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Measurement and control of electron-phonon interactions in graphene

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MEASUREMENT AND CONTROL OF ELECTRON-PHONON INTERACTIONS IN GRAPHENE

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MEASUREMENT AND CONTROL OF ELECTRON-PHONON INTERACTIONS IN GRAPHENE

(Order No. )

SEBASTIAN RÉMI

Boston University, Graduate School of Arts and Sciences, 2014
Major Professor: Bennett B. Goldberg, Professor of Physics

ABSTRACT

Despite the weak interaction between electrons and atomic vibrations (phonons) in the one-atom thick crystal of carbon called graphene, the scattering of electrons off phonons limits coherent electron transport in pristine devices over mesoscopic length scales. The future of graphene as a replacement to silicon and other materials in advanced electronic devices will depend on the success of controlling and optimizing electronic transport. In this dissertation, we explore the electron-phonon interaction via Raman scattering, elucidating the effects of filling and emptying charge states on the phonons in both the metallic state and when levels are quantized by an applied perpendicular magnetic field. In zero magnetic field, the phonon energy shifts due to electronic screening by charge carriers. Previously, a logarithmic divergence of the phonon energy was predicted as a function of the charge carrier density. For the first time, we observe signatures of this logarithmic divergence at liquid He temperatures after vacuum annealing on single layers. We also measure the electron-phonon coupling strength, Fermi velocity, and broadening of electronic quantum levels from Raman scattering and correlate these parameters to electronic transport. In a strong
perpendicular magnetic field, the energy bands split into discrete Landau levels. Here, we observe kinks and splitting of the optical phonon energy, even when the Landau level transitions are far from resonant with the phonons. We discover that the kinks are attributed to charge filling of Landau levels, as understood from a linearized model based on electron-phonon interactions. Moreover, we show that material parameters determined without magnetic fields also describe phonon behavior in high magnetic fields.
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<th>Full Form</th>
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<tr>
<td>2D</td>
<td>Two Dimensional</td>
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<tr>
<td>BZ</td>
<td>Brillouin Zone</td>
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<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
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<tr>
<td>EBL</td>
<td>Electron Beam Lithography</td>
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<tr>
<td>e-ph</td>
<td>Electron-Phonon</td>
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<tr>
<td>Eqn.</td>
<td>Equation</td>
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<td>FWHM</td>
<td>Full Width Half Maximum</td>
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<tr>
<td>GFET</td>
<td>Graphene Field Effect Device</td>
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<tr>
<td>hBN</td>
<td>Hexagonal Boron Nitride</td>
</tr>
<tr>
<td>LL</td>
<td>Landau Level</td>
</tr>
<tr>
<td>LN</td>
<td>Liquid Nitrogen</td>
</tr>
<tr>
<td>MPR</td>
<td>Magneto Phonon Resonance</td>
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<tr>
<td>NA</td>
<td>Numerical Aperture</td>
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<tr>
<td>NN</td>
<td>Nearest Neighbor</td>
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<tr>
<td>RT</td>
<td>Room Temperature</td>
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<td>Sec.</td>
<td>Section</td>
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<tr>
<td>SiO$_2$</td>
<td>Silicon dioxide</td>
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<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
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<tr>
<td>t.b.</td>
<td>Tight Binding</td>
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Chapter 1

Introduction

Graphene has received wide attention in the past decade due to its outstanding, fundamental physical properties. It shows high electrical conductivities and electronic mobilities, large thermal conductivity, high elasticity and breaking strength and is impermeable to gases, despite being a monoatomic layer of Carbon.

A wide range of potential applications using graphene has been proposed and is currently being developed across various scientific fields and disciplines. In the future, graphene could find its way into electronic devices, such as high frequency modulators as well as optical and photonic devices. Possible applications are investigated in life sciences, material science and new materials research (e.g. composite materials) and chemistry. Graphene has the potential to enable new, not yet invented technologies as well as replace current established technologies in these areas.

Some applications that are currently under development can be achieved using graphene of rather low quality that in certain cases can already be produced in large industrial quantities. Graphene flakes produced by liquid phase exfoliation are produced by the ton and CVD graphene can be grown in hundreds of meters length for uses in flexible displays and touchscreens (Segal, 2009; Kobayashi et al., 2013).

Other applications require fast and large production of high quality graphene currently only available in a few research labs in small quantities. The thickness of graphene is a challenge since, being a single atomic layer thin, it is a surface without bulk properties. Therefore it reacts extremely sensitive to external perturbations
such as the dielectric environment, charge impurity doping, residues from sample processing, substrate inhomogeneities, chemical modification, mechanical deformation and external fields.

To obtain the highest quality of graphene, understanding and knowledge of the fundamental scattering mechanisms is crucial such as the e-ph interactions. In this dissertation we describe experiments aimed at investigating and understanding the e-ph coupling mechanisms as a function of the density of charged carriers using electrical and optical methods.

In our lab we mainly perform experiments using Raman spectroscopy, where the inelastic scattered light off lattice vibrations and phonons is investigated. Raman has been established as a robust tool to investigate various properties of graphene and related carbon allotropes such as carbon nanotubes. Being sensitive to the e-ph coupling Raman can illuminate fundamental scattering mechanisms and due to screening effects the Raman modes are sensitive to the charge carrier density. Moreover mechanical, thermal and structural properties can be investigated by Raman since it is sensitive to strain, temperature and the stacking order of graphene sheets in multilayers.

We investigate the e-ph coupling in two regimes. First, in zero magnetic field and then in finite magnetic fields where the continuous band structure splits into discrete quantum levels. The structure of the thesis is as follows:

The first two chapters are devoted to the description of the fundamental theory and experimental methods.

In chapter 2 we describe mathematically some of the fundamental properties of graphene that are necessary for the understanding of the experimental work. We derive the expression of the electronic structure and discuss the relativistic Dirac Fermion states. We show the quantization of electron states into degenerate Landau
levels in magnetic fields and derive the degeneracy and filling factor as a function of charge carrier density. The transitions between Landau levels follow selection rules that are connected to the angular momentum of an exciting electro-magnetic wave. We then discuss the fundamental origin of the e-ph interactions through lattice distortions. The phonon properties are renormalized by the e-ph interactions and their frequency and broadening is derived from the phonon Greens function.

In chapter 3 we describe some of the experimental methods we used to process and characterize graphene samples. We describe how graphene is exfoliated, and identified using optical imaging and Raman spectroscopy. The production and principles of work of graphene field effect transitors (GFETs) are presented that allow us to tune the electron density in experiments and measure transport properties.

Our main experimental results are described in chapters 4 and 5.

We performed gate-voltage dependent Raman measurements on GFETs while simultaneously measuring the transport properties. The position and width of the Raman spectra are shifted and broadened by the e-ph interactions and charge inhomogeneity. We describe how we take account of inhomogeneities when fitting our data and determine the e-ph coupling strength. We discuss the connection between the electron density dependent phonon properties and the quantum level broadening of electron states. The transport of electrons through our samples is described by a diffusive process. The comparison of quantum scattering times with the scattering times from transport experiments is presented for different electron mobilities.

Finally in chapter 5 we describe experiments that probe the e-ph interaction in a magnetic field. We measure the influence of the level filling factor on the strength of the e-ph interactions and show how coupling to transitions between different Landau levels influence the Raman spectra. Our measurements can be well described by the same e-ph interaction strength measured in zero magnetic field experiments.
Chapter 2

The physics of Graphene

In this chapter we present the theoretical description of graphene related to the physics described in this work. We will first describe the honeycomb crystal structure of graphene and its Brillouin zone and calculate the electronic band structure in the tight binding approximation. The low energy approximation of the bands is the linear dispersion of massless Dirac Fermions and we derive the limits of this approximation. In a magnetic field the continuous bands split into discrete, highly degenerate LL. We present the energy spectrum, the electron wave function, expressions for the degeneracy and filling of levels and selection rules for inter-LL transitions. Finally we describe the origin of e-ph coupling and the derivation of phonons properties from the Greens function.

2.1 The electronic structure of graphene

2.1.1 The graphene lattice

The carbon atoms in graphene are arranged in a honeycomb lattice structure with nearest neighbor (NN) distance of \( a = 0.142 \) nm, measured by electron diffraction (Meyer et al., 2007) and scanning tunneling microscopy (STM) (Xue et al., 2011). The honeycomb structure is explained by the electronic structure of carbon with 4 valence electrons in configuration \( 2s^22p^2 \). In graphene the electrons form 3 sp\(^2\) hybridized planar orbitals oriented in 120\(^\circ\) angles and a \( p_z \) orbital perpendicular to the sp\(^2\) plane. The overlap of the planar orbitals form strong \( \sigma \)-bonds between NN
while the perpendicular $p_z$ orbitals form weak $\pi$ bonds. Fig. (2·1) shows a schematic view of the graphene lattice. Mathematically the honeycomb lattice is not a bravais lattice, but is described by a hexagonal (typically called triangular) bravais lattice with a basis of 2 atoms. Here we use a representation where the zig-zag edge of the graphene lattice is parallel to the x axis. The fundamental lattice translations can then be written as:

$$\vec{a}_1 = \sqrt{3}ae_x$$
$$\vec{a}_2 = \frac{\sqrt{3}a}{2} \left( e_x + \sqrt{3}e_y \right)$$

(2.1)

The 2 atoms in the basis form triangular A and B sublattices where atoms are connected directly by lattice vectors in Eqn. (2.1). In Fig. (2·1) atoms of the A, B sublattice are colored blue and red respectively.

It is useful to explicitly write out the vectors $\delta_i$ connecting the 3 NN atoms relative
to one of the sublattices. We define $\delta_i$ as in Fig. (2.1):

$$
\vec{\delta}_1 = \frac{a}{2} \left( \sqrt{3}e_x + e_y \right)
$$

$$
\vec{\delta}_2 = \frac{a}{2} \left( -\sqrt{3}e_x + e_y \right)
$$

$$
\vec{\delta}_3 = -ae_y
$$

(2.2)

The reciprocal lattice vectors $b_i$ are obtained by elementary methods (Kittel, 1986) using a relationship determined by translational symmetry:

$$
b_i a_j = 2\pi \delta_{ij}
$$

(2.3)

Solving the system of equations Eqn. (2.3) yields the reciprocal lattice vectors that also form a hexagonal lattice:

$$
\vec{b}_1 = \frac{2\pi}{\sqrt{3}a} \left( e_x - \frac{e_y}{\sqrt{3}} \right)
$$

$$
\vec{b}_2 = \frac{4\pi}{3a} e_y
$$

(2.4)

A small section of the reciprocal lattice is shown in Figure Fig. (2·2). The first Brillouin zone (BZ) is highlighted in blue.

Notably, the BZ is hexagonal and rotated relative to the crystal and reciprocal lattice. Traditionally, points of high symmetry are referred to as the $\Gamma$ point in the zone center, the 3 crystallographic equivalent M points in the center of the zone edges at

$$
M = \frac{1}{2} \vec{b}_1 = \frac{\pi}{\sqrt{3}a} \left( e_x - \frac{e_y}{\sqrt{3}} \right)
$$

(2.5)

Most important for the low energy physics of graphene are the K points in the corner of the BZ. There are two inequivalent K points (not connected by a primitive translation in the reciprocal lattice) labeled K and K’ that are related by time
The equivalent K (K') points are marked in Fig. (2·2). Goerbig emphasizes (Goerbig, 2011), that the presence of the inequivalent K points in the BZ is only related to the hexagonal bravais lattice and not the presence of a two atom basis.

2.1.2 Graphene band structure

The electronic band structure of graphene and related systems is well described by a tight binding model with hopping between NN atoms. The dispersion was first calculated by Wallace in 1947 (Wallace, 1947) to explain the band structure of graphite.
In general, the band structure graphene related systems (e.g. Carbon nanotubes) uses the dispersion of a single sheet of Graphene and is refined to match the specific physical system.

The band structure is fundamental to the remarkable properties of graphene, so we briefly discuss the t.b. calculation, closely following Goerbig and Bena et al. (Goerbig, 2011; Bena and Montambaux, 2009). The main result is that the effective Hamiltonian of graphene is formally equivalent to the relativistic Dirac equation describing massless fermions. Later we use this result to describe electronic states of Graphene in magnetic fields.

