodevices.

Growth of single crystals of Bi$_2$Se$_3$

The single crystals of Bi$_2$Se$_3$ were grown by a floating zone method. Bismuth and selenium were weighted in stoichiometric ratio and sealed under vacuum ($\sim$10$^{-3}$ mbar) in quartz ampoules. According to the Bi-Se phase diagram, Bi$_2$Se$_3$ has a congruent melting point at 705°C\cite{127}. To synthesize the compound, the mixture of elements was heated up to 750°C, kept at this temperature for 12 h and then quenched to room temperature. To assure a better mixing of the elements, during the isothermal time in the liquid state, the ampoule was shaken and rotated. This procedure was repeated three times. Finally the ampoule was heated up to 820 °C for 24 h and slowly cooled down to room temperature. At the end of this procedure, the sample was already formed by large single domains of good quality, suggesting a high growth rate for Bi$_2$Se$_3$. The sample was then crushed into small pieces and sealed inside a quartz ampoule with 5 mm of inner diameter and a conical bottom, which was vertically mounted in a homemade 2-lamp furnace. The sample was moved downwards through the hot zone at a speed of $\sim$0.33 mm h$^{-1}$, starting from the apex of the conical tip. In this way a single crystal started to grow in the tip. The ampoule was kept rotating all the time to avoid lateral thermal gradient. The advantage of the floating zone over other growth techniques consists in the large temperature gradient at the growth interface, the low travelling velocity, and the fact that the growing composition is prevented from local fluctuations in the melt composition. These differences can account for a different structural quality of the crystals – and in particular a lower density of defects – as compared with that of existing materials grown by different techniques. Large (1-10 mm size) crystals were cleaved from the solid rod formed inside the quartz. The high crystalline quality of the crystals was confirmed by X-ray diffraction that shows a single phase, single index diffraction pattern and narrow rocking curves. The cell parameters were found to be in good agreement with those reported in the literature.
Electronic transport through graphene on top of a high-$
\epsilon$ substrate

We report transport measurements through graphene on SrTiO$_3$ substrates as a function of magnetic field $B$, carrier density $n$, and temperature $T$. The large dielectric constant of SrTiO$_3$ screens very effectively long-range electron-electron interactions and potential fluctuations, making Dirac electrons in graphene virtually non-interacting. The absence of interactions results in an unexpected behavior of the longitudinal resistance in the $N = 0$ Landau level, and in a large suppression of the transport gap in nano-ribbons. The "bulk" transport properties of graphene at $B = 0$ T, on the contrary, are completely unaffected by the substrate dielectric constant.

4. Electronic transport through graphene on top of a high-\(\epsilon\) substrate

4.1 Introduction

Experiments on devices with SiO\(_2\)\(^1\) and BN\(^2\) gate dielectrics, as well as on suspended layers\(^3\),\(^4\), indicate that the substrate material has a strong influence on the transport properties of graphene. Whereas investigations have mainly aimed at minimizing the amount of disorder present, it should be possible to choose the substrate material to effectively control different aspects of the electronic properties of graphene. Here we discuss transport experiments through graphene on SrTiO\(_3\), a very well-known insulator where the presence of a low-energy phonon mode\(^5\),\(^6\) brings the material close to a ferroelectric instability. The softening of this low-energy mode causes the relative dielectric constant (\(\epsilon\)) of the material to increase from 200-300 at room temperature, to \(\approx 7000\) at liquid Helium temperature\(^7\), with most of the increase taking place when \(T\) is lowered from 50 to 10 K (see fig. 4.1). SrTiO\(_3\) substrates, therefore, allow the investigation of the effect of the dielectric environment on the charge carriers in graphene in a broad temperature range.

The effect of dielectric screening in graphene has been investigated previously. In one set of experiments, graphene devices were immersed in solvents with \(\epsilon\) up to 50 - 100\(^8\). Although revealing, these studies have been confined to temperatures above the solvent freezing point (\(T > 160\) K), which prevented the investigation of physical phenomena taking place at low temperature. In other work, the effect of the dielectric environment was investigated by comparing the transport properties of graphene on SiO\(_2\) with and without an adsorbed thin ice layer which slightly changed the dielectric environment seen by the charge carriers\(^9\). SrTiO\(_3\) offers the advantage of a very large tunable dielectric constant together with the possibility of measuring in a broad range of temperatures.

Our studies rely on transport measurements on graphene Hall-bars and etched nano-ribbons on SrTiO\(_3\). At zero magnetic field, transport through Hall-bar devices show no temperature dependence between 250 mK and 50 K, and graphene exhibits a behavior identical to that observed on SiO\(_2\) substrates\(^1\). The importance of the substrate, however, becomes clear in measurements at finite \(B\), and in nano-ribbons. In the quantum Hall regime, we observe that the longitudinal resistance peak measured in the \(N = 0\) Landau level decreases significantly with lowering \(T\), a trend different to what has been reported in previous experiments on SiO\(_2\) substrates\(^1\),\(^2\),\(^3\),\(^4\),\(^5\),\(^6\). In nano-ribbons, the magnitude of the transport gap is one order of magnitude smaller than in identical devices on SiO\(_2\)\(^7\),\(^8\),\(^9\). Both effects are manifestations of the suppression of electron-electron interactions due to substrate screening, which turns carriers in graphene into virtually non-interacting Dirac fermions. The
observation of such an effective screening also allows us to conclude that at
$B = 0$ T Coulomb interactions and long-range potentials do not significantly
influence transport through “bulk” graphene on SiO$_2$.

The devices investigated (Fig. 4.2(a)-inset) were prepared by exfoliating
graphene from natural graphite using an adhesive tape, and by its subsequent
transfer onto a 500$\mu$m thick SrTiO$_3$ single crystalline substrate. Graphene
layers were found by inspection under an optical microscope, with mono-, bi-, and tri-layer graphene giving a contrast of 1.25%, 2.5% and 3.75%, respec-
tively (see Fig. 4.2(b)); this contrast is measured on substrates with only one
face polished). Ti/Au contacts (10/50 nm) were defined by means of electron
beam lithography, evaporation, and lift-off. The gate electrode consisted of a
Au film evaporated on the substrate backside.

4.2 Electronic transport at B=0T

We first discuss measurements performed as a function of gate voltage $V_g$ and
at $B = 0$ T, at temperatures between 50 K and 250 mK. The increase in the
substrate dielectric constant $\epsilon$ upon lowering $T$ is visible in Fig. 4.2(a), where
the graphene resistance is plotted as a function of $V_g$, since, with lowering $T$, a
smaller $V_g$ range is needed to scan across the resistance peak around the charge
neutrality point (“Dirac peak”). At each gate voltage, the density of charge
carriers $n$ was extracted from the Hall resistance (shown in the Appendix
of this chapter). Fig. 4.2(c) shows that at a fixed value of $V_g$, $n$ increases
by approximately one order of magnitude as $T$ is lowered from 50K down
to 250mK, in agreement with the expected behavior of SrTiO$_3$ that we have
categorized separately through $T$-dependent capacitance measurements (see
fig. 4.1). Fig. 4.2(a) shows that, when plotted as a function of $n$, the Dirac
4. Electronic transport through graphene on top of a high-$\epsilon$ substrate

Figure 4.2: (a) Square resistance of graphene on SrTiO$_3$ as a function of gate voltage, measured for different temperatures between 50K and 250mK; the arrow points in the direction of lowering temperature. (a-inset) Optical microscope image with software enhanced contrast (left); the final device with contacts attached (right; scale bar is 3$\mu$m long). (b) Optical contrast of mono-, bi-, and tri-layer graphene on SrTiO$_3$. (d) Ratio of the carrier density measured by Hall effect at $V_g = 2$ V at temperature $T$ over the carrier density at $T = 250$ mK: this ratio is proportional to the dielectric constant of the substrate $\epsilon(T)$, and decreases by almost one order of magnitude when $T$ is increased from 250 mK to 50 K, as expected.

peaks measured at all different temperatures overlap nearly perfectly despite the large change in $\epsilon$ of the substrate.

Finding a complete insensitivity to temperature despite the large change in the SrTiO$_3$ dielectric constant may cause doubts that water or other adsorbed molecules are present in between the graphene layer and the substrate, effectively decoupling the two materials. To rule out this possibility, it is important to identify measurable effects sensitive to the substrate dielectric constant. Obvious candidates are phenomena that originate from long-range electron-electron interactions, which should be completely screened on SrTiO$_3$. Two such phenomena are the temperature dependence of the longitudinal resistance in the $N = 0$ Landau level in the quantum Hall regime \cite{97,103,132}, and low-temperature bias-dependent transport in nano-ribbons \cite{77,82,133,134}.

\footnote{Note that even in the presence of a 1-2 nm thick layer of adsorbates between graphene and the substrate, the long range effects of substrate screening due to the very large temperature dependent dielectric constant of SrTiO$_3$ should still be visible.}
4.3. Transport at high magnetic fields

Figure 4.3: (a) Square resistance of graphene on SrTiO$_3$ measured at different temperatures between 250 mK and 50 K, as a function of carrier density (extracted from Hall effect measurements shown in Fig. 4.4 of the Appendix). (b) Conductivity $\sigma$ of graphene on SrTiO$_3$ as a function of $n$ (in log scale) at different temperatures, showing the low density region where $\sigma$ is independent of $n$ (by extrapolating the $\sigma(n)$ curve measure at large density –dotted line– we estimate the width of this region to be approximately $\delta n = (6.0 \pm 0.5) \times 10^{11}$ cm$^{-2}$, independent of temperature). (c) (blue line) Fitting the experimental data to the dependence of $\sigma(n)$ by taking into account resonant scattering giving parameters ($n_i = 2.9 \times 10^{11}$ cm$^{-2}$, $R = 0.22$ nm) very close to those obtained for graphene on SiO$_2$.\

4.3 Transport at high magnetic fields

Figure 4.4 shows data measured in the presence of a 15 T perpendicular magnetic field. At high magnetic field, well-defined Hall plateaus in the Hall conductivity $\sigma_{xy}$ are observed up to the maximum temperature investigated (50 K; see Fig. 4.4(b)). The plateaus at $\sigma_{xy} = \pm 2e^2/h$ and $\sigma_{xy} = \pm 6e^2/h$ confirm that the device is of good quality and that it indeed consists of a single graphene layer[46, 47]. Note the temperature dependence of the peak in the longitudinal resistance observed at the charge neutrality, when the Fermi level is located inside the $N = 0$ Landau level: the height of this peak decreases monotonously with lowering temperature from 50 K to 250 mK. The effect is large, as the peak amplitude at 250 mK is more than three times smaller than at 50 K.

This behavior is different from what was observed for graphene on SiO$_2$ in all previously reported experiments. Early measurements on SiO$_2$ found that the height of the resistance peak associated to the $N = 0$ Landau level
4. Electronic transport through graphene on top of a high-$\epsilon$ substrate

Figure 4.4: (a) Longitudinal square resistance $R$ as a function of $V_g$ at $B = 15$ T, measured at different temperatures between 250 mK and 50 K. The height of the resistance peak at the charge neutrality ($N = 0$ Landau level) decreases significantly with lowering $T$, whereas the height of the peaks centered around the subsequent $N = \pm 1$ Landau show a slight increase in resistance with lowering $T$ (see panel (c); $N = 0$ (circles), $N = +1$ (squares) and $N = -1$ (triangles)). (b) The Hall conductivity measured at 50 K ($B = 15$ T) shows very well developed plateaus at $\pm 2, \pm 6 e^2/h$, as it characteristic for Dirac fermions in graphene.

decreases from room temperature upon cooling, but the temperature dependence nearly saturates for $T < 150$ K. Cooling down from 150 K to 4.2 K produces at most a 10% change in the peak resistance, i.e., contrary to what we observe on SrTiO$_3$, between 50 K and 250 mK essentially no temperature dependence is observed. More recently, an insulating temperature dependence was observed by different groups, accompanied by a very rapid (thermally activated below $T \approx 20$ K) increase in the resistance peak height with lowering $T$, which is the opposite of what we find on SrTiO$_3$. Importantly, the carrier mobility values in the devices used in these last experiments on SiO$_2$ were between 5000 and 10000 cm$^2$/Vs, comparable to those that we found in our devices on SrTiO$_3$ (see below), which implies that the different behavior of the resistance measured in the $N = 0$ Landau level on SiO$_2$ and SrTiO$_3$ cannot be simply attributed to a difference in the amount of disorder present. Since it is known that electron-electron interactions play an important role in determining the properties of $N = 0$ Landau level in graphene, finding a different behavior for graphene devices on SrTiO$_3$ and SiO$_2$ should be expected and provides a first indication of the
effectiveness of screening due to the substrate.

4.4 Graphene nanoribbons

The effect of substrate screening is also visible in bias-dependent transport measurements on etched nano-ribbons. When these nano-ribbons are gate-biased near the charge neutrality point, a transport gap opens, due to the joint effect of disorder and Coulomb interactions\cite{77,82,133}. Disorder causes electrons to localize in small regions of the ribbons, making charging effects important. In simple terms, a graphene nano-ribbon behaves as an array of Coulomb-blockaded quantum dots, and the transport gap originates from the charging energy of the individual islands\cite{134}. When the bias applied across the ribbon is sufficient to overcome the Coulomb gap, the differential conductance increases, providing the means to measure the gap magnitude.

Nano-ribbons on SiO$_2$ substrates have been investigated extensively\cite{77,82,133} and it has been found that the source drain gap increases with increasing length $L$ and decreasing width $W$. For very short nano-ribbons ($\approx 200$ nm or smaller), source-drain gaps as small as 2 meV have been reported\cite{133}. However, for nano-ribbons having a length and width comparable to those that we have studied on SrTiO$_3$ ($W = 70$ nm and $L = 1 \mu$m) the source-drain gap was found to range between 10 and 25 meV, and, for the majority of devices (approximately 80%), in between 15 and 20 meV (see Ref.\cite{133} and our own works on nano-ribbons on SiO$_2$\cite{S2}).

Figure 4.5(a) shows the conductance of a 70 nm wide and 1 $\mu$m long ribbon
4. Electronic transport through graphene on top of a high-$\epsilon$ substrate

on SrTiO$_3$ (one of the three devices that we measured, all showing similar behavior) as a function of gate and bias voltage ($V_{sd}$). It is apparent that the conductance is suppressed at low bias, i.e., a transport gap is present. The largest size of this gap is only 2 meV, i.e. one order of magnitude less than for devices SiO$_2$ with identical dimensions. The gap magnitude is more clearly seen in Fig. 4.5(b), which shows the bias dependence of the conductance measured for three different values of gate voltages. A large reduction of the transport gap in SrTiO$_3$ devices is expected due to the substrate dielectric constant, which strongly increases the self-capacitance of the islands in the ribbon, suppressing their charging energy (note that the remaining gap of 2 meV also includes a contribution due to single particle level spacing, which is present even if the charging energy is completely suppressed). The observation of a strongly suppressed gap in nano-ribbons on SrTiO$_3$, therefore, provides another clear indication of the effectiveness of substrate screening.

4.5 Discussion and conclusions

We now go back to discuss the behavior of graphene on SrTiO$_3$ observed at $B = 0$ T. We have measured approximately 10 different devices on SrTiO$_3$ (including several bilayers) and found mobility values in the range between 3000 and 10000 cm$^2$/Vs, which coincide with what we normally find for similar devices on SiO$_2$. Also the temperature independence of the conductivity, illustrated by the measurements in Fig. 4.3, is identical to what is normally found for graphene on SiO$_2$. From these results –carrier mobility values on SrTiO$_3$ in the same range as on SiO$_2$, showing no temperature dependence below 50 K– we directly conclude that the large dielectric constant of SrTiO$_3$ does not affect "bulk" transport through graphene at $B = 0$ T. These findings directly rule out long-range Coulomb potentials generated by charge impurities next to the graphene layers as the main, mobility-limiting scattering mechanism in graphene [55, 58, 136] (in agreement with the conclusions in Ref. [59], which only explored the high temperature regime).

Our experimental results can be explained by the presence of charge scatterers that are insensitive to the effect of the $\epsilon$ of the substrate, such as resonant scatterers or ripples and corrugations. In several works [72–75], the presence of resonant scatterers generated by strong short ranged potentials [72, 73, 137] (e.g. defects and monovalent impurities), have been considered to be responsible for limiting the carrier mobility in graphene. However, even if the presence of resonant impurities can satisfactorily explain our observations, the effects of strain resulting from ripples and corrugations, on the charge carriers can not be ex-

\[2\]In practice the dominant presence of the resonant impurities, leads to the following ex-
4.5. Discussion and conclusions

Inclined as an important scattering mechanism, because in principle they too, are able to (qualitatively) explain the observed dependence of the conductivity on the carrier density [63].

Note that the width $\delta n$ of the low density region where the conductivity $\sigma$ is independent of $n$ (for the device whose data are shown in Fig. 4.3(b) $\delta n \approx 6.0 \pm 0.5 \times 10^{11}$ cm$^{-2}$) also shows values essentially identical to those measured on devices on SiO$_2$ [44], where the dielectric constant is roughly 1000 times smaller. The magnitude of $\delta n$ is usually taken as a measure of potential fluctuations that give origin to the so-called "puddles", i.e. spatial fluctuation in carrier density whose presence has been observed in different kinds of experiments [56, 57, 138, 139]. Our findings indicate that the density fluctuations that affect the conductivity cannot be induced by Coulomb potentials: on SrTiO$_3$ these potentials are strongly suppressed as compared to SiO$_2$, and still the value of $\delta n$ on SrTiO$_3$ and on SiO$_2$ coincide. Consistently with this conclusion, $\delta n$ remains temperature independent despite the large increase in $\epsilon$ with lowering $T$ that occurs in the investigated temperature range. In contrast to long-range fluctuations, fluctuations of carrier density that vary on a length scale of at most a few nanometers (not much larger than the graphene-substrate distance) cannot be screened effectively by the substrate and can account for our observations. Indeed, density fluctuations on such a length scale are present in graphene on SiO$_2$, as it has been revealed experimentally by scanning tunnelling experiments [40, 73].

In summary, we have performed a study of low-temperature transport through graphene on SrTiO$_3$ which, through a comparison with results obtained on lower dielectric constant substrates, enables a direct identification of effects that originate from long-range electron-electron interactions and Coulomb potentials. Whereas these phenomena crucially determine the properties of the $N = 0$ Landau level and the size of the transport gap in nanoribbons, they do not play a significant role on the transport properties of "bulk" graphene at $B = 0$ T.

In fact the presence of strain in graphene can explain why the mobility and charge density fluctuations of devices made on top of SiO$_2$ and SrTiO$_3$ substrates coincide. This finding will be discussed in Chapter 5.

See Appendix for a discussion based on the dielectric function of SrTiO$_3$. 

Expression for the carrier density dependent conductivity $\sigma = \frac{2e^2}{\pi h} \frac{n}{n_i} \ln^2(\sqrt{n\pi R})$, where $n_i$, is the impurity concentration, and $R$ the potential range respectively. From the fit to our experimental data (see Fig. 4.3) we find $n_i = 2.9 \times 10^{11}$ cm$^{-2}$ and $R = 0.22$nm very close to those found for graphene on SiO$_2$ [44, 45].
Appendix
In this appendix we discuss the methods used for the extraction of the carrier density \( n \) in our hall-bar devices and also, why the magnitude of the charge density fluctuations (\( \delta n \)) close to the Dirac point in our graphene devices are not affected by the large dielectric constant of \( \text{SrTiO}_3 \).

Estimation of the carrier density in hall-bar devices
The carrier density of the devices discussed in section 4.2 was obtained through the measurement of the Hall Effect. The transverse resistance was measured as a function of gate voltage \( V_g \), first at \( B = +0.3T \) (Fig.4.6) and subsequently at \( B = -0.3T \) and \( R_{xy} \) was obtained by anti-symmetrizing the result of the two measurements, to avoid possible effects due to contact misalignment or to sample in-homogeneities

\[
R_{xy} = \frac{(R_{xy}(B) - R_{xy}(-B))}{2}
\]

(we have checked that extracting \( R_{xy} \) from measurement performed for a single magnetic field polarity gives essentially the same result). The carrier density \( n \) was obtained through the relation:

\[
n = \frac{B}{eR_{xy}}
\]

Where \( B \) is the magnetic field and \( e \) the elementary electron charge. The procedure is straightforward throughout the majority of the gate voltage range explored, except in the vicinity of the gate voltage where \( R_{xy} \) crosses zero, since a vanishing \( R_{xy} \) gives a diverging density. In our experimental data the range in carrier density which is affected by this problem is approximately \( \pm 2 \times 10^{11} \text{cm}^{-2} \) or less. In this range the carrier density was estimated by extrapolating the density measured at large gate voltage through a smoothing procedure using a local regression with weighted linear least squares (see blue line in Fig.4.6(b)). We emphasize that any possible uncertainty originating from this procedure does not affect any of our conclusions, which do not rely specifically on this small range of carrier densities (even the flat conductivity region which occurs for \( n < 6 \times 10^{11} \text{cm}^{-2} \) is determined by extrapolating the conductivity curve measured for higher carrier density values, where the Hall effect measurements are not affected by any uncertainty).

Finally, we notice that in all our measurements, a small non-linearity and asymmetry of the \( n-\text{vs}-V_g \) relation is observed (Fig.4.6(b)). Non-linearities
4.6. Appendix

Figure 4.6: (a) Hall resistance (R_{xy}) as a function of gate voltage (V_g) measured at B=0.3T and T=250mK. (b) Carrier density extracted from R_{xy} as a function of V_g (red circles) and fit to the experimental points (blue line). (c) Carrier density as a function of V_g for different temperatures, from 50K to 250mK. The arrow points in the direction of lowering temperature. (d) Carrier density as a function of temperature at V_g = 1V. The decrease in carrier density with increasing temperature is consistent with the measured temperature dependence of the dielectric constant of SrTiO_3 (see fig 4.1). Through (d) one can also estimate the gate capacitance, which varies from \sim 30nF/cm^2 at 50K up to \sim 190nF/cm^2 at 250mK, however, these values are limited to regions where the carrier density dependence on the gate voltage is linear, i.e. at small gate voltages.

of this order of magnitude are known to occur in SrTiO_3, owing to its vicinity to a ferroelectric state (the precise origin of the asymmetry has not been investigated). Indeed we found that the application of large gate voltages (much larger than those used in our studies) can also cause the substrate to exhibit hysteretic n−vs−V_g characteristics. These effects are not relevant here both because we intentionally kept the gate voltage to sufficiently low values where no hysteresis is observed and because the carrier density is measured directly using the Hall effect for every value of V_g.