**The tight binding basis**

The t.b. calculation starts with a fundamental basis of atomic orbitals \( \Phi(\mathbf{r}) \). The wavefunctions of the electrons in the crystal \( \Psi_k(\mathbf{r}) \) are then described by linear superpositions (Kittel, 1986; Ashcroft and Mermin, 1976) of atomic orbitals:

\[
\Psi_k(\mathbf{r}) = \sum_j c_{k,j} \Phi(\mathbf{r} - \mathbf{r}_j) \tag{2.7}
\]

where the orbital \( \Phi(\mathbf{r} - \mathbf{r}_j) \) belongs to the atom at position \( \mathbf{j} \) and the \( c_{k,j} \) are expansion coefficients. Due to translational symmetry the wavefunctions must be of the Bloch form

\[
\Psi_k(\mathbf{r}) = u_k(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} \tag{2.8}
\]

labeled by a wavevector \( \mathbf{k} \). Using the notation \( |\Psi_k\rangle \) the wavefunction is given by \( \Psi_k(\mathbf{r}) = \langle \mathbf{r} | \Psi_k \rangle \). The Bloch theorem Eqn. (2.8) requires the wavefunction to be of the form

\[
\Psi_k(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_j e^{i\mathbf{k}\cdot\mathbf{r}_j} \Phi(\mathbf{r} - \mathbf{r}_j) \tag{2.9}
\]

We apply the general form of the wavefunction in Eqn. (2.9) to the case of a basis
of two atoms. The basis states are written as superpositions

$$|\Psi_k\rangle = a_k |\Psi^A\rangle + b_k |\Psi^B\rangle$$

(2.10)

of the Bloch functions $|\Psi^A\rangle$ and $|\Psi^B\rangle$ on the A and B sublattice respectively. We now use Eqn. (2.9) to rewrite Eqn. (2.10) to obtain the general t.b. wavefunction for two sublattices:

$$|\Psi_k\rangle = \frac{1}{\sqrt{N}} \sum_j e^{ikr_j} (a_k |\Phi_A\rangle + b_k |\Phi_B\rangle)$$

(2.11)

### Diagonalization of the tight binding Hamiltonian

We now derive and diagonalize the hamiltonian of the system. The atomic orbitals must fulfill the t.b. condition $\langle \Phi_A | \Phi_B \rangle \ll 1$, i.e. the electrons are strongly bound to the respective crystal atom. The Hamiltonian describes hopping of electrons between lattice sites. We only consider NN hopping between the perpendicular $p_z$-orbitals of different sublattice atoms. These orbitals give rise to two bands which determine the low energy physics, while the planar $sp^2$ hybridized orbitals describe bands at higher energies. The hamiltonian restricted to NN hopping is:

$$\mathcal{H} = t \sum_{\langle i,j \rangle} |\Phi_{A,i}\rangle \langle \Phi_{B,j}| + h.c.$$ 

(2.12)

where the sum extends over all NN pairs $\langle i, j \rangle$ in the lattice. The hopping energy $t$ is given by the overlap integral:

$$t = \int d^2r \Phi^*_A(\mathbf{r} - \mathbf{R}_i) \mathcal{H}_{\text{hop}}(\mathbf{r} + \delta_i - \mathbf{R}_i) \Phi_B(\mathbf{r})$$

(2.13)

In general $t$ must be determined either by experimental measurements or first principle calculations. It is found that $t \approx -3 \, eV$ (Castro Neto et al., 2009).

We find the bands of the system by solving for the eigenvalues $\varepsilon_k$ of the Hamilton-
\[ \mathcal{H} |\Psi_k\rangle = \varepsilon_k |\Psi_k\rangle \implies \varepsilon_k = \langle \Psi_k | \mathcal{H} |\Psi_k\rangle \quad (2.14) \]

The states \( |\Psi_k\rangle \) are Bloch states of the form Eqn. (2.10). Using translational symmetry we find:

\[ \mathcal{H} |\Psi_k\rangle = t \begin{pmatrix} 0 & \gamma_k \\ \gamma_k^* & 0 \end{pmatrix} \begin{pmatrix} a_k \\ b_k \end{pmatrix} \quad (2.15) \]

where we wrote the hamiltonian in matrix form

\[ \mathcal{H}_k = t \begin{pmatrix} 0 & \gamma_k \\ \gamma_k^* & 0 \end{pmatrix} \quad (2.16) \]

The factor \( \gamma_k \) describes the phase change when the electron hops between nearest neighbors. The detailed form of \( \gamma_k \) is not unique and depends on the choice of basis and the definition of phases in the Bloch functions in Eqn. (2.11) (Bena and Montambaux, 2009). The physical results are independent of the form of the t.b. wavefunctions, however proper care has to be taken to not mix up expressions that are obtained for different basis definitions.

We place the origin of the coordinate system on one of the atoms in the A sublattices as in Fig. (2.1) where one of the nearest neighbor atoms of the B lattice atoms is considered to be on the same site. Then \( \gamma_k \) is given by:

\[ \gamma_k = 1 + e^{ika_2} + e^{ika_3} \quad (2.17) \]

where \( a_3 = (a_2 - a_1) \). There is no phase difference when hopping between sublattices on the same site, but a phase difference \( \exp(ika_i) \) to the remaining nearest neighbor sites.

The energy eigenvalues are the solution of the characteristic equation \( \det(\mathcal{H}_k - \)
\[ \varepsilon_\lambda = \pm |t\gamma_k| = \pm |t| \sqrt{3 + 2 \cos \left( \sqrt{3} k_x a \right) + 4 \cos \left( \frac{\sqrt{3} k_x}{2} a \right) \cos \left( \frac{3k_y}{2} a \right)} \]  

\( \varepsilon_k \) describes a positive and a negative band, with band index \( \lambda = \pm 1 \) (Goerbig, 2011). For \( \lambda = -1 \) we find the valence band \( \varepsilon_k < 0 \), often called the \( \pi \)-band. \( \lambda = +1 \) describes the conduction or \( \pi^* \) band with \( \varepsilon_k > 0 \). The full dispersion is illustrated in Fig. (2·3)(a) where we additionally included next NN hopping according to (Goerbig, 2011). Next NN hopping destroys the perfect electron-hole symmetry of Eqn. (2.18).

Fig. (2·3)(b) shows a cut through the band structure along the points of high symmetry \( \Gamma-M-K-\Gamma \). The \( \pi \) and \( \pi^* \) band touch in exactly one point where the energy \( \varepsilon = 0 \). Remarkably these points coincide with the K points of the Brillouin zone. They are called Dirac points due to the effective low energy behavior that will be described below. The coincidence of the Dirac points with the K points of the

**Figure 2·3:** Bandstructure of Graphene
Brillouin zone are not trivial and can be lifted, e.g. by the application of strain.

The eigenstates of the t.b. hamiltonian are:

\[ \Psi^\lambda_k = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -\lambda e^{-i\phi_k} \end{pmatrix} \]  

(2.19)

with the phase \( \phi_k = \text{arctan}(Im\gamma_k/Re\gamma_k) \). The two components of the eigenvector \( \Psi \) give the respective weight \( a_k, b_k \) of the electron wavefunction on the A and B sublattice.

2.1.3 Relativistic Dirac Fermions

Expansion around the K points

The physical properties of graphene are dominated by the low energy regime around the Dirac points K and K’ points in the BZ. The effective Hamiltonian can be calculated by expanding \( \gamma_K \) for low energies around K, K’:

\[ \gamma_{K+q} = 1 + e^{i(K+q)a_2} + e^{i(K+q)a_3} \]

\[ \approx 1 + e^{iK a_1} (1 - iq a_2) + e^{-iK a_3} (1 - iqa_3) \]

\[ = -\frac{3a}{2} (q_x + iq_y) \]  

(2.20)

Considering the expansion around both inequivalent points K and K’ the effective hamiltonian \( \mathcal{H}_{q,\text{eff}} \) takes on a block diagonal form:

\[ \mathcal{H}_{q,\text{eff}} = -\frac{3at}{2} \begin{pmatrix} 0 & q_x - iq_y & 0 & 0 \\ q_x + iq_y & 0 & 0 & 0 \\ 0 & 0 & 0 & -q_x - iq_y \\ 0 & 0 & -(q_x - iq_y) & 0 \end{pmatrix} \]  

(2.21)

The upper left block in \( \mathcal{H}_{q,\text{eff}} \) is related to the expansion around K and the lower right one to the expansion around K’. Each block is separately diagonalized by eigenvectors of the form Eqn. (2.19). The complete eigenstates are 4-spinors where the components
determine the weights on the A and B sublattices around K and K’ respectively:

\[ \Psi_q = \begin{pmatrix} \Psi^A_{q,+} \\ \Psi^B_{q,+} \\ \Psi^B_{q,-} \\ \Psi^A_{q,-} \end{pmatrix} \quad (2.22) \]

We interchanged the A and B sublattice components around K’ so the hamiltonian can be written in compact form:

\[ H_{q,\text{eff}} = \xi \hbar v_F \tau_z \otimes \sigma \cdot q \quad (2.23) \]

where \( \sigma_x, \sigma_y \) and \( \tau_z \) are the standard Pauli matrices and we introduced a valley pseudospin variable \( \xi = \pm \) that labels the two valleys K and K’. The Fermi velocity \( v_F \) is defined by:

\[ v_F = -\frac{3at}{2\hbar} \quad (2.24) \]

The Fermi velocity in graphene is roughly 1/300 of the speed of light in vacuum \( v_F \sim 1 \times 10^6 \text{ms}^{-1} \) (Kossacki et al., 2012; Elias et al., 2011). It is a straightforward exercise to calculate the eigenstates of the Hamiltonian Eqn. (2.23), using the eigenstates of Eqn. (2.19):

\[ \Psi^{\xi=\pm}_{q,\lambda} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -\lambda e^{i\varphi_q} \\ 0 \\ 0 \end{pmatrix}, \quad \Psi^{\xi=-}_{q,\lambda} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 0 \\ 1 \\ \lambda e^{i\varphi_q} \end{pmatrix} \quad (2.25) \]

where the phase \( \varphi_q \) is now defined by:

\[ \varphi = \arctan \left( \frac{q_y}{q_x} \right) \quad (2.26) \]
Similarity of the graphene Hamiltonian to the relativistic Dirac equation

The physics of charge carriers in graphene is formally equivalent to the dynamics of ultra-relativistic particles. For example the eigenvalues of the effective hamiltonian Eqn. (2.23) are:

$$\varepsilon = \hbar v_F q$$

This dispersion is linear in momentum. The energy of a relativist particle $E = \sqrt{p^2 c^2 + m^2 c^4}$ is linear in $p$ for ultra-relativistic velocities $v \approx c$ or particles with rest mass $m = 0$. Within the framework of quantum mechanics, particles obeying the relativistic Energy momentum relationship are described by the Dirac equation:

$$(c \alpha p + \beta mc^2) |\Psi\rangle = E |\Psi\rangle$$

Here $\alpha$ and $\beta$ are 4-dimensional matrices where $\alpha$ is given by Pauli matrices (Baym, 1969).

The Dirac equation equation describes relativistic spin-1/2 particles and its solutions are 2 component spinors. Semenoff showed in 1984 (Semenoff, 1984) that the linear approximation of the Graphene Hamiltonian is completely equivalent to the description of the Dirac equation with $m=0$. The translation symmetry of the honeycomb lattice forces the electrons to follow a linear dispersion with effective speed of light $v_F$. The eigenstates of the graphene hamiltonian are therefore referred to as relativistic, massless Dirac Fermions. Massless Dirac Fermions are chiral, i.e. the projection of (pseudo)spin onto the momentum is a conserved quantity. The chirality in graphene is defined in complete analogy when replacing the real spin by the sublattice pseudospin. Chiral eigenstates with eigenvalues $h = \pm 1$ have a spin projection parallel or antiparallel to the momentum. The band index $\lambda$ can then be uniquely
defined in terms of the helicity and the valley index $\xi$ as (Goerbig, 2011):

$$\lambda = \xi h$$

(2.29)

The chirality of Dirac fermions is very important for scattering processes, because it can be shown that the chirality is conserved for well behaved potentials that vary smoothly on length scales of the lattice constant (Goerbig, 2011). As a consequence intervalley and backscattering processes are strongly supressed (Shon and Ando, 1998).

**Validity of the small energy approximation**

The physics of graphene is very well described by the low energy approximation described in the previous sections. But what are the effective limits, where $\mathcal{H}_{\text{eff}}$ is a valid description of the physical processes? Interactions, that we have neglected so far, can significantly change the electron dispersion, because they break the symmetry of the Dirac Hamiltonian responsible for the linear band structure. Electron-electron interactions can cause measurable, sublinear deviation from the band structure where the Fermi velocity $v_F$ is larger close to the Dirac points (Elias et al., 2011). We did not consider electron-electron interactions to explain the experiments presented in this thesis.

In Fig. (2.4) we display the contours of equal energy around the $K$ point derived from the complete NN hamiltonian. Whereas energy contours derived from $\mathcal{H}_{\text{eff}}$ should have a circular shape, in the actual bandstructure significant deviations from polar symmetry are observed at energies $E \sim O(t) \sim 1eV$, where $t$ is the NN hopping energy.
Significant deviations from the low energy approximation occur at energies $E \approx 1\text{eV}$, where the contours of equal energy deviate from pure circular shape.