Influence of the dielectric function in high-\epsilon dielectrics
It is interesting to analyze the behaviour of graphene on SrTiO_3, whose large static dielectric constant should be expected to strongly affect the magnitude of the charge fluctuations due to electrostatic screening. Nevertheless, as we will show in Chapter 5, data obtained from graphene-on-SrTiO_3 follow the universal relation identified by analyzing the case of graphene-on-hBN (i.e., on a low dielectric constant substrate).
4. Electronic transport through graphene on top of a high-\(\epsilon\) substrate

The high static dielectric constant of the SrTiO\(_3\) substrates used in this chapter arises from an anharmonic transverse optical low frequency mode which shows a strong temperature dependence. We approximate the full dielectric function by

\[
\varepsilon(\vec{q}, \omega) \approx \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \frac{\omega_{TO}^2(\vec{q})}{\omega_{TO}^2(\vec{q}) - \omega^2 - i\gamma \omega}
\]

(4.3)

where \(\omega_{TO}(\vec{q})\) is the temperature dependent frequency of this mode, where we are maintaining its momentum dependence. We take for the low and high frequency limits of the dielectric function for \(|\vec{q}| \to 0\) the values \(\varepsilon_0 \approx 7000\) (as it is appropriate at low temperature, \(T \approx 4.2\) K) and \(\varepsilon_\infty \approx 5.2\). The dispersion of this mode can be written as

\[
\omega_{TO}^2(\vec{q}) \approx \omega_{TO}^2(0) + \lambda_1 q_x^2 + \lambda_2 (q_y^2 + q_z^2)
\]

(4.4)

with \(\lambda_1 \approx 500\) meV\(^2\) Å\(^{-2}\) and \(\lambda_2 \approx 1000\) meV\(^2\) Å\(^{-2}\). The value of \(\omega_{TO}^2(0)\) depends on the temperature. We assume here \(\hbar \omega_{TO}(0) \approx 1.8\) meV. The static dielectric function is shown in Fig. 4.7 where we use an average \((\lambda_1 + \lambda_2)/2 = \lambda_{av} = 700\) meV\(^2\) Å\(^{-2}\). This model for the dielectric function implies that SrTiO\(_3\) behaves like a low-\(\epsilon\) dielectric for momenta greater than \(q_c \approx 0.05\) Å\(^{-1}\).

The value of momentum separating the regions where SrTiO\(_3\) behaves as a high-\(\epsilon\) or low-\(\epsilon\) dielectric - \(q_c \approx 0.05\) Å\(^{-1}\) - corresponds to distances of a few

![Figure 4.7: Approximate q-dependence of the dielectric function for SrTiO\(_3\) discussed in the text.](image-url)
nanometers. Such distances are compatible with our observations discussed above, namely that interaction effects around charge neutrality in the presence of a magnetic field, as well as Coulomb gaps in nano-ribbons of approximately 50 nm width are suppressed. Indeed, both these phenomena involve distances much larger than a few nanometers, for which SrTiO$_3$ does behave as a high-$\epsilon$ dielectric. We find it important to emphasize this explicitly, to show that our explanation does account for the findings that we have reported in this chapter. We also emphasize that, for the same argument, SrTiO$_3$ is expected to cause a substantial increase in the carrier mobility if the dominant scattering mechanism is due to Coulomb potential generated by surface charges with a density up to at least a few times $10^{13}$ cm$^{-2}$. As mentioned previously, since no significant increase in mobility on SrTiO$_3$ is seen in the experiments (as compared to graphene-on-SiO$_2$), this provides one more indication that charge impurities are not the dominant scattering mechanism.
Strain-limited transport in high-quality graphene devices

By investigating low-temperature transport through many graphene devices on hBN substrates, we reveal a clear correlation between the carrier mobility $\mu$ and the width of the resistance peak around charge neutrality. The correlation –satisfied quantitatively also by devices realized in other laboratories, and on other substrates– indicates that a same, universal microscopic mechanism limits the carrier mobility and generates charge fluctuations for graphene-on-substrate. Weak-localization measurements show that the underlying random disorder potential is long-ranged, at least for devices whose mobility is between 1.000 and 80.000 cm$^2$/Vs. We propose a theoretical interpretation based on the effects of strain in graphene, which reproduces all key aspects of our observations.

5.1 Introduction

Hexagonal boron nitride (hBN) substrates enable the fabrication of graphene devices with strongly reduced disorder\cite{5,15,50,51}, exhibiting impressively high carrier mobility values, and leading to the observation of interesting physical phenomena\cite{6,13,18-20}. Progress in device quality, however, has not led to the identification of the nature of disorder affecting the properties of graphene-on-substrate. Many open questions remain\cite{6}. It is unclear, whether the dominant microscopic mechanism causing scattering of charge carriers is also responsible for the inhomogeneity in carrier density around the charge neutrality point (the so-called charge puddles). It is not yet established whether the dominant carrier scattering processes originate from short- or long-range potentials\cite{40,45,55,59,74,131,144}. It is also unclear if and how, microscopically, disorder is related to the specific substrate material.

Here we present an experimental study of graphene-on-hBN addressing these issues. While the best graphene-on-hBN devices exhibit impressive mobility, more modest values are also commonly found and the resulting broad range of electrical characteristics allows the identification of correlations between different quantities. We find an unambiguous correlation between the carrier mobility $\mu$ and the width of the resistance peak around charge neutrality $n^*$ with $\mu \propto (n^*)^{-1}$ – extending over nearly two orders of magnitude. This correlation is also satisfied by devices fabricated in other laboratories and, more surprisingly, by devices on other substrate materials. It demonstrates that the physical mechanism limiting the mobility in graphene-on-substrate is the same one responsible causing charge inhomogeneity, and points to its universality. Through weak localization measurements we establish that – at least for devices with $\mu$ in the range 1.000-80.000 cm$^2$/Vs – the mobility is limited by intra-valley scattering, implying that the dominant disorder is long-ranged. Our results point to deformations caused by strain in graphene as the dominant source of disorder for graphene-on-substrate, and we discuss in detail our data in this context.

5.2 High-quality graphene devices

The fabrication of graphene-on-hBN devices relies on a technique described in the literature\cite{15}. We exfoliate hBN crystals onto a heavily doped, oxidized Si wafer. Graphene flakes extracted from natural graphite are transferred onto a hBN crystal, following the procedure of Ref.\cite{15}. Metallic contacts (Ti/Au, 10/75 nm) are defined by electron-beam lithography, evaporation and lift-off (see Fig.5.1(a)). We find "bubbles" (as in Ref.\cite{50,51,52}) when transferring graphene on hBN: achieving high-$\mu$ requires etching Hall bar devices in parts of
the flakes with no bubbles (regions with “bubbles” exhibit lower $\mu$, comparable to SiO$_2$ devices). After an electrical characterization at 4K, we perform different low-temperature thermal annealing steps (150-250 C, in an environment of H$_2$/Ar at 100/200 sccm) and check each time the low-temperature transport characteristics. We find that the initial annealing step always results in a mobility increase (a factor of 2 in the very best cases), whereas subsequent annealing lead to a decrease in $\mu$, eventually to values similar to those obtained on SiO$_2$.

We analyzed approximately 15 distinct Hall-bar devices. Mobility values (at 4.2 K) between 30,000 cm$^2$/Vs and 80,000 cm$^2$/Vs at a carrier density of few $10^{11}$ cm$^{-2}$ were found regularly. Integer quantum Hall (QH) plateaus with $\sigma_{Hall} = 4(1/2 + N)e^2/h$ ($N$ integer) are fully developed starting from $B = 1$ T, and broken symmetry QH states with Hall conductivity $\sigma_{Hall} = \pm 1e^2/h$ appear from $B = 8$ T. Full degeneracy lifting of the $N = 0$ and $N = \pm 1$ Landau levels is observed below 15 T (Fig. 5.1(e)). In devices where
Conductivity $\sigma$ of a graphene monolayer on hBN as a function of carrier density $n$ in linear (a) and double-logarithmic (b) scale, measured after fabrication (blue line), after a first annealing at 150 C (green line), and after a second annealing at 250 C (red line). Panel (b) also illustrates the procedure to extract the value of $n^*$. (c) The blue full circles represent the low-temperature mobility $\mu$ (plotted versus $n^*$) for all the 15 graphene-on-hBN devices realized in our laboratory, measured after fabrication or after annealing. The triangles represent data for graphene-on-hBN extracted from Ref.\[13\] (orange triangles) and from Ref.\[51\] (green triangle). The green diamonds and red squares are from devices realized in our laboratory on SiO\(_2\) and SrTiO\(_3\) substrates, respectively.

The lattices of graphene and hBN were intentionally aligned, we observe the effect of a superlattice potential, with the appearance of satellite Dirac peaks in the measured $R(V_g)$ curve (Fig.\[18, 19\]). These results indicate that our devices have quality comparable to those reported in the literature, fabricated using a similar procedure.

5.3 Correlation between mobility and charge density inhomogeneities

To evaluate the quality of our graphene-on-hBN devices we focus on the low-$T$ mobility $\mu$ and on the width $n^*$ of the minimum in the conductivity $\sigma$-vs-$V_g$ curve. $\mu$ measures the elastic scattering time $\tau$ responsible for momentum relaxation, whereas $n^*$ quantifies the potential fluctuations present. Since these potential fluctuations are not a priori the dominant source of elastic scat-
5.3. Correlation between mobility and charge density inhomogeneities

Figure 5.3: (a) Same data as those of Fig. 2(c) plotted as $1/\mu$-vs-$n^*$, showing an overall linear relation. (b) Average inverse mobility as function of $n^*$ (obtained as indicated in the main text), showing clearly the linearity of the relation. In (a) and (b) the dashed lines corresponds to the prediction of Eq. (5). (c) For all our measured devices the $\sigma^* = en^*\mu$ was calculated from the data of Fig. 5.2(c) and compared with the measured minimum conductivity, $\sigma_{\text{min}}$, showing an excellent agreement between these two quantities.

tering, there is no reason to assume that $\mu$ and $n^*$ are related. Experimentally, the carrier mobility is obtained from $\mu = \sigma/ne$ (see Fig. 5.2(a)), with the density of charge carriers $n$ obtained through the Hall resistance. To extract $n^*$ we plot log($\sigma$) as a function of log($n$), and determine at which $n$ the constant value of log($\sigma$) measured at low density crosses the value of log($\sigma$) extrapolated (linearly) from high density (as shown in Fig. 5.2(b)). The mobility is estimated for $n > n^*$.

Fig. 5.2(c) shows $\mu$ as a function of $n^*$ for all devices, measured either immediately after fabrication, or after a subsequent annealing step. The presence of a correlation between $\mu$ and $n^*$ is unambiguous: devices with smaller density fluctuations have larger mobility. For hBN devices fabricated in our laboratory, this correlation extends from $\mu$ values of 5.000 cm$^2$/Vs (for devices after multiple annealing steps, see below) to 80.000 cm$^2$/Vs. Results reported in the literature\cite{13,15,51} quantitatively fit the same trend, extending the range to $\mu = 100.000$ cm$^2$/Vs. Surprisingly, the correlation is fulfilled also by devices on different substrate materials, (the red and green dots in Fig. 5.2(c) represent data obtained from graphene on SiO$_2$ and SrTiO$_3$. Plotting
5. Strain-limited transport in high-quality graphene devices

$1/\mu$-vs-$n^*$ (Fig. 5.3 (a)) shows that the relation between these two quantities is essentially linear. To reduce the statistical fluctuations we subdivide the $n^*$ axis into eight different intervals and plot the inverse averaged mobility as a function of the average charge density fluctuations (Fig. 5.3 (b)), which makes the linear scaling of $1/\mu$ with $n^*$ fully apparent. We also analyzed the minimum conductivity measured at the charge neutrality point $\sigma_{\text{min}}$, which nearly perfectly coincide in all devices, with the minimum conductivity $\sigma^* = n^* e \mu$ (see Fig. 5.3 (c)), calculated from the charge density fluctuations around charge neutrality and the measured mobility (i.e., $\sigma_{\text{min}} = \sigma^*$). We conclude that the microscopic mechanism limiting $\mu$ for graphene-on-substrate is the same that causes density fluctuations around charge neutrality. We also find that the process is "universal", i.e., independent of the specific substrate material or of details of the fabrications process, which only determines the strength of disorder.