**Figure 2.4:** Graphene bandstructure in the vicinity of the K point.
2.2 Graphene in magnetic fields

In the following we will describe the properties of Dirac fermions in graphene in perpendicular magnetic fields. We couple the Dirac Hamiltonian to an electromagnetic field by minimal substitution and show how the Hamiltonian can be written in terms of raising and lowering operators. We discuss the Landau level energy spectrum and the eigenstates of this Hamiltonian and derive the level degeneracy caused by the translational symmetry. Finally we discuss transitions between the Landau levels due to an electromagnetic field. We will present the selection rules and explain how the states are related to the angular momentum of the absorbed photon states. Inter-Landau level transitions play a crucial role in e-ph coupling in magnetic fields.

2.2.1 Graphene Hamiltonian in magnetic fields

We consider the low energy approximation of the graphene dispersion around the $K$ and $K'$ points Eqn. (2.23):

$$H_{\text{eff},q,\xi} = \xi \hbar v_F p \sigma$$

with the valley index $\xi = \pm$. We follow standard procedures to accomplish the coupling to a magnetic field by minimal substitution (Cohen-Tannoudji et al., 2006). The magnetic field is fully defined by a vector potential $A$ where $B = \nabla \times A$. The canonical momentum $p$ is redefined as:

$$p \rightarrow p = \Pi + eA = \hbar q$$

(2.30)

where we introduced the kinetic momentum $\Pi = m\nu = p - eA$, which is directly related to the velocity $\nu$. The canonical momentum is the conjugated variable to the position operator. However the hamiltonian is defined in terms of the kinetic momentum $\Pi$. The Hamiltonian describing coupling to the magnetic field is then simply given by:
\[ H_{\text{eff,}\xi}(\Pi) = \xi v_F (\Pi_x \sigma_x + \Pi_y \sigma_y) \]  

(2.31)

Due to the substitution Eqn. (2.30) the components of the kinetic momentum do not commute. Using the commutators between position and canonical momentum 
\[ [r_i, p_j] = i\hbar \delta_{ij} \] we find:

\[ [\Pi_x \Pi_y] = -i \frac{\hbar^2}{l_B^2} \]  

(2.32)

We introduced the magnetic length \( l_B \) defined by:

\[ l_B = \sqrt{\frac{\hbar}{eB}} \]  

(2.33)

The magnetic length has a simple physical illustration. \( l_B \) is the cyclotron radius of a charged particle having the ground state (vacuum) energy of a harmonic oscillator and the orbit encloses one magnetic flux quantum, see Fig. (2.6). The magnetic length is the relevant length scale for all quantum mechanical phenomena in a magnetic field considered in this thesis. For example, the effective continuum and low energy description of the discrete graphene lattice is valid as long as the magnetic length is much larger than the lattice constant. For all experimentally approachable magnetic fields this assumption is indeed valid.

The Hamiltonian Eqn. (2.31) can be formulated in analogy to the harmonic oscillator. We introduce the raising and lowering operators:

\[ \hat{a} = \frac{l_B}{\sqrt{2\hbar}} (\Pi_x - i\Pi_y) ; \quad \hat{a}^\dagger = \frac{l_B}{\sqrt{2\hbar}} (\Pi_x + i\Pi_y) \]  

(2.34)

which obey the harmonic oscillator algebra \([\hat{a}, \hat{a}^\dagger] = 1\). The inverted form of Eqn. (2.34) can be readily applied to the Hamiltonian

\[ \Pi_x = \frac{l_B}{\sqrt{2\hbar}} (\hat{a}^\dagger + \hat{a}) ; \quad \Pi_y = \frac{l_B}{i\sqrt{2\hbar}} (\hat{a}^\dagger - \hat{a}) \]  

(2.35)
Defining $\omega = v_F \sqrt{2/l_B}$, the Hamiltonian is now:

$$H_B = \xi \hbar \omega \begin{pmatrix} 0 & a \\ a^\dagger & 0 \end{pmatrix}$$  \hspace{1cm} (2.36)

For conventional two-dimensional electron systems the Hamiltonian is proportional to quadratic forms $\hat{a}^\dagger \hat{a}$. However for graphene Eqn. (2.36) is linear in the raising and lowering operators due to the relativistic, linear bandstructure of graphene. The physics is described by a spectrum of energy levels unique to graphene.

### 2.2.2 Landau levels

#### Energy spectrum

The LL are the eigenvalue solutions of the Hamiltonian Eqn. (2.36):

$$\varepsilon_n = \hbar \omega \sqrt{n} = v_F \sqrt{2\hbar e B n} = \hbar v_F \frac{\sqrt{2n}}{l_B} \hspace{1cm} (2.37)$$

In graphene $\varepsilon_n \propto \sqrt{n}$ and $\varepsilon_n \propto \sqrt{B}$, due to the linear dispersion, in contrast to conventional two-dimensional electron systems where $\varepsilon_{n,2DEG} = \hbar \omega_C (n + 1/2) \propto B$.

Fig. (2·5) compares the Landau level energy spectrum of a conventional 2DEG (left) and that of graphene (right side) where the different behavior as a function of the magnetic field strength is immediately visible. The bottom of the figure shows the position of energy levels for graphene and the conventional electron system at fixed magnetic field strength. The $\sqrt{B}$ behavior of the LL in graphene has been well observed in transport (Novoselov et al., 2005; Zhang et al., 2005) and IR absorption (Orlita and Potemski, 2010) experiments. Fig. (2·5) shows nicely that the LL are not evenly spaced. The energy difference of the lower LL is larger than the equidistant energy difference of conventional 2D systems. The large spacing between the LL makes graphene insensitive to thermal excitations of electrons, so quantum effects involving the lowest energy levels are especially robust, e.g. the quantum hall effect.
Figure 2-5: Position of Landau levels in conventional two-dimensional systems (left) and in graphene (right). The upper part of the figure shows the magnetic field dependence. The lower part illustrates the idealized density of states ($\delta$ peaks)
in graphene was observed even at room temperature (Novoselov et al., 2007). For correct quantitative evaluation of the LL energies, the Fermi velocity \( v_F \) needs to be known. Of course, \( v_F \) can be experimentally determined by precise measurement of \( \varepsilon_n \).

Besides the \( \sqrt{Bn} \) dependence of \( \varepsilon_n \), the LL at \( E = 0 \) does not exists in conventional 2D materials. The existence of the zero energy level is a consequence of the topological structure of the Dirac fermion state space. Dirac states described by Eqn. (2.25) acquire an additional geometric (Berry’s) phase \( \gamma = \pi \) under rotations of \( 2\pi \). The existence of Berry’s phase of \( \pi \) was directly observed in transport experiments (Zhang et al., 2005). Berry’s phase changes the quantization conditions for cyclotron orbits in magnetic fields thus leading to a Landau level at zero energy.

**Eigenstates**

The eigenstates of the Hamiltonian Eqn. (2.36) can be written as 2 component spinors in the A-B sublattice basis. We use the eigenstates \(|n\rangle\) of the number operator \(a^\dagger a\).

The result is:

\[
\Psi_{n,\xi} = \frac{1}{\sqrt{2}} \left( \begin{array}{c} |n-1\rangle \\ \xi |n\rangle \end{array} \right); \quad \Psi_{n=0,\xi} = \left( \begin{array}{c} 0 \\ |0\rangle \end{array} \right)
\]

(2.38)

The usual rules for the harmonic oscillator apply where \(a^\dagger a\ |n\rangle = n\ |n\rangle\), \(a\ |n\rangle = \sqrt{n}\ |n-1\rangle\), \(a^\dagger\ |n\rangle = \sqrt{n+1}\ |n+1\rangle\) and \(a\ |0\rangle = 0\). As before \(\xi\) is the valley pseudospin. By definition the components of the spinors represent the weight of the wavefunction on the A-B sublattice at the K point (\(\xi = +1\)) and the weights on the B-A sublattice at K’ (\(\xi = -1\)).

The \( E = 0 \) LL has a special structure. The two sublattices are decoupled, the wavefunction around K has only weight on the A sublattice, and the wavefunction at K’ only has weight on the B sublattice. We later show (Sec. (5.6.1)) the physical
impact when considering the strength of transitions between Landau levels. Goerbig (Goerbig, 2011) points out that the decoupling of the sublattices can be extended to the states at the Dirac point for $B = 0$. However while $B = 0$ involves 8 quantum states (electron and hole plus spin and valley degeneracy). The Landau levels are macroscopically degenerate.

**Degeneracy**

The discrete LL are strongly degenerate due to the guiding center degree of freedom of the cyclotron orbits (Goerbig, 2011). We schematically illustrate this in Fig. (2.6). The idea is to fill the sample area with cyclotron orbits. The area enclosed by one orbit is written in terms of the flux quantum $\Phi_0$:

$$A = \frac{\Phi_0}{B} = \frac{\hbar}{eB}$$

(2.39)

The degeneracy of each Landau level is determined by requiring that the area of the sample is continuously covered with cyclotron orbits, where neighboring orbits should not overlap. In the following we want to point out the connection of this picture to the relativistic Dirac eigenstates in graphene. Again we closely follow the very good description by Goerbig (Goerbig, 2011). In a magnetic field the particle position can be decomposed into two components: the position of the guiding center of a cyclotron orbit $R = (X, Y)$ and a cyclotron variable $\eta$:

$$r = R + \eta$$

(2.40)

The components of the guiding center variable build a set of dynamic, conjugate variables

$$[X, Y] = -i\hbar^2$$

(2.41)
Figure 2.6: Filling of the sample area with cyclotron orbits. The area enclosed by each orbit is given by the flux quantum $\Phi_0$. 
where again we used the magnetic length $l_B$. In analogy to the usual position and momentum operators, the guiding center operator is defined in terms of raising and lowering operators $b^\dagger$ and $b$. We define eigenstates of the number operator $b^\dagger b |m\rangle = m |m\rangle$.

Due to symmetry the guiding center is a constant of motion so the variable $m$ is a "good" quantum number. The LL eigenstates have to be labeled by the quantum numbers $m$ to express the degeneracy due to this symmetry. The complete eigenbasis is then given by:

$$\Psi_{\xi,n,m} = \frac{1}{\sqrt{2}} (1 + \delta_{n,0}) \left( \delta_{n,0} |n - 1, m\rangle_{\xi\lambda} |n, m\rangle \right)$$  \hspace{1cm} (2.42)

The magnitude of the degeneracy can be calculated using the following hand waving argument. Since $X$ and $Y$ are canonically conjugate variables there is an uncertainty relation, i.e. the guiding center position is smeared out over a surface

$$\Delta X \Delta Y = 2\pi l_B^2$$  \hspace{1cm} (2.43)

which is equal to the area derived using the flux quantum Eqn. (2.39). The degeneracy $N_B$ is the number of states necessary to completely covere the sample surface:

$$N_B = \frac{A}{\Delta X \Delta Y} = n_B A$$  \hspace{1cm} (2.44)

with the flux density $n_B = 1/2\pi l_B^2$.

A convenient measure for the total occupancy of states is the filling factor $\nu$ defined by the ratio between the total density of charge carriers and the flux density:

$$\nu = \frac{n_{el}}{n_B} = n_{el} 2\pi l_B^2 = \frac{n_{el} h}{eB}$$  \hspace{1cm} (2.45)

Whenever $n_{el} l$ takes on integer multiple values of the flux density all degenerate states in a Landau level are completely filled. When the fourfold spin and valley degeneracy
in graphene is included, filling one LL will increase $\nu$ by 4.

The filling factor can be experimentally adjusted using either the magnetic field strength or the charge carrier density. The dependence of $\nu$ on $B$ is shown in Fig. (2.7)(a). For increasing field strength the degeneracy increases (smaller cyclotron radii) and the filling factor decreases $\sim (\sqrt{B})^{-1}$. For determination of the highest filled Landau level we have to consider the special role of the energy level at $E = 0$. For the charge neutral system $n_{el} = 0$ the filling factor is $\nu = 0$. The $E = 0$ level is located between $-2 < \nu < 2$. For $\nu > 0$ electrons are filling up the states whereas holes are introduced for $\nu < 0$. Due to the macroscopic but finite number of states in each Landau level according to eqn. 2.44 the position of the highest filled Landau
level changes with the magnetic field if $n_{el} = \text{const.}$. We illustrate this in Fig. 2.7(b) and (c) for two different values of $n_{el}$. For constant magnetic field the highest filled level is at larger energy if $n_{el}$ is larger.

### 2.2.3 Inter Landau level transitions

The quantization of the electron energy levels in magnetic fields drastically changes the system response to external perturbations since electrons can only be excited between the discrete Landau levels. Electron excitations can occur by coupling to electromagnetic fields or to lattice vibrations. Symmetry imposes selection rules that allowed LL transitions have to obey.

To understand the selection rules we consider the coupling of Dirac electrons to an electromagnetic plane wave. In Sec. (5) we will investigate coupling to lattice vibrations (phonons) to describe the Raman scattering in magnetic fields.