5.4 Weak localization in high mobility devices

To gain additional insight, we analyze the scattering times in graphene, extracted from weak-localization measurements\cite{86, 88, 90}. Specifically, we compare the inter-valley scattering time $\tau_{\text{iv}}$ to the elastic scattering time $\tau$ determined from the carrier mobility. Either $\tau_{\text{iv}} \simeq \tau$, implying that the mobility is determined by inter-valley scattering processes (i.e., the dominant source of disorder are short-range potentials), or $\tau_{\text{iv}} \gg \tau$, indicating that $\mu$ is limited by intra-valley scattering (i.e., long-range disorder potentials dominate). Surprisingly, this straightforward argument has not been used systematically in previous work to identify the dominant disorder, nor it has been suggested in theoretical work (for an exception, see Ref.\cite{92} dealing with rather low mobility devices, $\mu \simeq 1.000 \text{ cm}^2/\text{Vs}$).

Fig. 5.4 (a) shows the low-field magneto-resistance of a Hall bar device with $\mu \simeq 60.000 \text{ cm}^2/\text{Vs}$, for different values of $V_g$ around $V_g = 8 \text{ V}$. A narrow dip in conductivity (width $\simeq 1 \text{ mT}$ or less) is seen around $B = 0 \text{ T}$, originating from weak localization. Aperiodic conductance fluctuations due to random interference are also visible, which we suppress by averaging measurements taken for slightly different $V_g$ values \cite{145}. "Ensemble-averaged" curves obtained in this way around three different $V_g$ values are shown in Fig. 5.4 (b). The data are fit to existing theory\cite{SN}, from which we extract $\tau_{\text{iv}}$, the phase coherence time $\tau_\phi$, and the time $\tau_*$ needed to break effective single-valley time reversal symmetry. At $T = 250 \text{ mK}$ $\tau_\phi$ is much larger than $\tau_{\text{iv}}$, which is why weak-localization is observed. More importantly throughout the density range investigated $\tau$ and $\tau_*$ nearly coincide (which, as we discuss below, gives important indications as
5.5. The effect of strain on transport

Figure 5.4: (a) B and $V_g$ dependence of the resistivity measured at $T = 250$ mK. (b) The circles represent magneto-conductivity curves $\Delta \sigma(B)$ that have been ensemble averaged, by averaging traces in a range of gate voltages around $V_g = -7$ (blue circles), 7 (green circle), and 30 V (red circles), to suppress sample specific fluctuations. The continuous lines are fit to the theory of weak-localization in graphene. (c) Characteristic times extracted at 250 mK for different values of carrier density, either from the fit of weak localization curves ($\tau_\phi$, $\tau_{iv}$, and $\tau_*$) or from the conductivity ($\tau$). The elastic scattering time $\tau$ is always at least one order of magnitude smaller than the inter-valley scattering time $\tau_{iv}$.

to the origin of the dominant source of disorder), and $\tau_{iv} \gg \tau$ by at least one order of magnitude, (and by nearly two at low $n$). This last observation implies that intra-valley scattering due to long-range potentials is the process limiting $\mu$, a conclusion that – in conjunction with previous measurements on graphene-on-SiO$_2$ – holds at least in the mobility range between 1.000 and 80.000 cm$^2$/Vs.

5.5 The effect of strain on transport

The two sources of long-range disorder that have been proposed theoretically to play a role in graphene are potentials originating from a low density $n_{imp}$ of charged impurities at the substrate surface, and strain present in graphene. Different aspects of our data consistently indicate that strain dominates. A first indication comes from the observation that

\footnote{We consider pristine graphene. Clearly, if defects are created –e.g., through ion bombardment– or ionic impurities are introduced –e.g., by dosing graphene with alkali}
This finding is naturally explained by strain, which generates random pseudo-magnetic fields\cite{68} that not only scatter charge carriers, but also break the effective time reversal symmetry in a single valley\cite{62,66,70} on a comparable time scale. On the contrary, for long range potentials generated by charges on the substrate, \( \tau \) is determined by the Fourier components with \( k \approx k_F \), whereas \( \tau_s \) is determined by random fluctuations in the potential difference between the A and B atoms in the individual unit cells of graphene, i.e. by the Fourier component with \( k \approx 1/a \). Through Fermi golden rule, a potential generated by charge impurities leads to \( \tau_s \sim n_{imp} \omega_q \gg \tau \), incompatible with the experimental observations. The evolution of \( \mu \) upon annealing also points to the effect of strain. As discussed above, repeated annealing at low temperature (\( \sim 200 \) C) in an inert atmosphere systematically reduces \( \mu \) by one order of magnitude. These annealing processes have no significant chemical effect, and therefore are not expected to change the density of charge at the surface of hBN by one order of magnitude (as it would be needed to explain the changes in \( \mu \)\cite{55}). On the contrary, they do lead to visible mechanical deformations, compatible with strain causing a decrease in mobility. Finally, having \( \mu \) limited by strain-induced pseudo-magnetic fields also explains why the use of high-\( \epsilon \) substrates does not lead to a very large increase in mobility: a high-\( \epsilon \) substrate can screen electrostatically the scalar potentials induced by strain, but not the effect of a pseudo-magnetic field.

Following these considerations, we need to determine whether strain can explain the observed relation between \( 1/\mu \) and \( n^* \) (see Fig.\ref{fig:5.3}(a)-(b)). We do not attempt to discuss theoretically the full universality, and focus on the case of low dielectric constant (\( \epsilon_0 \)) substrates, such as hBN and SiO\(_2\), which concerns the majority of the experimental data. We treat graphene as an elastic membrane\cite{62,66,70}, and consider strain associated to random ripples, described by the correlation function for the height fluctuations \( \langle h(q)h(-q)\rangle = A/|q|^4 \) (\( A = T_q/\kappa \), with \( T_q \) quenching temperature of the height fluctuations, and \( \kappa \) bending rigidity of graphene). Strain due to in-plane deformations also contributes, but does not change our conclusions). From this expression, the correlation functions for the random scalar and vector (gauge) potential \( V_s(q) \) and \( A(q) \) –which describe how strain couples to electrons in graphene– are calculated (see Ref.\cite{70} and at the Appendix). The scalar and the gauge potential scatter the electrons with comparable (on low-\( \epsilon \) substrates) rates (\( 1/\tau_s \) and \( 1/\tau_g \) respectively), and limit \( \mu \). The magnitude of the charge fluctuations \( n^* \), on the contrary, is determined by the scalar potential only. We calculate \( 1/\tau_s \) and \( 1/\tau_g \) using Fermi golden rule, and obtain the total scattering time as

\( \tau \approx \tau_s \).
5.5. The effect of strain on transport

\[ \frac{1}{\tau} = \frac{1}{\tau_s} + \frac{1}{\tau_g}. \] Specifically,

\[
\frac{1}{\tau_s} = \frac{2\pi N(E_F)}{\hbar^2} \times \frac{4\pi^2}{4\pi^2} \times \int_0^{\pi} d\theta \frac{1 - \cos^2(\theta)}{2} \frac{\langle V_s(q)V_s(-q)\rangle}{e^2(q)} |q|=2k_F \sin(\theta/2)
\]

(5.1)

and

\[
\frac{1}{\tau_g} = \frac{2\pi N(E_F)}{\hbar^2} \times \frac{4\pi^2}{4\pi^2} \times \int_0^{\pi} d\theta [1 - \cos(\theta)] \langle A_\perp(q)A_\perp(-q)\rangle |q|=2k_F \sin(\theta/2),
\]

(5.2)

where \( A_\perp(q) \) is the component of \( A \) perpendicular to \( q \), \( N(E_F) = \frac{k_F}{2\pi\hbar v_F} \) is the one-valley density of states at the Fermi energy, \( \epsilon(q) = (\epsilon_0 + 1)/2 + 4e^2k_F/v_F|q| \) is the dielectric function including the substrate contribution, and \( k_F, v_F, \) and \( E_F \) are the Fermi momentum, velocity, and energy. We extract the mobility from \( \mu = \sigma/ne = 2e^2h^2/E_F\tau \) (the factor of 2 accounts for the two valleys). To calculate the magnitude of charge fluctuations we use the relation \( n(r) = \frac{1}{\pi}(\frac{V_s(r)}{hv_F})^2 \) between local charge density and potential, from which:

\[
n^* = \frac{1}{\pi} \frac{\langle V_s(r)^2 \rangle}{(hv_F)^2} = \frac{1}{4\pi^3\hbar v_F^3} \int d^2q \frac{\langle V_s(q)V_s(-q)\rangle}{e^2(q)}.
\]

(5.3)

Since the correlation functions of all the potentials are determined by \( \langle h(q)h(-q) \rangle \), \( \mu \) and \( n^* \) are related, and we find:

\[
\frac{1}{\mu} \approx n^* \frac{\hbar^2v_F^2}{4e} \left[ \frac{h^2v_F^2}{8e^4} + \frac{g_2^2(\lambda_L + \mu_L)^2}{g_1^2\mu_L^2} \right] \frac{1}{\log[1/(k_F(n^*a))]},
\]

(5.4)

with \( g_1 = 4 \) eV and \( g_2 = 2.3 \) eV quantifying the strength of electron-phonon coupling in graphene, \( \mu_L = 9.4 \) eV/Å² and \( \lambda_L = 3.3 \) eV/Å² Lamé coefficients\(^{[146]}\), and \( \frac{\hbar v_F}{e} = 2.2 \) (\( a \) is the lattice constant of graphene and the logarithm appears when cutting off the integrals at large \( q \)-values, at \( q = 1/a \)).

\(^{[2]}\)for the calculation details see Appendix.
Eq.(4) shows that the relation between $1/\mu$ and $n^*$ is linear (the deviations caused by the logarithm are within the fluctuations in the data) as found experimentally, and it only depends on fundamental constants and on the elastic properties of graphene (i.e. the intrinsic properties of graphene). It is therefore fully compatible with the universality found experimentally. With the value of all the constants known (and using $n^* = 10^{11} cm^{-2}$ as a characteristic value to calculate the logarithm) we obtain

$$\frac{1}{\mu} \approx \frac{h}{e} n^* \times 0.076 \quad (5.5)$$

which reproduces the slope of the relation measured experimentally with a remarkable accuracy (see Fig.5.3(a)-(b)), without having introduced any free parameter. This last result shows that strain does not only explain the qualitative aspects of our observations, but also account for the measured relation between $\mu$ and $n^*$ at a quantitative level.

5.6 Conclusions
We conclude that our observations provide compelling evidence for the role of mechanical deformations in graphene as the dominant source of disorder, that both cause scattering of charge carriers, and spatial fluctuations in their density. The important implication of this finding is the remarkable universality of the behavior of graphene-on-substrate: it suffices to provide one quantity (equivalently, $n^*$, $\mu$, the magnitude of the mechanical deformations) to characterize in a rather complete manner the low-energy transport properties of a graphene device.
5.7 Appendix

This section contains the details of the calculations of the mobility and amplitude of charge density fluctuations due to the effect of strain in graphene. The estimation of these quantities is particularly relevant for the discussion of the experimental correlation between mobility and charge density fluctuations in section 5.5.