We present a simple model for coupling to the electromagnetic field by Pudlik (Pudlik, 2012). Consider a circular polarized electromagnetic plane wave. Without loss of generality we choose the wave to move in the $z$-direction. The electric field can be written as:

$$E = \tilde{E} \sin (\omega t - kz) \quad (2.46)$$

For circular polarized light the complex amplitude $\tilde{E}$ is:

$$\tilde{E} = \begin{pmatrix} 1 \\ \pm i \end{pmatrix} \quad (2.47)$$

There is no static field so the electrostatic potential is $\Phi = 0$. $E$ is then related to the vector potential $A_p$ by $E = -\mu_0 \partial_t A_p$ with:

$$A_p = \frac{E}{2\omega} \begin{pmatrix} 1 \\ \pm i \end{pmatrix} \cos (\omega t) \quad (2.48)$$

We place a graphene sheet at $z = 0$. In the presence of $E$ the effective hamiltonian
is obtained by the minimal substitution in Eqn. (2.30):

\[ \mathcal{H} = \xi v_F \sigma (p - eA_B - eA_p) = \mathcal{H}_B + \mathcal{H}_{\text{pert}} \tag{2.49} \]

with \( B = \nabla \times A_B \). \( \mathcal{H}_{\text{pert}} \) is the contribution due to the electromagnetic wave. We find:

\[ \mathcal{H}_{\text{pert}} = \xi v_F \sigma eA_p = \xi v_F \mathcal{A} \sigma_z (\sigma_x \pm i\sigma_y) (e^{i\omega t} + e^{-i\omega t}) \tag{2.50} \]

We are interested in the transitions between Landau level states Eqn. (2.42) as a response to this Hamiltonian. When the field amplitude \( E \) is small \( \mathcal{H}_{\text{pert}} \) is a small perturbation to the static field Hamiltonian \( \mathcal{H}_B \). The transition rate between the initial state \( |i\rangle \) and final state \( |f\rangle \) can then be calculated using Fermi’s Golden rule. We are not interested in the quantitative details of the calculation of the transition rate, thus we can neglect all constants and only consider the transition matrix elements

\[ \mathcal{M} = |\langle f | \sigma_x \pm i \sigma_y | i \rangle|^2 \tag{2.51} \]

These matrix elements are easily calculated using the Form Eqn. (2.42) for the initial and final states \( |i\rangle \) and \( |f\rangle \) and using the orthogonality

\[ \langle f, m_f | i, m_i \rangle = \delta_{f,i} \tag{2.52} \]

The result is the selection rule for inter-Landau level transitions due to a circular polarized electromagnetic field

\[ \Delta n = \pm 1 \tag{2.53} \]

with the Landau level index \( n \). Eqn. (2.53) is independent of the index \( m \), since the guiding center operator is a constant of motion.

The interpretation of the selection rule 2.53 is as follows. Circular polarized light can be connected to the angular momentum where (depending on convention) left and
right circular polarization carry angular momentum $l = \pm 1$. Changing the Landau level index must therefore be connected to a transfer of angular momentum. This is not only true for electromagnetic waves but for phonons coupling to the Landau levels as well, e.g. the fundamental phonon states coupling to Landau level transitions are formally circular polarized superpositions of the doubly degenerate G-band phonon states (Goerbig, 2011; Goerbig et al., 2007).

Transitions can be classified into interband transations between conduction and valence band states and intraband transitions where the band index is not changed. Fig. (2.8) shows a schematic representation of allowed interband and intraband transitions. There is a symmetry of LL transitions with pairwise equal energy. For each index pair $i, f$ allowed by Eqn. (2.53) one can select either the transition with $\Delta n = +1$ or $\Delta n = -1$. Due to symmetry, energies of LL transition are pairwise equal. The energies of inter- and intraband transitions behave different as a function of the index $n$. While the energy of interband transitions increases, the energy of intraband transitions decreases. The energy of the transitions follows immediately from Eqn. (2.37). For interband transitions it is given by:

$$T_n = T_0(\sqrt{n + 1} + \sqrt{n})$$

(2.54)

$T_n$ labels the energy of the interband transition between levels $-n \rightarrow n + 1$ and $-n - 1 \rightarrow n$ with $T_0 = v_f \sqrt{2e\hbar B}$. The energy of intraband transitions $S_n$ between $n \rightarrow n + 1$ and $-n - 1 \rightarrow -n$ is given by:

$$S_n = T_0(\sqrt{n + 1} - \sqrt{n})$$

(2.55)

The role of the $T_0/S_0$ transition is somewhat ambiguous, since the $n = 0$ Landau level is a mixture between conduction and valence band states, so transitions to the $n = 0$ have the character of both, interband and intraband transitions. Due to the
special form of the $n = 0$ LL Eqn. (2.42) the weight is restricted to only on one of the sublattices. Since the eigenstates are not normalized by a factor $1/\sqrt{2}$, transitions involving the LL $n = 0$ appear twice as strong, for both of the two possible signs of $\Delta n$ (i.e. independent of the angular momentum transferred).

### 2.3 Electron-phonon interactions

In this section we are providing a short overview over the theoretical framework needed to describe electron-phonon (e-ph) interactions in graphene. The e-ph coupling has a strong influence on the phonon energies, due to screening of the lattice vibrations. E-ph interactions are responsible for the existence of Kohn anomalies at the $\Gamma$ and $K$ points of the phonon dispersion that strongly soften the optical
phonon energy (Kohn, 1959). E-ph interactions can also significantly affect physical properties, e.g. scattering in transport (Piscanec et al., 2004).

In this dissertation, we will mainly focus on optical phonons near the Γ point of the Brillouin zone. Only phonons with small wavevectors directly satisfy energy and momentum conservation requirements of the Raman process. These long wavelength phonons are responsible for the G-band, one of the main Raman lines found in graphene and Carbon nanotubes (Malard et al., 2009).

The origin of the e-ph interaction is easily understood considering the hopping between nearest neighbor atoms. Lattice vibrations will lead to a change in bond length between the crystal atoms and cause distortions in the electronic bands. In two dimensional graphene the displacement field can be written as \( u = (u_x, u_y) = 1/\sqrt{2}(u_A - u_B) \), where \( u_A \) and \( u_B \) are the displacements of the atoms on the A and B sublattices. General expressions for the displacement field are derived in basic solid state theory texts (Ashcroft and Mermin, 1976). \( u(r) \) is given by:

\[
u(r) = \sum_{q, \mu} \sqrt{\frac{\hbar}{2NM\omega}} (b_{q, \mu} + b_{q, \mu}^\dagger) e_{\mu}(q) e^{iqr} \tag{2.56}\]

where \( N \) specifies the number of unit cells, \( M \) is the mass of carbon and \( \omega \) is the phonon frequency. \( b_q \) and \( b_q^\dagger \) are the creation and annihilation operators for phonons.

While the complex details of the calculation depend on the specific crystal structure and composition, some insight can be gained from simple approximations. Within a tight binding model the changes in bond length will change the overlap integral, i.e. the hopping energy, between the sublattice atoms should be:

\[
t \rightarrow t + \frac{\partial t}{\partial a} \delta a \tag{2.57}\]

where \( a \) is the bond length. Goerbig estimates (Goerbig, 2011), that the coupling energy for small deformations, where \( \delta a/a \ll 1 \) using the hopping energy described by
Harrison (Harrison, 1981): \( t = \frac{\hbar^2}{Ma^2} \) with some constant factor \( c \). The length scale \( \delta a \) can be estimated from the energy of a harmonic oscillator \( \frac{p^2}{2m} + \frac{1}{2}m\omega^2a^2 = \frac{1}{2}\hbar\omega \). The e-ph coupling strength \( g \) is then:

\[
g = c \frac{\partial t}{\partial a} \delta a = c \frac{2t}{a} \sqrt{\frac{\hbar}{M\omega G}} \approx 0.26eV
\]

Still following Goerbig (Goerbig, 2011) we use a value of \( c = \frac{3}{2} \).

The exact form of the coupling was first derived for acoustic (Suzuura and Ando, 2002) and optical phonons (Ishikawa and Ando, 2006) in Carbon nanotubes. The changes to the continuum Hamiltonian induced by the lattice displacements can be calculated using a tight binding model of graphene. The e-ph coupling t.b. hamiltonian \( H_{e-ph} \) is given by (Goerbig, 2011):

\[
H_{e-ph} = g \sqrt{\frac{2M\omega}{\hbar}} [\sigma_x u_y + \sigma_y u_x]
\]

The application of \( H_{e-ph} \) to graphene has been achieved using density functional theory methods (Piscanec et al., 2004; Lazzeri and Mauri, 2006) and later analytical solutions were presented (Ando, 2006; Neto and Guinea, 2007; Ando, 2007; Goerbig et al., 2007).

The propagation of optical phonons under the perturbation \( H_{e-ph} \) can be obtained from the phonon Greens function in a many particle theory. While this calculation is beyond the scope of this experimental work we will nevertheless present the central results and ideas. The most general form of the phonon Greens function is:

\[
D_{\mu}(q, \omega) = \frac{2\varepsilon_0}{\varepsilon^2 - \varepsilon_0^2 - 2\varepsilon_0 \Pi_{\mu}(q, \omega)}
\]

where \( \varepsilon_0 \) is the unperturbed phonon energy. The index \( \mu \) labels longitudinal and transversal modes respectively. The quantity \( \Pi_{\mu}(q, \omega) \) is the self-energy of the phonon due to the polarization by electron-hole pairs. In lowest order the calculation of \( \Pi \)
only includes the renormalization of the phonon frequency due to the excitation of virtual electron-hole pairs due to $\mathcal{H}_{e-ph}$. The renormalized phonon frequency and broadening are defined by the poles of the Greens function $\mathcal{D}_\mu$ (Ando, 2006). From Eqn. (2.60) we find:

$$\varepsilon^2 - \varepsilon_0^2 = \frac{2}{\varepsilon_0} \Pi_\mu(q, \omega)$$  \hspace{1cm} (2.61)

The phonon frequency is calculated from the real part of $\Pi$, the broadening from the imaginary part.

In the following chapters several experiments will be described that probe the real and imaginary part of the self energy by measuring the optical phonons as a function of charge density and magnetic field strength. The theoretical task will be to calculate the self energy as function of the external parameters to provide meaningful comparison to the experimental observations.
Chapter 3

Experimental methods

The extraordinary achievements in understanding the fundamental properties and applications of graphene have been possible due to the robustness and quality of graphene when integrated into existing micro fabrication processes. For example, graphene field effect devices allow tuning of the number of free charge carriers and provide probes for studying the properties of electronic transport. Using exfoliation, transfer and lithography techniques graphene can be integrated in countless other devices such as composite materials, suspended structures or photonic devices.

In this chapter we present some of the experimental methods we used to prepare graphene devices for experiments and data acquisition. We describe how single layers of graphene are isolated, located and identified. A series of micro fabrication steps are described to process field effect devices that allow for flexible tuning of the physical properties of graphene in experiments.

3.1 Processing of graphene samples

3.1.1 Exfoliation

We use the exfoliation technique developed by Geim and Novoselov (Novoselov et al., 2005; Novoselov et al., 2004) to produce thin graphene crystals. The source material are pieces of natural graphite such as the on shown in Fig. (3-1)(a). Thin layers of graphite are removed from the source crystal either by using a piece of adhesive tape (e.g. Scotch tape) or by carefully peeling thin layers with sharp tip stainless steel
Figure 3-1: Exfoliation of graphene using the Scotch tape exfoliation technique. (a) Crystal of natural graphite used as source for exfoliation. (b) Thin graphite flakes on a piece of scotch tape. (c) Low magnification image of graphite on Si/SiO$_2$ wafer. Areas that appear greenish, faint and cloudy are residues from the adhesive tape. (d) High magnification optical image of a piece of single and bi-layer graphene.

tweezers. The pieces are attached to a piece of adhesive tape which is repeatedly folded over to produce thin sections of the original crystallite see Fig. (3-1)(b).

The as-prepared tape is pressed on a target wafer of Si that is covered with a layer of thermally grown SiO$_2$. The thickness of the SiO$_2$ is selected to produce the highest optical contrast of the single layer graphene flakes (see Sec. (3.1.2)). Finally the tape is slowly peeled of the the wafer to be investigated in an optical microscope. A typical exfoliation results is shown in the optical image in Fig. (3-1)(c). The surface is covered
with graphite crystals of varying thickness that appear as regions of different color. Single layers of graphene can typically be found among the thicker graphite crystals using higher microscope magnifications (see Fig.3.1(d)).

**Best practices for exfoliation**

Exfoliation is not an arbitrary process where a single layer of graphene is deposited at a well defined location. It is rather a stochastic process where the number and locations of the graphene sheets are random. The size and number of sheets depend on the details of the graphene-surface interaction strength, but also on the skill and abilities of the exfoliator. For example, we found that the adhesion can be controlled by the surface properties of the substrate. When the SiO$_2$ surface was too hydrophobic, exfoliation results were typically poor, i.e. most samples wouldn’t show any or only very small single layers of graphene. Samples where the surface was prepared to be hydrophilic by O$_2$ plasma ashing, seemed to be favorable in terms of size and yield of graphene. Typical exfoliations would produce several graphene sheets between 10µm and 50µm in size.

**Surface contamination and sample cleaning**

Other aspects of exfoliation are surface contaminations. Typically, the exfoliation process leaves residues on the surface. In the wide field image of Fig.3·1(c) there appear regions of faint, greenish color that are residues from scotch tape. Residues can negatively influence the quality of the graphene layers. The amount of residues from exfoliation can be minimized by choosing clean room grade adhesive tape instead of conventional Scotch brand tape. In addition we cleaned samples immediately following exfoliation using bathes of warm acetone and iso-propanol. Afterwards the optically visible residues are mostly removed.
3.1.2 Identification

Once potential single layers of graphene are located their thickness or number of layers has to be determined. We used a combination of Raman spectroscopy and optical contrast measurements and show how identification was performed in each case.

Identification by Raman spectroscopy

The two most prominent and strongest lines in the Raman spectrum of graphene are the G-band around 1580\,\text{cm}^{-1} and the 2D-band around 2650\,\text{cm}^{-1} (Malard et al., 2009). The identification of single layer graphene is based on the substantial change in shape of the Raman spectral lines of the 2D band when the number of graphene layers is changed (Ferrari et al., 2006) while the G-band always shows a symmetric, lorentzian line shape. The 2D-band lineshape of single layer graphene shown in Fig. (3-2)(a) is symmetric as well. However for Bernal stacked bi-layer graphene the line shape significantly deviates from the lorentzian form shown in Fig. (3-2)(b).

Unlike the G-band the 2D-band is not a first order Raman process since it involves phonons around the K-point of the Brillouin zone. The 2D-band is created by a process schematically illustrated in the lower half of Fig. (3-2). The quantum mechanical amplitude of the process involves the creation of a virtual electron-hole pair and the creation of 2 phonons with equal, but opposite momentum that scatter between the $K$ and $K'$ points. This process creates the symmetric lineshape for single layer graphene.

However in the band structure of bi-layer graphene additional bands appear in the vicinity of the $K$ points due to the presence of inter-layer coupling. Phonon scattering can connect each of the sub-bands and the 2D band splits up into 4 discrete lines due to the different energies of each of the processes, creating a distorted Raman line. Calculations show (Ferrari et al., 2006) that the line splitting indeed originates...
Figure 3.2: Raman 2D-band spectrum of (a) single layer graphene and (b) bi-layer graphene. The bottom half of the figure shows the underlying double resonance process.
from the splitting of the electronic bands and not from a much smaller splitting that appears in the phonon bands of bi-layer graphene.

**Identification by optical contrast**

Raman identification is closely connected to the different band structures of graphene layers of different thickness in a well defined stacking order. However randomly oriented layers such as the turbostratic graphene created by CVD growth, will always show symmetric 2D bands and behave like decoupled single layers of graphene, due to the low inter-layer interactions in the absence of a well defined-stacking order.

A precise determination of layer thickness can still be accomplished by measurement of the optical contrast. We showed in Fig. (3·1) that a rough characterization of layer thickness can be accomplished using the distinct colors of graphene on Si/SiO\textsubscript{2} substrates.

For more precise determination of the number of layers we acquire a monochromatic microscope image such as in Fig. (3·3) which shows a region covered with single and bi-layer graphene. For each layer of interest we calculate a histogram of pixel intensity values (typically using the software ImageJ) of a region of interest involving the bare substrate and substrate covered with graphene. The resulting histogram seen in Fig. (3·3)(b) will show two separate peaks. The position of the peaks is a measurement of the reflected intensity on the substrate \( I_{\text{sub}} \) and on graphene \( I_G \). The optical contrast is evaluated by:

\[
c = \frac{I_{\text{sub}} - I_G}{I_{\text{sub}}} \tag{3.1}
\]

Adding layer by layer the optical contrast will show discrete jumps (see Fig. (3·3)(b)).

For constant wavelength of probing light and well defined thickness of the SiO\textsubscript{2} layer, precise identification is even without using Raman spectroscopy measurements.
Figure 3.3: Determination of optical contrast. (a) Monochromatic image of a region with single and bi-layer graphene. (b) Histogram of pixel intensities from the regions of interest shown in (a)
The magnitude of the contrast changes can be engineered by tuning the wavelength of the probing light and the thickness of the SiO$_2$ layer. In Fig. (3-4) we present the results of a simulation of the optical contrast of single layer graphene. The image was created using a matrix propagation model describing the reflectivity of electromagnetic waves incident on a layered dielectric medium (Saleh and Teich, 2007). We only consider light at normal incidence. While this model captures the qualitative features correctly, quantitative changes will occur in real experimental situations due to the high NA of microscope objectives.

Recent experiments and theories (Gaskell et al., 2009; Goncalves et al., 2013) show that the coefficient of refraction of the air/SiO$_2$ interface has to be adjusted in regions with a air/graphene/SiO$_2$ interface by the optical conductance of $\pi \alpha$, which has been measured in experiments on suspended graphene membranes (Nair et al., 2008). The Fresnel coefficients for the reflectivity between air and SiO$_2$ is then given by:

$$r_s = \frac{n_{air} \cos \theta_i - n_{ox} \cos \theta_t - \pi \alpha}{n_{air} \cos \theta_i + n_{ox} \cos \theta_t + \pi \alpha} \quad (3.2)$$

The model can easily be extended to multiple layers by using integer multiples of the conductance $\pi \alpha$ in Eqn. (3.2).

In Fig. (3-4)(a) we show the values obtained for the optical contrast of single layer graphene on SiO$_2$/Si as a function of the wavelength of the incident electro-magnetic wave and the thickness of the oxide layer. Very visibly the optical contrast fluctuates when the optical path length is changed. Contrast values above 3 – 4% can be easily seen by the human eye, but maximal contrast values of up to 12% can be achieved by selecting the ideal combination of oxide thickness and wavelength of the probing light beam.

In Fig. (3-4)(b) we show the contrast as a function of oxide thickness for constant wavelength $\lambda$ for $\lambda = 460nm, 514nm, 600nm$. We typically choose an oxide thickness
Figure 3-4: Numerical simulation of the optical contrast of a single layer of graphene under light of normal incidence on a substrate of Si and SiO$_2$ as a function of the oxide thickness and the light wavelength. Bottom shows 3 line cuts at the specified wavelength.
slightly below 300nm where both the red and green wavelength show reasonably high contrast.

3.1.3 Graphene Field effect devices

A basic description of GFETs

The workhorse used in the experiments described in this work are samples where graphene is embedded in a field effect structure. We show a schematic drawing of a GFET in Fig. (3·5). Practically GFETS are produced by exfoliation of graphene on top of substrates of degenerately doped Si (\( \rho < 0.005 \Omega \text{cm} \)) that are covered by a dielectric layer of SiO\(_2\) and thickness \( d \).

Determination of the charge carrier density \( n \)

In the GFET structure the charge carrier density can be controlled by applying a backgate voltage \( V_{bg} \). The substrate and the graphene sheet build the two plates of a parallel plate capacitor. The capacitance per unit area of the graphene sheet is given by

Figure 3·5: Schematic drawing of a graphene field effect transistor on top of a SiO\(_2\) substrate of thickness \( d \). Charge carrier density can be controlled by applying a backgate voltage \( V_{bg} \).
\[ C^{2d} = \varepsilon_0 \varepsilon_{SiO_2} \frac{1}{d} \sim 11.5 \frac{nF}{cm^2} \quad (3.3) \]

The charge carrier density is then calculated as a function of the applied back gate voltage \( V_{bg} \). For an oxide thickness of \( d = 300\,nm \) used in many studies, e.g. by Geim in the first experiments on exfoliated graphene (Novoselov et al., 2004), we obtain:

\[ \frac{n}{V_{bg}} = 7.19 \times 10^{10}\,cm^{-2} \quad (3.4) \]

A reasonable choice to select a gate voltage at this oxide thickness is \( V_{bg} = \langle -100V, 100V \rangle \). Charge densities up to \( 10^{13}\,cm^{-2} \) can be achieved. This is about a factor of \( 10^{-2} \) smaller than the density of carbon atoms in the graphene lattice \( \rho_c = 3.8 \cdot 10^{15}\,cm^{-2} \), so about one additional electron per 100 carbon atoms is introduced at the highest electron density. Due to breakdown of the SiO\(_2\) at high voltages, densities beyond \( 10^{13}\,cm^{-2} \) need to be created by different methods, e.g. polymer electrolyte top gates (Das et al., 2008).

**Determination of the Fermi energy \( E_F \)**

In a charge neutral graphene layer all electron states in the valence band up to the Dirac point are occupied. Higher electron densities will populate unoccupied states in the conduction band. Applying a gate voltage (i.e. changing the charge carrier density) changes the level of the Fermi energy \( E_F \). Since the bandgap in graphene is zero it can be continuously filled with electrons or holes (by removing electrons) (Novoselov et al., 2005). The number of available states is described by the density of states \( \rho^{2D}(E) \) per unit area. In graphene \( \rho^{2D}(E) \) is given by:

\[ \rho^{2D}(E) = \frac{2}{\pi \hbar^2 v_F^2} \frac{E}{\hbar^2 v_F^2} \quad (3.5) \]
Figure 3.6: (a) The density of states $D(E)$ describes the number of states within a small slab on the surface of a cone, shown in orange color. (b) Gate-voltage dependence of the Fermi energy $E_F$ (blue lines) and the charge carrier density $\tilde{n}$. Solid blue line calculated for $v_F = 1.1 \cdot 10^6 ms^{-1}$, dashed blue line for $v_F = 1.0 \cdot 10^6 ms^{-1}$.

$\rho^{2D}(E)$ takes into account the fourfold spin(2) and valley(2) degeneracy. A simple geometric interpretation of $\rho^{2D}(E)$ in graphene is shown in Fig. (3.6)(a). Around the K point $\rho^{2D}(E)$, the number of states between $\langle E, E + dE \rangle$, is describing all quantum states within the orange shaded area on the Dirac cone.

The total number of electron states between the Dirac point and the Fermi level, the charge carrier density $\tilde{n}$, is obtained by integration of Eqn.3.5:

$$\tilde{n}(E_F) = \int_0^{E_F} \rho^{2D}(E) dE = \frac{E_F^2}{\pi (\hbar v_F)^2} = \frac{k_F^2}{\pi}$$

(3.6)

with the Fermi momentum $k_F$. In Fig. (3.6)(b) we show the behavior of $\tilde{n}$ and $E_F$ as a function of the applied gate-voltage for graphene field effect device with oxide thickness $d = 300nm$. Clearly visible is the square root dependence of the Fermi energy as a function of the gate-voltage $E_F \propto \sqrt{V_g} \propto \sqrt{\tilde{n}}$ shown as blue curve. The red curve shows $\tilde{n}$ changing linearly with the gate-voltage.
The value of the Fermi energy depends sensitively on the material parameter of the Fermi velocity. To illustrate we plotted the value of \( E_F \) for two different values of \( v_F \). The solid blue line is calculated using \( v_F = 1.1 \cdot 10^6 \text{ms}^{-1} \) while the dashed blue line is calculated using \( v_F = 1.0 \cdot 10^6 \text{ms}^{-1} \). The curves deviate by 10% of the value of the Fermi energy, so by precise determination of \( E_F, v_F \) can be measured experimentally.

**Fabrication of backgates**

Graphene field effect devices were fabricated in the following way. We use degenerately doped Si wafers that have been covered with a layer of thermally grown \( \text{SiO}_2 \). Using a standard photo lithography process the wafers are first covered with a layer of SI813 photoresist. After exposure and development we removed the resist from squares of size \( 500 \mu \text{m} \times 500 \mu \text{m} \). The \( \text{SiO}_2 \) is removed in a wet etch using hydrofluoric acid. Finally we use electron beam evaporation to deposit 5nm Cr/50nm Au films on the substrate followed by liftoff. For quality assurance the backgate is tested before use by measurement of the resistance between two neighboring backgate contacts. For a resistivity \( < 0.005 \Omega \text{cm} \) the backgate resistance should be ohmic (linear I-V curve) with a value of about \( 1 - 3 \Omega \).

**Electron beam lithography**

Once suitable sheets of single layer graphene are exfoliated and identified on backgated samples, we perform a series of fabrication steps for electrical contacts to the sample. The complete fabrication flow is schematically illustrated in Fig. (3.7).