Gauge and scalar potentials induced by corrugations

We consider the effect of corrugations of the graphene sheet on its low energy electronic states (in-plane strain has analogous effects), which are described by the Dirac equation. The height profile \( h(\vec{r}) \) of these corrugations was found to lead to strains, which induce the following scalar and a gauge potential on the electrons\[^15\]:

\[
V_s(\vec{q}) = -g_1 \mu_L \lambda_L + 2 \mu_L \frac{q_x^2 + q_y^2}{|\vec{q}|^4} F(\vec{q})
\]

\[
A_x(\vec{q}) = g_2 \frac{\lambda_L + \mu_L}{\lambda_L + 2 \mu_L} \frac{q_x^2 - q_y^2}{|\vec{q}|^4} F(\vec{q})
\]

\[
A_y(\vec{q}) = -2g_2 \frac{\lambda_L + \mu_L}{\lambda_L + 2 \mu_L} \frac{q_x q_y}{|\vec{q}|^4} F(\vec{q})
\]

where \( g_1 \) and \( g_2 \) are parameters with dimensions of energy, \( \lambda_L \) and \( \mu_L \) are the elastic Lamé coefficients, and \( F(\vec{q}) = \sum_{i,j} q_i q_j f_{i,j}(\vec{q}) - |\vec{q}|^2 \sum_i f_{i,i}(\vec{q}) \), with \( f_{i,j}(\vec{q}) \) the Fourier transform of \( f_{i,j}(\vec{r}) = \partial_i h(\vec{r}) \partial_j h(\vec{r}) \). Estimations for the parameters \( g_1, g_2 \) are \( g_1 = 4 \text{ eV} \) and \( g_2 = 3c^2 \gamma_0 / 4 \), with \( \gamma_0 \approx 2.7 \text{ eV}, \beta = \partial \log(\gamma_0)/\partial \log(a) \approx 2 \) and \( c = \mu_L / (\sqrt{2}(\lambda_L + \mu_L)) \approx 0.59 \)\[^14\].

Calculation of the scattering rate

Using eq.(5.6) we can calculate the contribution to \( \tau^{-1} \) of the scalar and gauge potentials\[^7\]

\[
\tau^{-1} = \tau_s^{-1} + \tau_g^{-1}
\]

\[
\tau_s^{-1} = \frac{2\pi N(E_F)}{\hbar^2} \int_0^\pi d\theta \frac{1 - \cos^2(\theta)}{2} \left\langle V_s(\vec{q}) V_s(-\vec{q}) \right\rangle_{|\vec{q}| = 2k_F \sin(\theta/2)}
\]

\[
\tau_g^{-1} = \frac{2\pi N(E_F)}{\hbar^2} \int_0^\pi d\theta \left[ 1 - \cos(\theta) \right] \left\langle \vec{A}_\perp(\vec{q}) \vec{A}_\perp(-\vec{q}) \right\rangle_{|\vec{q}| = 2k_F \sin(\theta/2)}
\]

where \( \epsilon(\vec{q}) = (\epsilon_0 + 1)/2 + (4e^2k_F)/(\hbar v_F |\vec{q}|) \) is the dielectric function of the system, \( \epsilon_0 \) is the dielectric constant of the environment, \( e \) is the electronic
charge, \( k_F \) is the Fermi wavevector, and \( v_F \) is the Fermi velocity. Note that the scalar potential is screened, while the gauge potential is not. The scalar potential includes a factor \([1 - \cos^2(\theta)]/2\), which is responsible for the suppression of backscattering. In eq. (5.7) only the component of \( \mathbf{A} \) perpendicular to \( \mathbf{q} \) contributes to \( \tau_g \). There are no interference terms between the scalar and gauge potentials within Fermi’s Golden Rule.

Model for the height profile
We assume that the height correlations are such that

\[
\langle h(\mathbf{q})h(-\mathbf{q}) \rangle = \frac{A}{|\mathbf{q}|^4} \tag{5.8}
\]

where \( A \) is a constant. This dependence corresponds to the profile of a membrane with temperature \( k_B T \propto \kappa \), where \( \kappa \) is the bending rigidity of graphene\[62\]. This assumption leads to

\[
\langle F(\mathbf{q})F(\mathbf{q}) \rangle = \frac{\bar{A}}{|\mathbf{q}|^2} \tag{5.9}
\]

where \( \bar{A} \) is a dimensionless constant. It is given, approximately, by

\[
\bar{A} \sim \frac{h_r^4}{\ell_r^4} \tag{5.9}
\]

where \( h_r \) and \( \ell_r \) are typical values for the height and size of the ripples. This assumption leads to the following scattering times from eq (5.7):

\[
\tau_s^{-1} = \frac{2\pi N(E_F)}{\hbar} \frac{g^2 \mu_L^2}{4\pi^2 (\lambda_L + 2\mu_L)^2} \times 2 \times \int_0^{\pi} d\theta \frac{1 - \cos^2(\theta)}{2} \left( \frac{A}{|\mathbf{q}|^2} \right) \left[ \frac{\epsilon_0 h v_F}{e^2} \right] |\mathbf{q}|=2k_F \sin(\theta/2)
\]

\[
\approx \left\{ \frac{v_F g^2 \mu_L^2}{32\pi(\lambda_L + 2\mu_L)^2} A + \cdots \frac{\epsilon_0 h v_F}{e^2} \leq 1 \right\} \quad \left\{ \frac{v_F g^2 \mu_L^2}{8\pi(\lambda_L + 2\mu_L)^2} A + \cdots \frac{\epsilon_0 h v_F}{e^2} \geq 1 \right\}
\]

\[
\tau_g^{-1} = \frac{2\pi N(E_F)}{\hbar} \frac{g^2 (\lambda_L + \mu_L)^2}{4\pi^2 (\lambda_L + 2\mu_L)^2} \times 2 \times \int_0^{\pi} d\theta \frac{1 - \cos(\theta)}{2} \left( \frac{A}{|\mathbf{q}|^2} \right) \left[ \frac{\epsilon_0 h v_F}{e^2} \right] |\mathbf{q}|=2k_F \sin(\theta/2)
\]

\[
= \frac{g^2 (\lambda_L + \mu_L)^2 A}{4\pi h v_F k_F (\lambda_L + 2\mu_L)^2} \quad (5.10)
\]

The mobility is given by \( \mu = \sigma/(ne) = 2e^2 \frac{v_F k_F \tau}{h} = 2e^2 \frac{v_F}{h} k_F \), and when considering the limit of \( \epsilon_0 \ll e^2/(\hbar v_F) \), we find
\[ \frac{1}{\mu} = \frac{\hbar A}{e} \left[ \frac{g_1^2 \mu_L^2}{32\pi e^4 (\lambda_L + 2\mu_L)^2} + \frac{g_2^2 (\lambda_L + \mu_L)^2}{4\pi (hv_F)^2 (\lambda_L + 2\mu_L)^2} \right], \quad (5.11) \]

while, for case of \( \epsilon_0 \gg 1 \), the mobility is then

\[ \frac{1}{\mu} = \frac{\hbar A}{e} \left[ \frac{g_1^2 \mu_L^2}{8\pi \epsilon_0^2 (hv_F)^2 (\lambda_L + 2\mu_L)^2} + \frac{g_2^2 (\lambda_L + \mu_L)^2}{4\pi (hv_F)^2 (\lambda_L + 2\mu_L)^2} \right] \quad (5.12) \]

### Charge density inhomogeneities near the Dirac point

We calculate the amplitude of charge puddles near the neutrality point by using

\[ n^* (\vec{r}) = \frac{1}{\pi} \left( \frac{V(\vec{r})}{h v_F} \right)^2 \quad (5.13) \]

Only the scalar potential in \eqref{5.6} are able to generate to charge density fluctuations. The average value of the charge density fluctuations are found to be

\[ n^* = \frac{\langle V^2 (\vec{r}) \rangle}{\pi h^2 v_F^2} = \frac{1}{4\pi^3 h^2 v_F^2} \int d^2 \vec{q} \frac{\langle V_s (\vec{q}) V_s (-\vec{q}) \rangle}{\epsilon^2 (\vec{q})} \]

\[ \approx \frac{g_1^2 \mu_L^2 A}{2\pi^2 (\lambda_L + 2\mu_L)^2 (hv_F)^2} \times \left\{ \frac{\log \left( \frac{\Lambda}{k_F} \right)}{4\epsilon_0^2 \log \left( \frac{\Lambda_{\epsilon_0}}{\Lambda_{\epsilon_0}} \right)} \right\} \frac{\hbar v_F \epsilon_0}{e^2} \lesssim 1 \quad (5.14) \]

where \( \Lambda \sim 1/a \) is a high momentum cut-off. In the presence of a dielectric with a large value of \( \epsilon_0 \), the momentum cut-off, \( \Lambda_{\epsilon_0} \) is given by the condition \( \epsilon_{\text{dielectric}} (\Lambda_{\epsilon_0}) \sim \epsilon_0 \), and it is determined by the \( \vec{q} \) dependence of the dielectric function (see next section). The lower cut-off is \( \Lambda'_{\epsilon_0} \approx (4e^2 k_F^* \epsilon_0) / (\epsilon_0 hv_F) \) .

Here and in \eqref{5.14} \( k_F^* = \sqrt{\pi n^*} \). Using the expressions for the mobility in \eqs\( \ref{5.11} \) and \( \ref{5.12} \), we obtain for \( \epsilon_0 \lesssim 4 \) (i.e., for the case of hBN and SiO\(_2\) substrates)

\[ \frac{1}{\mu n^*} \approx \frac{h}{4e} \left[ \frac{(hv_F)^2}{8e^4} + \frac{g_2^2 (\lambda_L + \mu_L)^2}{g_1^2 \mu_L^2} \right] \frac{1}{\log \left( \frac{\Lambda}{k_F} \right)} \quad (5.15) \]
and, for $\epsilon_0 \gg 4$

$$
\frac{1}{\mu n^*} \approx \frac{h}{e} \left[ 1 + \frac{\epsilon_0^2 g_2^2 (\lambda_L + \mu L)^2}{g_1^2 \mu L^2} \right] \log \left( \frac{\Lambda_{vg} \epsilon_0 \hbar v_F}{4e^2 \hbar F} \right)
$$

(5.16)
Three-dimensional (3D) topological insulators are characterized by the presence of a band gap in their bulk and gapless Dirac fermions at their surfaces. New physical phenomena originating from the presence of the Dirac fermions are predicted to occur, and to be experimentally accessible via transport measurements in suitably designed electronic devices. Here we study low-temperature transport through superconducting junctions fabricated on thin Bi$_2$Se$_3$ single crystals, equipped with a gate electrode. In the presence of perpendicular magnetic field B, sweeping the gate voltage enables us to observe the filling of the Dirac fermion Landau levels, whose character evolves continuously from electron- to hole-like. When B=0 T, a supercurrent appears, whose magnitude can be gate tuned, and is minimum at the charge neutrality point determined from the Landau level filling. Our results demonstrate how gated nano-electronic devices give control over normal and superconducting transport of Dirac fermions at an individual surface of a 3D topological insulators.

The content of this chapter has been published in Nature Communications: Benjamin Sacépé, Jeroen B. Oostinga, Jian Li, Alberto Ubaldini, Nuno J.G. Couto, Enrico Giannini and Alberto F. Morpurgo Gate-tuned normal and superconducting transport at the surface of a topological insulator Nature Communications 2 575 (2011)
6. Electronic transport through a topological insulator

6.1 Introduction

The classification of crystalline solids in terms of their electronic properties as metals and insulators is one of the early successes of quantum mechanics. Metals are those materials in which a finite density of states at the Fermi energy enables electrons to move freely, and to conduct electricity. On the contrary, when the Fermi energy lies in an energy gap with no electronic state available, electrons cannot propagate, causing the insulating behaviour. Remarkably, it has been recently discovered\cite{28,30} that this long-established classification is incomplete: topological insulators (TIs), realized in compounds with very strong spin-orbit interaction, represent a third class of materials, possessing an energy gap in their bulk – similarly to insulators – and electronic states that remain ungapped – such as in a metal – at their surfaces.