Using a high magnification image we design the layout of contacts onto the graphene sheet making sure to avoid graphene or graphite pieces in the vicinity of the sample that could short circuit contacts. Afterwards the sample is spun with photo resist for electron beam lithography. In order to facilitate the lift off process we spin
Figure 3-7: Fabrication flow for processing contacts onto single layer graphene sheets using electron beam lithography. (I) Exfoliation result, (II) spincoat PMMA, (III) expose and develop, (IV) Evaporate metals and liftoff, (V) Spin coat PMMA, (VI) expose etch mesas, (VII) RIE etch and removing leftover PMMA.
first PMA copolymer resist (Microchem) followed by PMMA950 (Microchem) resist. The higher solubility of the shorter copolymer undercuts the PMMA950 resist after development.

The sample is aligned and exposed to an electron beam followed by development in a solution of Methylisobuthylketone and Isopropanol (mixture 1:3) at room temperature for 30s. We evaporate a thin layer of Cr, typically 3-5nm, followed by a thicker layer of Au, 50-60nm and liftoff the metal layer in warm acetone around 60C without using sonication.

**Etching**

For certain types of experiments it is favorable to produce graphene sheets of well defined shape, e.g. bars with side contacts for Quantum Hall effect type experiments. It also often necessary to remove graphene sheets other than the main sample that short circuit adjacent contacts. Our samples are going through an etch step to remove these artefacts. First an etch pattern is defined, again using electron beam lithography. For etching we spin a single layer of PMMA950. Graphene is easily removed in a O$_2$ dry etch in an RIE system.

However the O$_2$ etch shows suboptimal selectivity between graphene and the PMMA layer. Therefore it was important to determine the etch rate of PMMA. Fig. (3·8) shows the thickness of a PMMA layer as a function of etch time using our standard recipe. Etch times were selected to remove maximally half of the PMMA etch mask.
Figure 3-8: Determination of PMMA etch rate using and optimized reactive ion etching recipe. Gas: O$_2$, Flow-rate: 15 sccm, Pressure: 200 mtorr, Power: 50 W. The etch rate determined from a linear fit is determined to be 4.3 nm/sec.
Chapter 4

Correlation of Raman and Transport measurements

4.1 Introduction

In this chapter we describe measurements of simultaneous Raman and transport measurements as a function of the charge carrier density in single layer graphene GFETs. The electron-phonon interaction strength in graphene depends sensitively on screening by charge carriers (Kohn, 1959; Piscanec et al., 2004). The energy of the optical G-band phonons increases as a function of charge carrier density (Ando, 2006; Lazzeri and Mauri, 2006) because the adiabatic Born-Oppenheimer approximation is not applicable in graphene (Pisana et al., 2007) typical for metallic materials without a bandgap. The increase in the phonon energy has been observed in multiple studies as a function of an applied electric field that changes the concentration of charge carriers (Yan et al., 2007a; Yan et al., 2007b; Das et al., 2008; Stampfer et al., 2007). Theoretical work additionally predicts strongly enhanced renormalization of the phonon energy when the Fermi level is tuned to the threshold where excitations of real electron-hole pairs by phonon decay become Pauli blocked (Ando, 2006; Lazzeri and Mauri, 2006).

The chapter is structured in the following way. We first describe theoretically the effects of electron-phonon interaction in graphene as a function of charge carrier density and discuss the interpretation in terms of a Kohn anomaly at the Γ point.
of the phonon dispersion. We then describe the experimental setup and measurements of the G-band position and width as a function of the charge carrier density. We present a quantitative discussion of our observations including broadening due to charge inhomogeneity and show how to extract the Fermi velocity, electron-phonon coupling strength, homogeneous broadening and magnitude of inhomogeneity of the charge carrier distribution. We present the results of transport measurements performed simultaneously with Raman experiments. We describe the diffusive transport model we use to describe our observations and determine the mobility due to charged impurities, the amount of short range scatterers and the total transport scattering time. Finally we compare the transport scattering times to quantum scattering times obtained. Their relative size is determined by the dielectric constant of the substrate and the dominant type of scattering mechanism. We consider scattering by charged impurities and short range scattering from lattice defects.

4.2 Electric field dependent electron-phonon coupling

4.2.1 Gate voltage dependent phonon behavior

The electron-phonon interactions in doped graphene layers were first obtained by DFT methods (Lazzeri and Mauri, 2006) and an analytic model by Ando (Ando, 2006). The properties of the optical phonons can be obtained from the self-energy as we showed in Sec. (2.3). For interactions with massless Dirac electrons near the K points Eqn. (2.23), the self-energy in the limit \( T \to 0 \), in lowest order perturbation theory is given by (Ando, 2006):

\[
\Pi(\varepsilon) = \lambda E_F - \frac{\lambda}{4} (\varepsilon + i\delta) \left( \ln \left( \frac{\varepsilon + 2E_F + i\delta}{\varepsilon - 2E_F + i\delta} \right) + i\pi \right)
\]  

(4.1)

\( E_F \) is the Fermi level, \( \lambda \) is the dimensionless electron-phonon coupling, \( \delta \) is a phenomenological broadening factor describing electronic level broadening and \( \varepsilon \) is the
phonon energy. The coupling parameter $\lambda$ is obtained by comparing the energy scales of electron-phonon coupling and electron hopping (Goerbig, 2011)

$$\lambda = \frac{2\pi}{\sqrt{3}} \left( \frac{g}{t} \right)^2$$

(4.2)

with the electron-phonon coupling constant $g \sim 0.26 \, eV$ from Sec. (2.3) and electron hopping energy $t \sim 3 \, eV$. Theoretical estimates for the value of $\lambda$ range from $\lambda \approx 3 \cdot 10^{-3}$ (Ando, 2006) to $\lambda \approx 4.43 \cdot 10^{-3}$ (Lazzeri and Mauri, 2006).

The phenomenologic parameter $\delta$ is introduced to describe broadening of quantum states. Ando relates $\delta$ to level broadening due to electron scattering (Ando, 2006). In the study by Lazzeri et al. broadening only appears as a small parameter without further discussion, but finite temperature effects are taken into account (Lazzeri and Mauri, 2006). Present experimental studies do not consider the homogeneous broadening term in their data analysis (Yan et al., 2007a; Yan et al., 2007b; Pisana et al., 2007), due to the dominating influence of inhomogeneous broadening mechanisms.

We assume that in a typical experimental situation the shifts of the phonon energy are small ($\sim 1\%$) so the self energy must be small as well (Ando, 2006). The shift and broadening are then approximated by the real and imaginary part of the self energy defined in Eqn. (2.61):

$$\varepsilon_G = \varepsilon_0 + \text{Re}\Pi(\varepsilon_0)$$

(4.3)

$$\Gamma_G = \delta_0 + 2\text{Im}\Pi(\varepsilon_0)$$

(4.4)

In this approximation the self energy $\Pi$ has to be evaluated at the unperturbed phonon energy $E = \varepsilon_0$. We numerically calculated the energy and FWHM of the phonon Raman signal from Eqn. (4.3). In the following sections we separately discuss the behavior of the phonon energy and FWHM obtained from the simulations.
4.2.2 Phonon energy shift

In Fig. (4.1) we show the behavior of the phonon energy $\varepsilon_G$ as a function of the Fermi energy $E_F$ using the parameters $\lambda = 4.8 \times 10^{-3}$ and $\varepsilon_0 = 1582.0 \, cm^{-1}$. The black solid line is calculated using $\delta = 10 \, meV$, the dashed line using $\delta = 50 \, meV$. The phonon energy increases for large $E_F$. According to Eqn. (4.1) the increase in $\varepsilon_G$ is proportional to the Fermi energy. The asymptote $\propto \lambda E_F$ is shown as red line in Fig. (4.1). The increase of the phonon energy for increased doping can be explained by the presence of a Kohn anomaly at the $\Gamma$ point of the phonon dispersion (Piscanec et al., 2004). Kohn anomalies occur in metals at wavevectors that connect electron states on the Fermi surface $q \sim 2k_F$ (Kohn, 1959) and are characterized by a discontinuity in the slope of the phonon dispersion. The nesting behavior increases the screening of the lattice vibrations, so the phonon energy decreases. The Kohn anomalies in graphene can be studied by changing the doping density (Fermi energy) using a gate voltage (Lazzeri and Mauri, 2006). Increasing $E_F$ will shift the Fermi surface away from the $\Gamma$ point and influence the condition $q \sim 2k_F$. However Raman measurement only probe phonons at low momentum $q \sim 0$ with energy $\varepsilon_G$. The less efficient screening leads to an increase in the energy of the Raman lines. Experimental studies report that the increase in $\varepsilon_G$ is not expected if calculations are based on the adiabatic Born Oppenheimer approximation (Pisana et al., 2007), where the electrons stay in the instantaneous ground state of the band structure obtained when the lattice atoms change their positions. However this approximation has been shown to be invalid in graphene (Pisana et al., 2007; Lazzeri and Mauri, 2006), which is often the case in metallic system due to the lack of an energy gap between ground and excited electron states.

Eqn. (4.1) has two logarithmic divergences at $E_F = \pm \hbar \omega_G/2$. For low disorder $\delta$ the phonon energy strongly decreases at these points located symmetrically around
the Dirac point $E_F = 0$, as seen in Fig. (4·1), where the position of the logarithmic divergences are marked by vertical lines. The singularities are located precisely where electrons are excited between the valence and conduction band by decay of G-band phonons. Increasing the broadening $\delta$ diminishes the effect of the divergence, e.g. while phonon softening is still visible at $\delta = 50$ meV, it is significantly reduced.

$$\epsilon_G \propto \lambda E_F - \hbar \omega_G/2 + \hbar \omega_G/2$$

Figure 4·1: Phonon energy calculated from the model Eqn. (4.3). Black solid lines are calculated for $\delta = 10$ meV and black dashed lines are calculated for $\delta = 50$ meV. Red solid lines are the asymptotic lines to the G-band frequency with slope $\lambda$ (the electron-phonon coupling)

Another effect of electron level broadening $\delta$ is to shift the phonon energy near the Dirac point at $E_F = 0$ eV. In the limit $\delta \to 0$, the phonon energy approaches its unperturbed value $\epsilon_0$ and blueshifts for increasing $\delta$. Thus the electronic broadening is directly measurable from the position of the G-band Raman line if no other broadening mechanisms such as charge inhomogeneity are considered.

The most common application of the G-band energy shift is to measure the distri-
bution of doping density on a graphene sheet, e.g. by measurement of doping density maps (Stampfer et al., 2007). Typical graphene sheets show considerable amount of doping due to processing residues and due to the roughness of the underlying SiO$_2$ substrate. The impurities lead to particular large values of broadening $\delta$ and strong charge inhomogeneity so the logarithmic divergence of the e-ph coupling does not strongly affect the phonon energy. In a typical experimental situation the G-band position is therefore a good measure of the local charge density.

### 4.2.3 Blocking of phonon decay channels

We now discuss the behavior of the Raman line width. Depending on $E_F$ the line broadening shows a transition between a region of large and small FWHM (see Fig. (4·2)). The transition is located around $E_F = \pm \hbar \omega_G/2$. Qualitatively this behavior is easily understood considering the filling of electron states that can be excited by phonon decay into electron-hole pairs. The decay is allowed for $|E_F| < \hbar \omega_G/2$ when valence band states are filled with electrons, but the electronic states around $E_F = \hbar \omega_G/2$ are unoccupied. Once the Fermi energy is tuned to $|E_F| > \hbar \omega_G/2$, conduction band states that can be excited by a phonon are filled. The decay of optical phonons into electron hole pairs is then prohibited due to Pauli blocking. The lack of the additional decay channel is seen in a decrease of FWHM (increase in phonon lifetime) of the G-band (Fig. 4·2(b)).

The change in decay rate $\Delta \Gamma$, illustrated by a red line in Fig.4·2, can be mathematically linked to the e-ph coupling strength, $\Delta \Gamma \propto \lambda$ (Yan et al., 2007b; Pisana et al., 2007). Thus the e-ph coupling strength can be independently determined either from the behavior of phonon broadening or energy described in Sec. (4.2.2).

The width of the transition region between large and small G-band FWHM strongly depends on the electron level broadening $\delta$. We try to illustrate this connection in Fig. (4·2) where we show the FWHM calculated for $\delta = 10 \text{ meV}$ (black solid
Figure 4.2: FWHM of the G-band optical phonon with electron level broadening $\delta = 10 \text{ meV}$ (black solid line) and $\delta = 50 \text{ meV}$ (black dashed line). The Dirac cones symbolize the level occupation (orange) at the Dirac point, where only the valence band states are filled, and for $E_F \gg 0$. The shaded regions at vertical and horizontal bars are located at $E_F = |\hbar \omega_G/2|$ and illustrate the broadening $\delta = 10 \text{ meV}$. $\Delta \Gamma$ is the total change in G-band linewidth.

Or for small temperatures, $\delta$ would then be equal to the width of the single electron quantum states $\delta_q$ at $E_F = \hbar \omega_G/2$. Using this naive point of view we directly extract electronic properties from a Raman measurement. Later Sec. (4.5) we relate $\delta_q$ to the transport scattering times.
4.3 Experimental measurements of the electron-phonon coupling

We study the gate voltage dependence of the e-ph coupling by experiments on single layer graphene GFETs. We simultaneously perform optical Raman and transport conductivity measurements. This is in contrast to previous, similar measurements that only collect Raman data (Yan et al., 2007a; Yan et al., 2007b; Stampfer et al., 2007) or do not report details about transport measurements except device mobilities (Pisana et al., 2007).

4.3.1 Setup and samples

We prepare GFETs by exfoliation from natural graphite (www.graphit.de) and process with EBL using the procedures outlined in Sec. (3.1.3). The thickness of the dielectric SiO$_2$ layer was 285 nm. Immediately before ball bonding with Au wire, the sample was annealed in Ar/H$_2$ gas at atmospheric pressure at $T = 300\, ^\circ\, C$. Samples are mounted in a cryogenic $\mu$-Raman microscope. A schematic view of the measurement setup in Fig. (4·3)(a). The samples are mounted on top of a piezo electric x-y-z positioning stage. The sample is positioned to be in the focus of a confocal microscope that is inserted into a vacuum tight cylinder. The microscope is initially evacuated at room temperature and then inserted into a bath cryostat to be cooled to $T=77K$ in liquid nitrogen. For thermal equilibration the microscope volume is filled with low pressure He as thermal exchange gas.

Raman spectra are excited using the $\lambda = 488\, nm$ line of an Ar-Ion laser using a NA=0.68 aspheric objective lens. For efficient collection of Raman light, the collection arm of the microscope is aligned to collimate a green HeNe laser at $\lambda = 543\, nm$ which is located close to the expected G-band wavelength $\lambda_G \sim 528\, nm$ ($\varepsilon_G \sim 1582\, cm^{-1}$). This minimizes the effects of chromatic abberations. Excitation and Raman light are
transported to/from the microscope using single mode optical fibers. The excitation light is spectrally cleaned from plasma lines and fiber fluorescence by a small bandpass line filter. A longpass filter cuts out the laser light before the collection fiber, thus only low power Raman signal is transported to an analyzing spectrometer.

We show the Raman G-band and 2D band spectra from our sample in Fig. (4·3)(b) and Fig. (4·3)(c). A symmetric, lorentzian shaped 2D band identifies the sample as single layer (see Sec. (3.1.2)(Ferrari et al., 2006)).

Sample and microscope remained in vacuum and/or low temperature experimental conditions for a duration of several weeks while experiments were performed. Throughout the experiment duration we regularly perform gatevoltage dependent transport measurements to obtain information about the quality of the sample. The
measurement of the gate voltage dependent resistance is quick and accomplished in a few minutes. Raman measurements have spectral acquisition times of several minutes per spectrum and are not suitable for a quick characterization of the sample quality. A detailed discussion of transport measurements to monitor sample quality is presented in Sec. (4.4). However in this section we will only refer to the sample mobility $\mu$ as a measure of sample quality. Experimentally determined $\mu$ values in graphene range from $10^2 \text{ cm}^2/\text{Vs}$ for low quality graphene (e.g. CVD graphene (Song et al., 2012)) to $10^6 \text{ cm}^2/\text{Vs}$ for the high quality graphene that is suspended (Bolotin et al., 2008a; Bolotin et al., 2008b; Du et al., 2008) or on ultraflat, inert substrates such as hBN (Mayorov et al., 2011; Dean et al., 2010). For single layer graphene on SiO$_2$ $\mu$ ranges from 1000 $\text{ cm}^2/\text{Vs}$ to about 25000 $\text{ cm}^2/\text{Vs}$ (Tan et al., 2007). Often the sample quality is reduced by surface contamination from processing. In this case cleaning procedures such as current or high temperature annealing can be used to improve quality as measured by the device mobility.

During the first Raman gate sweeps on our sample, the mobility was $\mu \sim 4900 \text{ cm}^2/\text{Vs}$. After several attempts of cleaning by current annealing and temperature cycling we were able to increase the mobility to $\mu \sim 7800 \text{ cm}^2/\text{Vs}$. To characterize the charge carrier density dependence of the e-ph coupling we perform Raman measurements of the G-band optical phonon as a function of back-gate voltage. All Raman measurements were performed at liquid nitrogen temperatures $T=77\text{K}$. Transport data is collected simultaneous to Raman measurements with low currents of $I \sim 200 \text{ nA}$ to avoid heating of the sample.

4.3.2 Observation of phonon stiffening

In Fig. (4·4)(a) & (b) we show the gate voltage dependence of the energy and FWHM of the G-band extracted from the experimental Raman spectra by double lorentzian fits as described in Sec. (B).
Figure 4.4: Gate voltage dependence of the Raman G-Band. (a)&(b) G-band energy and FWHM as a function of gate voltage. (c)&(d) as a function of the Fermi energy. Data represented by grey circles measured when the device mobility was $\mu = 4900 \text{cm}^2/\text{V}s$, brown triangles were measured when the mobility was $\mu = 7800 \text{cm}^2/\text{V}s$. 
Brown triangles show measurements while the device was in a state with mobility $\mu = 4900 \text{cm}^2/\text{Vs}$, while grey points were measured for a device mobility $\mu = 7800 \text{cm}^2/\text{Vs}$. For both measurements the Dirac point was located at $V_D \sim 8 \text{ V}$. The equivalent charge density $\tilde{n}_d = 0.6 \cdot 10^{12} \text{cm}^{-2}$, calculated using Eqn. (3.4), is a measure of the density of charged impurities on the sample.

We clearly observe phonon stiffening due to change in screening described previously. Also the FWHM of the Raman line increases around the Dirac point as expected from the Pauli blocking of phonon decay. More details are visible when the data is plotted against the Fermi energy $E_F$ (using Eqn. (3.6)) with $E_F = 0$ at the position of the Dirac point. As shown in Fig. (4-4)(c)&(d) the region around the Dirac points are stretched horizontally since $E_F \propto \sqrt{V_{\text{Gate}}}$. 

There are significant differences in the behavior of the phonon energy and width between the measurements at different $\mu$ as well:

1. The Raman frequency around the Dirac point is significantly shifted. While for $E_F \gg 0$ the phonon energies overlap, the energy around $E_F = 0$ is increased when measured at lower mobility.

2. The width of the transition between high and low FWHM is wider for lower $\mu$.

The data suggests that increased scattering in transport, that leads to small $\mu$, is directly correlated to the scattering and broadening observed in the gate-voltage dependent G-band properties. Broadening in the Ando model from Sec. (4.2.1) is described by the phenomenological parameter $\delta$, but what broadening mechanisms are described by $\delta$? How is $\delta$ connected to the physical parameters of electron transport? Are other parameters in the Ando model e.g. the coupling strength $\lambda$ also connected to the transport properties? To answer these questions we first need to determine quantitative measurements from our experimental data that can be compared to transport measurements.
4.3.3 Quantitative analysis of Raman gatesweps

Charge inhomogeneity and electron-hole puddles

In homogeneous samples the G-band energy and FWHM can be calculated from Eqn. (4.3). For single layer graphene previous experiments (Yan et al., 2007b; Pisana et al., 2007; Stampfer et al., 2007) confirm the increase of the G-band energy for large $E_F$ but fail to observe softening due to the logarithmic divergence in the e-ph coupling at $E_F = \hbar \omega_G / 2$ due to large system broadening. The origin of the large broadening is related to the inhomogeneous distribution of charged impurites. The energy scale of fluctuations $\delta \tilde{n}$ in the charge carrier density in single layer graphene are:

$$E_{inh}^{sl} = \hbar v_F \sqrt{\pi \delta \tilde{n}}$$

The influence of charge inhomogeneity is confirmed by observations on bilayer graphene, where the energy scale of inhomogeneous broadening is weaker $E_{inh}^{bl} \propto \tilde{n}$. Phonon softening due to the logarithmic divergence in the phonon self energy is easily observed in experiments on bilayers (Yan et al., 2008).

Charge inhomogeneity is found in many other experiments as well. Spatial Raman maps show G-band shifts on large scales ($\sim 10 \ \mu m$) corresponding to changes in charge carrier density. For graphene on SiO$_2$ fluctuations as large as $\delta \tilde{n} \sim 1.6 \cdot 10^{12} cm^{-2}$ or $E_{inh} \sim 162 \ meV$ (Stampfer et al., 2007; Forster et al., 2013) have been observed and $\delta \tilde{n} \sim 0.6 \cdot 10^{12} cm^{-2}$ or $E_{inh} \sim 100 \ meV$ for graphene on hBN (Forster et al., 2013). Scanning probe studies observe the distribution of charge inhomogeneity into e-h puddles on length scales of $\sim 100 \ nm$ (Martin et al., 2007; Xue et al., 2011). The density fluctuations are found to be up to $\delta \tilde{n} \sim 4.0 \cdot 10^{10} cm^{-2}$, $E_{inh} \sim 25 \ meV$ on SiO$_2$ substrates vs. $\delta \tilde{n} \sim 2.9 \cdot 10^9 cm^{-2}$, $E_{inh} \sim 6 \ meV$ on hBN. The large differences of up to two orders of magnitude compared to the larger length scales might be explained by the low temperatures for STM measurements and the length scale being
on the order of the puddle size (Forster et al., 2013).

There are several competing mechanisms contributing to the creation of charge inhomogeneity and e-h puddles (Das Sarma, 2011). The charge inhomogeneity due to rippling of the graphene sheet is \( \sim 10^{11} \text{cm}^{-2} \) already for small height fluctuations on the subnanometer scale (Brey and Palacios, 2008). The surface of SiO\(_2\) substrates is naturally uneven and rough and graphene follows the nanoscale wrinkles in the substrate due to its low bending rigidity (Cullen et al., 2010). However substrate effects should not play a significant role on atomically flat hBN substrate.

The main influence on charge inhomogeneity seems to be the density of charged impurities on or nearby graphene (Das Sarma, 2011). The charge density distribution might be non-trivial (i.e. not Gaussian) and can change as a function of the density of charge impurities \( \tilde{n}_{imp} \) and the applied back gate voltage (Rossi and Sarma, 2008).

**Modelling of inhomogeneous broadening**

A complete understanding of our observations can only be achieved when the influence of charge inhomogeneities is included. Due to the large energy scales found for charge inhomogeneity (see previous section), previous Raman studies exclusively consider broadening \( \delta \tilde{n} \) due to charge inhomogeneities and neglect homogeneous broadening mechanisms (Yan et al., 2007b). However in our simulations, described in this section, we find that homogeneous broadening \( \delta \) and inhomogeneous broadening \( \delta \tilde{n} \) might be nevertheless be differentiated in experimental measurements.

In the model presented here, we assume that the length scale of charge carrier density fluctuations are much smaller than the focal spotsise in our experiment \( \delta \tilde{n} \ll 1 \mu m \). We consider a gaussian distribution of \( \tilde{n} \) around the mean charge density \( \tilde{n}_\mu(V_{gate}) \) and standard deviation \( \delta \tilde{n} \) in the area of interest probed by the laser. Locally the energy and FWHM of the G-band are given by the local charge density and the overlap of the different contributions within the probe area are measured. The charge
carrier distribution is given by:

\[ f(\tilde{n}_\mu, \delta \tilde{n}) = \frac{1}{\delta \tilde{n} \sqrt{2\pi}} e^{-\frac{(\tilde{n}_\mu - \tilde{n})^2}{2\delta \tilde{n}^2}} \]  

(4.6)

The simulation proceeds in the following way:

1. Select a random set of \( \tilde{n}_\mu \) values normally distributed according to Eqn. (4.6). Reasonable fast performance is achieved using 1000-5000 values. The result is a distribution shown in Fig. (4.5)(a).

2. The charge carrier distribution is converted in a \( E_F \) distribution. \( \tilde{n} \) is connected to the Fermi energy by Eqn. (3.6). Directly calculated \( E_F \) for each value of \( \tilde{n}_\mu \).

3. Calculate the phonon energy \( \varepsilon_G \) and width \( \Gamma_G \) using the model Eqn. (4.3). A reasonable choice has to be made to select the initial values of the parameters \( \lambda, \delta, \varepsilon_0 \). For example \( \lambda \) and \( \varepsilon_0 \) can be determined from the slope and position of the phonon energy for \( E_F \gg 0 \). Eventually the parameters are iteratively adjusted with \( \delta \tilde{n} \) until the best values are found.

4. Create distribution of lorentzian lines using the distributions of \( \varepsilon_G \) and \( \Gamma_G \). We assume that the spectral weight of each line is the same, independent from position and width. All lorentzians are thus normalized to area \( A = 1 \).