The nature of the surface states in TIs depends on their dimensionality. In two-dimensional (2-D) TIs, they consist of one-dimensional helical modes propagating at the system edges\cite{28,30}, whose existence has been revealed in transport experiments\cite{33,34}. In the three-dimensional (3-D) case, the surface states are 2-D gases of Dirac fermions\cite{35,115,147–149}. Following theoretical predictions\cite{147,149}, Dirac fermions have been observed in several bismuth-based materials in angle-resolved photoemission experiments\cite{37,150,151} and scanning tunnelling spectroscopy\cite{152,153}. Contrary to the 2-D case, however, for 3-D TIs probing and controlling Dirac fermions in transport measurements\cite{154–158} is difficult, because a large parallel conductance originating from bulk states is usually present\cite{157,159–162}. This hinders the use of nano-fabricated devices based on 3-D TIs, which is essential to gain control over the Dirac fermions and to probe some of their most unique properties.

Here we study transport through thin ($\sim 10$ nm) Bi$_2$Se$_3$ layers exfoliated from single crystals and transferred onto (doped) Si/SiO$_2$ substrates functioning as gates, and we show that the ability to modulate the carrier density is a powerful tool to investigate Dirac surface fermions. As superconductor/TI junctions are of interest for the investigation of so-called Majorana fermions\cite{163,164} the Bi$_2$Se$_3$ layers were contacted with two closely separated Al/Ti superconducting electrodes ($T_c \sim 1$ K; Fig.6.1), enabling us to investigate in a same device the normal state transport at high magnetic field $B$, and the possibility to gate-control induced superconductivity at $B = 0T$. 
6.2 Gate-tuned Shubnikov-de Haas oscillations of Dirac fermions

We realized several similar devices and here we discuss data measured on one of them that are representative of the overall behaviour observed (data from the other devices are shown in the Appendix). We first discuss the dependence of the normal state resistance measured at $T = 4.2$ K on gate voltage $V_g$ and magnetic field $B$, focusing on the qualitative aspects of the data, which are sufficient to conclude that Dirac surface fermions are present and can be gate controlled. The sample resistance is $R = 70\,\Omega$ and shows a 15-20% variation when $V_g$ is swept from -80 V to +50 V, roughly symmetrical with respect to $V_g^{CN} \sim -10$ V (Fig. 6.2(a)). This non-monotonic dependence is a manifestation of ambipolar transport involving both electrons and holes, and indicates that...
Gate voltage dependence of the normal state resistance. The maximum at $V_g \sim -10$ V, provides a first indication of ambipolar transport. The $V_g$ dependence originates from the modulation of the conductivity of the surface close to the gate, and can be quantitatively described as $\delta\sigma(V_g) = n_{\text{Dirac}}(V_g) e \mu$ (inset of panel (a): the yellow line corresponds to the calculated $\delta\sigma(V_g)$). (b) Full dependence of the resistance on $V_g$ and magnetic field $B$ (the measurements are performed by sweeping $V_g$ at fixed $B$, for different values of $B$). As a function of $B$ the resistance increases approximately linearly, exhibiting clear oscillations that are enhanced by deriving the data with respect to either $V_g$ or $B$. (c) Oscillations in $-d^2R/dB^2$ ($V_g = -62$ V), periodic in $1/B$, as it is typical for the Shubnikov-de Haas (SdH) effect (Fig. 6.3(b)). The oscillations are gate-voltage-dependent and disperse in opposite directions when $V_g$ is swept across $V^CN_g$, which indicates that the character of the charge carriers changes from electron ($V_g > V^CN_g$) to hole ($V_g < V^CN_g$). These oscillations are not present when the magnetic field is applied parallel to the surface of the Bi$_2$Se$_3$ flake, which is seen in Fig. 6.3. Additional information can be obtained if the amplitude of the oscillations is enhanced by looking at the quantities $d^2R/dB^2(B,V_g)$ and $d^2R/dV^2_g(B,V_g)$ (Fig. 6.4(a)-(b) respectively)
6.2. Gate-tuned Shubnikov-de Haas oscillations of Dirac fermions

Figure 6.3: The left panel shows the magnetoresistance as a function of gate voltage and in-plane magnetic field. It is apparent that the application of the magnetic field parallel – rather than perpendicular – to the crystal has only a small effect on the resistance. No fine features are present in this measurement. This is confirmed by taking the second derivative with respect to magnetic field (shown in the right panel), where only noise is seen.

or by subtracting the positive magnetoresistance background\[^1\]. The two methods give fully consistent results, and here we focus on the discussion of the second derivative, which is free from any possible arbitrariness associated to the background subtraction. Figure 6.4(a) shows that – next to the oscillations dispersing with $V_g$ – features that do not depend on gate voltage are also present. These features are also periodic in $1/B$: indeed the Fourier spectrum of the data plotted versus $1/B$ (Fig. 6.4(c)) shows a peak dispersing with gate voltage as well as a peak whose position is $V_g$-independent. Interestingly, at $V_g = 0$ V the frequency of the two peaks – the one dispersing with gate voltage and the $V_g$-independent one – are nearly the same.

These observations give clear indications as to the nature of the electronic states that are involved. Finding an electron-to-hole crossover that occurs in a small gate voltage range ($\sim -10$ V) – which corresponds to a rather small amount of accumulated charge (few times $10^{11}$ cm$^{-2}$) – implies that the electronic states responsible for the SdH oscillations cannot be in the bulk band of the material. As the bulk bands are separated by a gap of 300 meV\[^1\], crossing over from electron to holes would require a change in gate voltage that is well more than one order of magnitude larger. A continuous crossover from electron to hole SdH is known to occur (and has been observed) only in gapless systems of chiral fermions (for example, graphene or bilayer graphene\[^2\]). Indeed, gapless Dirac fermions are known to be present at the surface of Bi$_2$Se$_3$ (refs.\[^1\]|\[^2\]|\[^3\]). The electron-to-hole crossover as a function of gate voltage that we observe in the SdH oscillations, therefore, is a clear

\[^1\]The technical details behind these methods can be found in the Appendix.
Figure 6.4: (a) Plot of $-d^2R/dB^2$ (in arbitrary units) as a function of $B$ and $V_g$ (fan diagram). The features dispersing with $V_g$ originate from the formation of Landau levels of Dirac fermions on the bottom surface of the Bi$_2$Se$_3$ crystal. Features with a $V_g$-independent position are associated to Landau levels on the top surface. The white dashed lines (and the numbers indexing the LLs) indicate the condition for the Fermi level to fall between two Landau levels for holes on the bottom surface (see discussion in the main text). They correspond to $B = n(h/e)(1/(N+1/2))$ ($n$ is the density of Dirac holes), as expected for Dirac fermions. A similar indexing also works for electrons (i.e., positive gate voltage). (b) $-d^2R/dV^2$ plot showing dispersing features corresponding to those observed in the $-d^2R/dB^2$ plot (the $V_g$-independent features disappear when taking the $V_g$ derivative). An asymmetry between electrons and holes at high magnetic field – already visible in the $-d^2R/dB^2$ plot – is present, which is likely to originate from the opening of a small Zeeman gap\cite{160}, which shifts the position of the zero-energy LL to either positive or negative energies depending on the sign of the g-factor. (c) Fourier spectrum of $-d^2R/dB^2$, as a function of $V_g$ and frequency $B_F$. From the position maxima in the spectrum we extract the density of carriers according to the relation $n = B_F e/h$. Again, the features dispersing with $V_g$ originate from Landau levels of Dirac fermions on the bottom surface, and the $V_g$-independent features (pointed to by the red arrow), from states on the top surface. At $V_g = 0$ V, the peaks of the dispersing and non-dispersing features occur approximately at the same frequency, implying that the density of electrons on the two surfaces of the crystal are also the same. The blue line is the frequency of the SdH oscillations calculated using equation (6.1) ($B_F = n_{\text{Dirac}}(V_g)h/e$) with no free parameter, in good agreement with the gate dependent position of the (broad) peak in the Fourier spectrum.

Indication of the presence of Dirac fermions in our devices. It also confirms, as it was already concluded from the observation of ambipolar transport at $B = 0$T, that the Fermi level at the surface is inside the gap of the bulk bands of Bi$_2$Se$_3$.

The conclusion that Dirac fermions are responsible for the $V_g$-dependent
SdH oscillations also explains the presence of SdH oscillations with a $V_g$-independent frequency. In fact, Dirac fermions are not only present on the bottom surface of the Bi$_2$Se$_3$ flake but also on the top surface. As this top surface is further away from the gate electrode, it is electrostatically screened by carriers that are accumulated on the bottom surface and by states that are present in the 'bulk' of the flake (see below). Accordingly, sweeping the gate voltage does not lead to a change in the carrier density on the top surface, and the frequency of the SdH oscillations associated to these carriers is constant. The finding that at $V_g = 0$ V, the $V_g$-independent and the $V_g$-dispersing oscillations have roughly the same frequency can be explained naturally, as when no gate voltage is applied the two surfaces of the Bi$_2$Se$_3$ flake host approximately the same carrier density. This finding could not be explained if the two families of SdH oscillations had different origin. We conclude that the presence of surface Dirac fermions at the surface of Bi$_2$Se$_3$ explains all the qualitative aspects of our observations – continuous evolution from electron to hole SdH, the presence of two families of SdH with different response to the gate voltage and having the same frequency at $V_g = 0$ V, and the observation of ambipolar transport. No other known scenario can account for these findings.

6.3 Bulk contribution to the magnetoresistance

Having established the presence of Dirac surface fermions from qualitative aspects of the data only is important, because it ensures that this conclusion does not depend on any specific assumption that needs to be made to interpret detailed aspects of the data quantitatively. To proceed with such a more quantitative analysis, we first note that in our devices another transport channel in parallel to the surface states is present, which gives a dominant contribution to the measured conductance. Indeed, the device resistance – approximately 70Ω – is much smaller than what can be expected from the presence of surface Dirac fermions alone. To estimate the conductivity of Dirac fermions, a carrier mobility $\mu$ of 1000-2000 cm$^2$/Vs$^{-1}$ can be taken, corresponding to the best values reported in the literature for Bi$_2$Se$_3$ (refs [165, 166]; see also below).

The surface Dirac states therefore coexist with other states in the system present inside the Bi$_2$Se$_3$ flake, at the same energy (that is, inside the gap.

---

2Both the bulk electronic states($\sigma_{1B}$) and the surface states($\sigma_{SS}$) contribute to the total conductivity ($\sigma_T$) as $\sigma_T = \sigma_{SS} + \sigma_{1B}$. The $\sigma_{SS}$—roughly estimated from the carrier density $n$ (obtained from the SdH oscillations) and assuming the typical mobility values found in our (and other related) work—only contributes approximately 10% to $\sigma_T$, which indicates that bulk the electronic states bulk dominating transport.
between bulk conduction and valence band). We attribute the origin of these states to the presence of an impurity band caused by the disorder present in Bi$_2$Se$_3$, which is known to be large even in the best crystals. Indeed, a rather large density of states inside the gap, coexisting with the surface Dirac fermion states, is reproducibly seen in scanning tunnelling spectroscopy experiments. The density of states $\nu_{\text{Bulk}}$ coexisting with the Dirac surface states can be estimated by comparing the density of charge extracted from the SdH frequency $B_F$ with that obtained from the known capacitance to the gate voltage. At $V_g - V_{g \text{CN}} = -70$ V, for instance, the frequency of the SdH oscillations corresponds to a density $n = B_F e/h = 1.05 \times 10^{16} m^{-2}$, whereas $n_{\text{Tot}} = C(V_g - V_{g \text{CN}})/e = 5.1 \times 10^{16} m^{-2}$. The discrepancy is only apparent, because with changing $V_g$ charge is accumulated near the surface on a depth given by the Thomas-Fermi screening length ($\lambda_{TF} \sim 3 - 4$ nm) and the occupation of states in the impurity band reduces the density of Dirac fermions $n_{\text{Dirac}}(V_g)$ to (only a fraction of the accumulated charge occupies Dirac fermion states):

$$n_{\text{Dirac}} = \pi (h v_F)^2 \left[ -\nu_{\text{Bulk}} \lambda_{TF} \sqrt{\left(\nu_{\text{Bulk}} \lambda_{TF}\right)^2 + \frac{n_{\text{Tot}}}{\pi (h v_F)^2}} \right]^2$$

with $v_F = 5 \times 10^5$ m/s. By imposing that at $V_g = -80$ V $n_{\text{Dirac}}(V_g)$ coincides with the density extracted from the fan diagram, we obtain $\nu_{\text{Bulk}} \lambda_{TF} = 3.6 \times 10^{13} \text{ cm}^{-2} \text{ eV}^{-1}$, corresponding to $\nu_{\text{Bulk}} \sim 7 \times 10^{19} \text{ cm}^{-3} \text{ eV}^{-1}$, comparable to literature estimates for similar crystals.

In fact this impurity band originates from defect states with a large Bohr radius – about 4-5 nm, owing to the large relative dielectric constant of the material $\epsilon \sim 110$ (ref. [160]). This large radius causes a strong overlap of the impurity states, as well as a strong overlap of the impurity states with the surface Dirac fermion states (the Bohr radius of the impurity states is also comparable to the Bi$_2$Se$_3$ layer thickness), resulting in a high conductivity in the impurity band. The large value of $\epsilon$ also suppresses Coulomb effects, which are usually the dominant mechanism lowering the conductivity of impurity bands, and tends to cause a more insulating-like behaviour through the opening of a Coulomb gap.

To find the relation between $n_{\text{Dirac}}$ and $n_{\text{Tot}}$ we imagine to vary $V_g$ starting from the charge neutrality point, and we impose that in equilibrium, the highest occupied states in the Dirac surface band and in the bulk impurity band have the same energy $E_F$. In terms of the density of states of the Dirac electrons and of the impurity band we have:

$$n_{\text{Tot}}(V_g) = n_{\text{IB}}(V_g) + n_{\text{Dirac}}(V_g) = \nu_{\text{Bulk}} \lambda_{TF} E_F + \frac{1}{4\pi (h v_F)^2} E_F$$

We solve this equation for $E_F$ as a function of $n_{\text{Dirac}}$ and and insert the value found in the expression for the density of Dirac fermions to obtain eq. (6.1).

Note that the density of bulk impurity band states extracted from the data, is comparable to the density of states of the impurity band that forms in degenerately doped silicon. For silicon, an impurity band (that causes the material to be conducting at very low...
6.4 Landau levels for Dirac fermions

We can then use equation (6.1) to calculate the frequency of the SdH oscillations for all values of $V_g$, $B_{F}(V_g) = (h/e)n_{\text{Dirac}}(V_g)$, and we find quantitative agreement with the position of the peak in the Fourier spectrum with no adjustable parameters (blue line in Fig. 6.3(c)). Equation (6.1) also naturally reproduces the $V_g$ dependence of the conductivity ($\delta\sigma(V_g)$) at $B = 0$ T. The inset of Fig. 6.2(a) shows that $\delta\sigma(V_g) = n_{\text{Dirac}}(V_g)e\mu$ is in excellent agreement with the measured data with $\mu = 2500 \text{ cm}^2/\text{Vs}$. This value is comparable, but slightly higher, than what has been reported previously for Bi$_2$Se$_3$ surface states [165, 166]; when inserted in the criterion for the occurrence of SdH oscillations, $\omega_c\tau = \mu B \geq 1$ (ref. [167]) it gives $B \geq 4T$, which agrees with experiments (oscillations due to top-surface Dirac electrons start at approximately half this field – implying $\mu \sim 5000 \text{ cm}^2/\text{Vs}$ – probably because contact with SiO$_2$ slightly reduces $\mu$ at the bottom surface).

6.4 Landau levels for Dirac fermions

We now proceed to discuss the indexing of the Landau levels responsible for the SdH. For massless Dirac fermions, when $n = (N+1/2)B/(h/e)$, the $N$th LL is completely filled and the Fermi energy is located in between the $N$th and the $(N+1)$th LLs (here $n$ is the density of surface Dirac fermions, $N$ the integer LL index and $B/(h/e)$ is the LL degeneracy [6]). A quantitative interpretation of the data measured in our samples, however, requires an assumption to be made: it is a priori unclear whether maxima or minima of the measured oscillations correspond to having completely filled LLs at the surface, because both conductance of the Dirac fermions and parallel conductance depends on magnetic field. As the background conductance is $10\times$ larger than the conductance of the surface states, its contribution to the oscillations is likely to dominate. We therefore assume that the dominant contribution to the magnetoresistance oscillations is due to the background conductance itself, which is modulated by the formation of surface LLs. Specifically, with the flake being only 10 nm thick, carriers responsible for the background conductance are strongly coupled to the surface states (this is indicated by the fact that the diffusion constant of these carriers and of the Dirac surface fermions is temperature) develops at doping concentrations of a $3 - 4 \times 10^{19} \text{ cm}^{-3}$ (ref. [168]). The states responsible for this impurity band are close to either the valence or the conduction band (depending on the sign of the dopants), and they are distributed in a fraction of 1 eV (corresponding to the gap of silicon). The resulting density of states (equal to the concentration divided by this energy range) coincides with the value that we estimated for Bi$_2$Se$_3$. However, due to the larger $\epsilon$ of Bi$_2$Se$_3$, the conductivity in the impurity band is much larger when compared with silicon.
6. Electronic transport through a topological insulator

According to the relation characteristic for massless Dirac fermions, $N = \frac{(nh/e)}{B} - \frac{1}{2}$, where $n$ is the density of charge carriers (electrons or holes), whereas for normal fermions $N = \frac{(nh/e)}{B}$. Therefore, looking at how $N$ extrapolates for $\frac{1}{B} \to 0$ allows us to discriminate between massless Dirac and normal fermions. The continuous lines are linear least square fits to the data $N = a \frac{1}{B} + b$. They show that as, $N$ extrapolates to close to $-1/2$ as expected for massless Dirac fermions. The inset shows the extrapolation value $(b)$ obtained by least square fitting for $\sim 20$ different values of gate voltage (in the region with $V_g$ in between $\sim -40$ and $+15$ V, the oscillations are not sufficiently pronounced to perform the analysis). The data show that $b$ fluctuates close to $-1/2$ (and not around 0). Consistently, the average of $b$ over gate voltage is $<b> = -0.4 \pm 0.1$.

approximately the same). When the Fermi level at the surface is inside (in between) LLs, the density of states at the Fermi energy associated to the surface LLs has a maximum (minimum), so that carriers responsible for the background conductance have maximum (minimum) probability to scatter, and the background resistance is also maximum (minimum); in other words, the formation of surface LLs modulates the diffusion constant of the carriers responsible for the background conductance). On this basis, we index the LLs

---

6 The Diffusion constant of the bulk carriers can be estimated through the Einstein relation as $D_{\text{Bulk}} = \frac{\sigma_{\text{Bulk}}}{\rho_{\text{Bulk}} e^2} \simeq 1.5 \times 10^{-2} \text{m}^2/\text{s}$, where $t = 10\text{nm}$ is the thickness of the crystal. For the case of the Dirac carriers their diffusion constant is given by $D_{\text{Dirac}} = \frac{1}{2} v_F \tau = \frac{h k_F v_F e}{2 e} \simeq 1.5 \times 10^{-2} \text{m}^2/\text{s}$.
6.5 Gate-tuned supercurrent through surface states

Measurements at $B = 0$ T and $T=30$ mK, with the Al/Ti electrodes in the superconducting state ($T_c \sim 1$ K), show that the ability to gate-control the device is also essential to establish that the Dirac fermions contribute to mediate the superconducting correlations induced by the contacts. In the measured differential resistance, a large suppression is observed when the bias is decreased below twice the superconducting gap (Fig. 6.6(a)), a distinctive signature of Andreev reflection, indicating the high transparency of the contacts [120]. At zero bias, a supercurrent is present (Fig. 6.6(b)), with critical current $I_c \sim 200$ nA. It is apparent that the critical current depends on the gate voltage, and that it has a minimum in correspondence of the charge neutrality point extracted from the LL fan diagram. This finding shows the ambipolar character of the supercurrent, and makes clear directly from the experimental data that at least part of the supercurrent is carried by either Dirac electrons or holes at the bottom Bi$_2$Se$_3$ surface (and not only by the carriers in the bulk states). By enabling to separate the contributions of the surface and bulk channels to superconducting transport, gate control of supercurrent certainly provides an effective tool for the investigation of proximity effect in 3-D TIs (whose complete understanding – for example, the very small $R_nI_c$ product, $\sim 15 \mu V \ll 2\Delta/e \sim 300 \mu V$ (Fig. 6.6(c)) – goes beyond the scope of this thesis).
Figure 6.6: (a) Differential resistance of the junction in the superconducting state ($B = 0$, $T = 30$ mK), as a function of bias voltage $V$ ($V_g = +50$ V). A large decrease is seen upon lowering $V$ below $2\Delta/e \sim 300\mu$eV, due to Andreev reflection (the sharp feature around $V = 0$ originates from the presence of the supercurrent; the origin of the split peak at $V \sim 2\Delta/e$ is currently unknown). (b) Junction I-V curves showing a gate-tunable supercurrent. The critical current exhibits a minimum at $V_g \sim -10$ V, corresponding to the $V_g$ value at which the maximum of the normal state resistance occurs. (c) $R_nI_c$ product of the junction obtained using for $R_n$ the measured normal state resistance. Its value ($\sim 15\mu$ eV) is about 20 times smaller than expected ($R_nI_c \sim 2\Delta/e \sim 300\mu$eV).

6.6 Discussion and Conclusions

Our experiments clearly show how the use of a gate electrode to tune the surface density of charge carriers is a very effective tool to identify and explore the contribution to transport of surface Dirac fermions in devices based on 3-D TIs. The possibility to tune the carrier density electrostatically, for instance, enables the observation of Dirac electron and hole transport in a single device, making it possible to control the filling of their Landau levels. It also allows the identification of transport properties associated with the two opposite material surfaces, owing to their different electrostatic coupling to the gate electrode. Finally, it is crucial to establish that Dirac fermions are capable of mediating superconducting correlations induced by the contacts, a conclusion drawn directly from the experimental data that – in the presence of a large parallel contribution to transport – would be difficult to draw in any other way. It appears from our experiments that the quality of the BiSe-based 3-D topological materials currently available would greatly benefit from considerable improvements, which should aim at decreasing the...
amount of states present in the bulk bandgap of the crystals and at increasing the carrier mobility. Nevertheless, even with the quality of the existing materials, performing new and interesting transport experiments, to investigate the physics of Dirac surface fermions is certainly possible. These experiments should address, among other, the detailed behaviour of the Dirac fermions as a function of the crystal thickness \cite{170, 171} – where ARPES experiments have shown an interesting dimensional crossover to occur \cite{172} – and the nature of proximity effect \cite{163, 164}, both of which currently remain phenomena virtually unexplored experimentally.
6.7 Appendix

In this section we briefly discuss the methods and experimental data obtained from the measurement of other Bi$_2$Se$_3$ nanodevices.

Temperature dependence

As characterization of the Bi$_2$Se$_3$ crystals used in our experiments, we have also measured the temperature dependence (from 250 to 4.2 K) of the resistance for two devices, and compared the results to measurements reported in the literature. The two devices were fabricated using nearby layers ($\sim$100 µm apart) found on a same substrate, implying that they originate from a same region of the starting bulk Bi$_2$Se$_3$ crystal. The thickness of one of the layers was $\sim$ 4 nm (as estimated using a Keyence microscope equipped with a laser interferometer) and that of the other was $\sim$10 nm. The temperature dependence of the resistance is shown in Fig. 6.7 (unfortunately the 4 nm device broke early after starting the experiments). Although both layers were rather highly conducting ($\rho \sim 1$mΩcm, in the range reported in the literature$^{[159-162]}$), the thinnest one (Fig. 6.7(a)) was found to exhibit a weak insulating temperature dependence (resistance slightly increasing with lowering T), whereas in the thicker one (Fig. 6.7(b)) the resistance decreased with lowering T. This difference may indicate the opening of a gap in the surface states due to hybridization of the Dirac bands on opposite surfaces, which for a 4nm thickness should lead to a gap of about 10 meV (for a 10-nm thickness the gap is predicted to be negligible).

![Figure 6.7: Temperature dependence of the resistance of two different Bi$_2$Se$_3$ devices. One is 4 nm thick (a) and shows a weakly insulating behavior; the other (b) corresponds to the device whose data are shown above: it is approximately 10 nm thick and it exhibits metallic behavior.](image-url)
Experimental data from other Bi$_2$Se$_3$ nanodevices.

We show data from two additional Bi$_2$Se$_3$ devices that we measured, which exhibit the same behaviour that we have discussed in section 6.2. In both these two other devices, the fan diagram of Landau levels is clearly seen in the magnetoresistance measurements as a function of gate voltage and magnetic field. In particular, clear signatures of LLs due to electrons and holes dispersing in opposite directions, as the gate voltage is tuned across the charge neutrality point, are present (note that the position of the charge neutrality point in gate voltage is comparable in the different devices always ranging between -10 and -20 V). Also in these devices the evolution as a function of gate voltage is continuous, pointing to the absence of a gap, consistently with the massless character of the carriers. For one of the devices (see Fig. 6.8) the quality of the data is sufficient to check the extrapolation of the $N$ vs $-1/B$ plot and also in this case we find that the extrapolation is only compatible with “-1/2”.

![Surface state Shubnikov-de Haas oscillations measured on a second device.](image)

**Figure 6.8:** Surface state Shubnikov-de Haas oscillations measured on a second device. Left panel: Fan diagram of Landau levels measured on a second device (the plot shows $-\frac{d^2R}{dB^2}(V_g, B)$). The overall behavior is identical to that of the device shown in the main text, exhibiting gate-dependent features fanning out from the charge neutrality point (which in this device is close to -20V) and gate-independent features that originate from SdH oscillations due to carriers at the surface far away from the gate. At a quantitative level, the quality of the data is not as good as that of the measured data on the device discussed in section 6.2, but a quantitative analysis of the $N$ vs $-1/B$ relation is possible. This is shown in the right panel, for different values of gate voltage (when the gate voltage is close to the charge neutrality point, a quantitative analysis is not feasible, as discussed in section 6.2). Also in this case, the result is compatible with an extrapolated value of -0.5 and not of 0 (see inset). Note in the inset of the right panel that the points that deviate the most from -0.5 are also those on which the error – obtained from the linear fitting procedure – is the largest. Points for which the error is small are close to -0.5.
Electronic transport through a topological insulator

Figure 6.9: Fan diagram measured on a third device. Both the dispersing, gate-dependent features and the "vertical" gate-independent features are clearly visible in the data, even though they are less pronounced as compared to the data measured in the device shown in the and that shown in Fig. 6.8. As a consequence (and also because the number of LLs that can be resolved is smaller), it is not possible to perform an accurate indexing of the levels on this device. Nevertheless, the data shown here represent an additional confirmation that the qualitative behavior observed in the other two devices is reproducible, and that the ambipolar transport and gate-tunable quantum resistance oscillations that we discuss are a robust phenomenon, commonly present in our devices.

For the other device (see Fig. 6.9), the number of LLs visible is not enough to perform a quantitative analysis of the LL indexing.

Together with the device whose data are shown in the previous sections, the two other devices discussed here show that: (1) ambipolar transport and SdH oscillations due to electrons and holes evolving smoothly as a function of gate voltage are present in several devices, (2) in all cases where we can index the LLs, the indexing is only compatible with massless Dirac fermions (as it should be expected from the absence of a gap in the fan diagram).

Background magnetoresistance

Here we discuss in detail several more technical aspects related to the analysis of our magnetoresistance measurements \( R(V_g, B) \), and to the analysis of the SdH effect by removing this positive magnetoresistance background. We emphasize that in section 6.4 we have discussed the quantity \(-\frac{d^2R}{dB^2}(V_g, B)\), because this quantity can be obtained directly from the experimental data without any "arbitrariness" that may be present in removing the background magnetoresistance. However, as we will show, removing the background is particularly useful to analyze the data at high magnetic field, and it allows to find clear features originating from Landau levels \( N = 1 \) and 2, that are not easy to extract from the analysis of \(-\frac{d^2R}{dB^2}(V_g, B)\). As discussed in section 6.4, the measured magnetoresistance is due to the change in the conduction mediated
Figure 6.10: Temperature dependence of the magnetoresistance oscillations. (a) Temperature dependence of the resistance oscillations observed in the second derivative of the resistance with respect to $B$ (measured at $V_g = -40$ V). Despite the fact that oscillations remain visible up to fairly large temperature (as it can be expected, owing to the large energy spacing between LLs that is characteristic of Dirac fermions), their amplitude increases only slowly with lowering temperature. This is a consequence of the presence of the continuous density of states associated to the bulk impurity band. (b) Magnetoresistance measured at $V_g = -80$ V and $T=4.2$ K. Note how at high magnetic field, the oscillations do resemble true plateaus: at these high field values, the analysis of SdH by looking at the derivative with respect to magnetic field starts not to be appropriate, because the effect of LLs cannot be any more thought of as that of small oscillations superimposed onto smooth background. That is why in Fig.6.4(a) of section 6.4, features at high field are not sharply defined.

by carriers in the impurity band, which can scatter in the states of the Landau Levels of the surface Dirac. This mechanism leads to a maximum in resistance when the Fermi level at the surface is in the middle of a Landau level and a resistance minimum when the Fermi level at the surface is in between two Landau levels (also in the two-terminal measurement configuration employed in our work). At low magnetic field, where the SdH effect starts to be visible, the modulation of the magnetoresistance is small, and the features can be well described as a sinusoidal oscillation superimposed on a background. Under these conditions, looking at the quantity $-\frac{d^2R}{dB^2}(V_g, B)$ provides an effective way to analyze the data. At higher magnetic field, however, the degeneracy of the Landau levels becomes larger and their effect leads to extended plateaus (see Fig.6.11(b), for instance). In this regime, the features originating from LLs are not any more well described by sinusoidal oscillations superimposed on the positive background.

To analyze the data at high field, we show here that features become visible after removing the positive magnetoresistance background (the presence of these features does not depend on the way in which the background is removed, which at most affect their precise position and sharpness). The data obtained
6. Electronic transport through a topological insulator

Figure 6.11: Fan diagram obtained after background subtraction. Color plot of the measured magnetoresistance as a function of magnetic field $B$ and gate voltage $V_g$, after subtracting a smooth background. The green dotted lines denote the position of the Landau levels (indexed by the corresponding numbers), as expected from the analysis of $-\frac{d^2 R}{dB^2}(V_g, B)$ discussed in Chapter 6. The good agreement with the position of the measured features shows that subtracting a background allows a correct analysis of the LLs. This analysis is particularly useful at high magnetic field, since it makes clearly apparent the LLs with $N = 1$ and $2$, which could not be identified in the color plot of $-\frac{d^2 R}{dB^2}(V_g, B)$ after removing the positive magnetoresistance background are shown in the color plot in Fig. 6.11. It is apparent that the $N = 1$ and $N = 2$ Landau levels are clearly visible, at values of $B$ and $V_g$ in agreement with what is expected from the analysis performed on $-\frac{d^2 R}{dB^2}(V_g, B)$. Note that, for the indexing of the Landau levels, it is in any case important to confine the analysis to small magnetic field range, in order to ensure that the Zeeman effect (which contributes to the opening of a gap, thereby suppressing the half-integer quantization) is negligible. A good indication for this is the presence of electron-hole symmetry in the Landau level filling, since the opening of a gap shifts the zero energy Landau level either in the conduction or the valence band and breaks this symmetry. In the range where we have analyzed $-\frac{d^2 R}{dB^2}(V_g, B)$ as discussed in section 6.4, symmetric Landau level filling is rather well satisfied. At the largest fields reached in the experiment, violation of this symmetry starts to appear, indicating that these large magnetic fields should not be included in the analysis.

Finally, we comment on the presence of states in the impurity band with a continuous density of states, which coexist (at the same energy and overlapping in space) with the Landau levels. As discussed above, the electrons in the impurity band (which give a large contribution to transport in parallel to that of the surface Dirac electrons) are strongly hybridized with the surface
states, which is why the formation of LLs affects the transport through the bulk. Therefore, contrary to the usual case where at sufficiently large $B$ the Landau level separation becomes larger than their broadening, in the present case the Landau levels co-exist for all values of $B$ with the continuous density of states in the impurity band. This has several consequences. For instance, it weakens the temperature dependence of the Shubnikov-de Haas oscillations (as compared to the usual exponential dependence), which indeed we observe experimentally (see Fig. 6.11(a)). For Dirac fermions, whose LL energy scales proportionally to $B^{1/2}$, it also can affect the linearity of the fan diagram, since the added electrons do not have only to fill states in the Landau levels but also in the impurity band. A consequence of the non-linearity that can still be detected for $B \to 0$ is that the Landau levels of electrons and holes extrapolate to two slightly different (only a few Volts) values of gate voltage.
References


6. ELECTRONIC TRANSPORT THROUGH A TOPOLOGICAL INSULATOR


112 6. Electronic transport through a topological insulator


References


6. ELECTRONIC TRANSPORT THROUGH A TOPOLOGICAL INSULATOR


References


6. ELECTRONIC TRANSPORT THROUGH A TOPOLOGICAL INSULATOR


Curriculum Vitae

Nuno José Guimarães Couto

04/12/1984  Born in Joane, Portugal

Education

21/07/2014  PhD defense: *Quantum transport through Graphene and Topological Insulators*
University of Geneva, Switzerland

Committee:  Prof. Alberto Morpurgo (UNIGE)
Prof. Nuno Peres (UMINHO)
Dr. Alexey Kuzmenko (UNIGE)

2009-2014  PhD research in Physics,
University of Geneva, Switzerland
Advisor: Prof. Alberto Morpurgo

2003-2009  Licenciatura em Física (Bachelor + Master in Physics),
University of Minho-Braga, Portugal
Thesis Advisor: Prof. Michael Belsley

2001-2003  High School, Científico-Natural (Natural Sciences)
Escola Secundária Padre Benjamin Salgado - Joane, Portugal

Work Experience

2002  Trainee as automobile electrician
Electro Firmino, Joane, Portugal
Random strain fluctuations as dominant disorder source for high-quality on-substrate graphene devices
Nuno J. G. Couto, Davide Costanzo, Stephan Engels, Dong-Keun Ki, Kenji Watanabe, Takashi Taniguchi, Christoph Stampfer, Francisco Guinea and Alberto F. Morpurgo.

In-plane electronic confinement in superconducting LaAlO$_3$/SrTiO$_3$ nanostructures

Gate-tuned normal and superconducting transport at the surface of a topological insulator
Benjamin Sacépé, Jeroen B. Oostinga, Jian Li, Alberto Ubaldini, Nuno J.G. Couto, Enrico Giannini and Alberto F. Morpurgo.
Nature Communications 2, 575 2011

Transport through Graphene on SrTiO$_3$
Nuno J. G. Couto, Benjamin Sacépé, and Alberto F. Morpurgo.

Controllable transport mean free path of light in xerogel matrixes embedded with polystyrene spheres
Optics Express 17, 6976 2009