5. The complete simulated Raman line \( \mathcal{L}_{\tilde{n}_\mu}(\varepsilon) \) is then given by the sum of each lorentzian function in the distribution.

\[ \mathcal{L}_{\tilde{n}_\mu}(\varepsilon) = \sum_{\varepsilon_\mu, \Gamma} \frac{2}{\pi \Gamma} \left( \frac{\varepsilon - \varepsilon_\mu}{\Gamma/2} \right)^2 + 1 \right)^{-1} \]  

(4.7)

6. Fit a single lorentzian line profile to the simulated G-band \( \mathcal{L}_{\tilde{n}_\mu} \).

7. Repeat simulation for additional \( \tilde{n}_\mu \).
We show a simulated Raman line with inhomogeneity $\delta n = 0.3 \cdot 10^{12} cm^{-2}$ in Fig. (4-5)(b) as a black line. The red dashed line is the best lorentzian fit to the data. Unless unnaturally large values of $\delta n$ are assumed, the deviations of the simulated G-band to a lorentzian lineshape are very small. In particular we are not able to produce asymmetric lineshapes that we observe in our data. We explain this result by two observations. Large shifts of the phonon energy (larger than the line width $\Gamma_{FWHM}$) only occur for small $\delta$ and in a very narrow region $\Delta E \sim 1 \text{ meV}$ around $\hbar \omega_G/2$. The corresponding phonons only contribute weakly to the overall signal. Also the shift of the phonon energy, that is sampled by the charge carrier distribution, is small compared to the phonon linewidth, so no significant deviations from a lorentzian lineshape can occur. Unusual charge carrier distributions, which are not Gaussian, might be able to explain the asymmetric lineshapes we observe in our experiments (Rossi and Sarma, 2008), but the main idea will stay the same. A single Raman
measurement effectively measures the probability distribution function of the charge carrier density within the laser focus. Results for different charger carrier distributions have to be reported later in a different study.

The effect of charge inhomogeneity within our model on the position and FWHM of the G-band line is significant, which we demonstrate by simulated Raman gatesweeps for a selection of $\tilde{\delta}n$ values:

$$\tilde{\delta}n = \{0.05, 0.1, 0.2, 0.3, 0.5, 0.7, 1.0\} \cdot 10^{12} cm^{-2}$$

The simulated energy and FWHM are shown in Fig. (4·6).

The phonon energies are the same for $E_F \gg 0$. As for increased homogeneous broadening $\delta$ Eqn. (4.1) the logarithmic divergence around $E_F = \hbar \omega_G / 2$ broadens and disappears for large $\delta \tilde{n}$.

However the behavior of the phonon energy at $E_F = 0$ deviates from the homogeneous broadened model. Consider Fig. (4·6)(c) where we show the value of the phonon energy $\varepsilon_G(E_F = 0)$ for different $\delta \tilde{n}$. Initially the energy decreases and reaches a minimum around $0.5 \cdot 10^{12} cm^{-2}$. Without inhomogeneity the energy will increase monotonically shown in Fig. (4·6)(d).

The effect on the FWHM is significant as well as shown in Fig. (4·6)(b). Similar to homogeneous broadening the transition width between high and low FWHM increases with $\delta \tilde{n}$, though counter intuitively the FWHM at $E_F = 0$ decreases, due to the width of the transition region being larger than the distance $\Delta E = \hbar \omega_G$ between the transitions. In Fig. (4·6)(e) we show the development of the FWHM for increasing $\delta \tilde{n}$. Already small charge inhomogeneities have a significant effect due to the effective energy broadening in graphene single layers.
Figure 4.6: Effect of inhomogeneous line broadening on the phonon energy and FWHM as determined from single lorentzian fits. We show for separate values of $\delta \tilde{n}$ the energy (a) and FWHM (b) of the phonon Raman line. Behavior of the phonon energy at $E_F = 0$ for inhomogeneous broadening (c) and only homogeneous broadening (d). The behavior of the FWHM at $E_F = 0$ is shown in (e).
Fit to experimental data

We now describe our measurement data using the e-ph coupling model with charge inhomogeneity. The (in our opinion) best fit to the data is shown in Fig. (4·7). The model is adjusted to the data by eye using the following procedure.

1. Select Fermi velocity so position of divergence falls right on $E_F = \hbar \omega_G / 2$. Since the Fermi velocity is the only free parameter in the Voltage-Energy conversion this allows measurement of the Fermi velocity. This is described in more detail in Sec. (5.4.3).

2. select $\lambda$ and $\varepsilon_0$ to match the slope and position for $E_F \gg 0$.

3. Select $\delta_0$ to describe minimal FWHM. Due to relationship between $\lambda$ and $\Delta \Gamma$ the maximal width should overestimate the phonon width at the Dirac point since no inhomogeneous broadening has been included yet.

4. Adjust $\delta \tilde{n}$ and $\delta$ iteratively while observing the effect on $\Delta \omega_G$ at the Dirac point, $\Gamma_{max}$ and the broadening of the transition region.

A good fit (by eye) is obtained when selecting $\lambda = 3.5 \cdot 10^{-3}; \varepsilon_0 = 1586 \text{ cm}^{-1}; \delta_{\text{high} - \mu} = 20 \text{ meV}, \delta_{\text{low} - \mu} = 60 \text{ meV}$. The charge inhomogeneity was set to $\delta \tilde{n} = 0.5 \cdot 10^{12} \text{ cm}^{-2}$ for both mobilities.

The value obtained for the e-ph coupling strength is close to theoretical estimations of $\lambda \sim 3 \cdot 10^{-3}$ (Yan et al., 2007b; Goerbig et al., 2007), but DFT studies found $4.43 \cdot 10^{-3}$. Experimental evidence supports the latter value with $\lambda$ values of $4.5 \cdot 10^{-3}$ obtained from gate sweep measurements (Yan et al., 2007b) and $4.8 \cdot 10^{-3}$ from measurements in magnetic fields (Faugeras et al., 2009). On a different sample Sec. (5.4) we also measure a value of $4.8 \cdot 10^{-3}$. The SiO$_2$ layer used on the present sample was treated with Cl atoms during the oxide growth, presumably reducing surface charges. However we don’t think this is sufficient to explain the low value of $\lambda$. 
Figure 4.7: Quantitative description of the e-ph coupling. Top row shows the G-band energy, bottom row the G-band FWHM. Fits by eye to the grey dots ($\mu = 7800 \text{cm}^2/\text{Vs}$) is shown as black lines and fits to brown triangles ($\mu = 7800 \text{cm}^2/\text{Vs}$) as red lines. The white shaded figures only include inhomogeneous broadening $\lambda = 3.5 \cdot 10^{-3}, \omega_0 = 1586 \text{ cm}^{-1}, \delta_{\text{high}-\mu} = 20 \text{ meV}, \delta_{\text{low}-\mu} = 60 \text{ meV}$. Blue shaded figures additionally include charge inhomogeneity $\delta \tilde{n} = 0.5 \cdot 10^{12} \text{cm}^{-2}$. 
We have used a model by Ando to describe the gate voltage dependence of the G-band. Our model also simulates the effect of an inhomogeneous charge carrier density which is assumed to be normal distributed. We determine the width $\tilde{n}$ of the charge carrier distribution as well as the size of the phenomenological broadening parameter $\delta$ used in the Ando model. We find $\delta = 20\text{meV}$ for $\mu = 7800 \text{cm}^2/\text{Vs}$ and $\delta = 60\text{meV}$ for $\mu = 4900 \text{cm}^2/\text{Vs}$.

4.4 Transport characterization and electron scattering

The strong influence of charge inhomogeneity and the inability to observe characteristic phonon behavior (logarithmic divergence), make it necessary to study the sample properties in more detail. GFETs enable us to study electron transport as a function of $E_F$ simultaneously to Raman measurements.

Significant progress in graphene research has been driven by study of transport through graphene. GFETs were used in the nobel-prize awarded work by Novoselov and Geim about discovery of Dirac Fermions in graphene (Geim, 2011; Novoselov, 2011; Novoselov et al., 2005; Novoselov et al., 2004) and for discovery of new forms of the integer quantum hall effect in single and bilayer graphene (Novoselov et al., 2005; Zhang et al., 2005) Transport provides a general measure of sample quality as well as direct access to electron and hole scattering times. The properties of transport scattering can then be correlated to our Raman data.

4.4.1 Fundamentals of transport

We acquire transport data from GFETs in the device configuration shown in Fig. (4·8). We apply a well defined current $I$ through the Au source-drain contacts and measure the voltage drop $V_{\text{sig}}$ across the GFET. We then determine the resistivity and conductivity as a function of the charge carrier density $\tilde{n}$. Device are prepared in a four probe geometry shown in Fig. (4·8)(c) eliminating the influence of the con-
Figure 4-8: (a) Schematic drawing of setup for transport measurements. (b) Top view of measurement setup for transport measurements. (c) Particle trajectories for diffusive and ballistic transport.

tact resistance between metal electrodes and graphene which can significantly change transport behavior (Blake et al., 2009). We measure the transport limited charge scattering times and make conclusions about the mechanisms of scattering in our device.

Determination of basic transport parameters

Let’s consider the transport through a rectangular graphene bar of length $L$ and width $W$ with large aspect ratio $L \gg W$ in zero magnetic field. From the resistance $R = U_{\text{sig}}/I$ we determine the two dimensional resistivity $\rho^{2D}$:

$$\rho^{2D} = R \left( \frac{W}{L} \right)$$  \hspace{1cm} (4.8)
More specifically we use the length between the side contacts that are used to measure $U_{sig}$. Unlike a bulk 3D, sample the dimensions of the resistivity $\rho^{2D}$ in two dimensions equal the dimensions of the resistance. Finally the conductivity in zero magnetic field is given by the usual relation $\sigma = \rho^{-1}$. The conductivity directly links the current density $j$ to the applied electric field $E$:

$$j = \sigma E = \bar{n}e\mu E$$  \hspace{1cm} (4.9)$$

Here we introduced the mobility $\mu$, where $\sigma = \bar{n}e\mu$. The mobility is a basic measure of sample quality and preferably used in the characterization of semiconductors since the mobility of electrons and holes can be defined separately. $\mu$ connects the drift velocity $v_D$ of the charge carriers to the applied electric field:

$$v_D = -\mu E$$  \hspace{1cm} (4.10)$$

**Scattering time in diffusive transport**

Classically the transport conductivity can be related to the effective mass $m^*$ and the scattering time $\tau$ that defines the mean free path $l = v_D\tau$ between scattering events:

$$\sigma = \frac{e^2\tau\bar{n}}{m^*}$$  \hspace{1cm} (4.11)$$

The transport effective mass in graphene can be defined by the group velocity of wave packets and is given by (Ariel and Natan, 2012):

$$m^* = \hbar^2 k \left(\frac{\partial E}{\partial k}\right)^{-1} = \frac{\hbar k}{v_F}$$  \hspace{1cm} (4.12)$$

The often used expression for the effective mass based on the curvature of the band structure $m^* \sim 1/(\partial^2 E/\partial k^2)$ is invalid for graphene since it is derived assuming parabolic bands.
Combined with Eqn. (4.11) we find the expression for the scattering time:

\[ \tau = \frac{\hbar \sigma}{v_F e^2 \sqrt{\tilde{n}}} \]  

(4.13)

\( \tau \) is understood to be the total scattering time due to all active scattering mechanisms.

### 4.4.2 Diffusive transport in Graphene

There are many factors influencing and limiting the diffusive conductivity in graphene. Experiments show that the conductivity in single layer graphene at large carrier densities is dominated by scattering due to charged impurities, described by a screened Coulomb potential \( V \sim e/\kappa r \). Here \( \kappa \) is the dielectric permittivity of the substrate and \( r \) the electron-impurity distance. The conductivity due to charged impurity scattering \( \sigma_l \), has a characteristic dependence on the charge carrier density \( \tilde{n} \). It is found that \( \sigma_l \propto \tilde{n} \) for a random distribution of charged impurities (Hwang et al., 2007a). In graphene \( \sigma_l \) can be written as:

\[ \sigma_l = \tilde{n} e \mu + \sigma_{min} \]  

(4.14)

with the sample mobility \( \mu \). The universal minimum conductivity \( \sigma_{min} \) is included phenomenologically in agreement with experimental observations (Miao et al., 2007; Tan et al., 2007).

Short range scattering, caused by lattice defects and described by \( \delta \)-function potentials, is orders of magnitude weaker compared to Coulomb potential scattering (Das Sarma, 2011). The influence of short range scattering is visible on samples showing high mobility. The total conductivity increases sublinear in \( \tilde{n} \). This is visible in the data shown in Fig. (4·11) where sublinear behavior is clearly observed for higher mobility (red curve) but not for lower mobility (green curve). The conductivity \( \sigma_s \)
due to short range scattering is found to be $\sigma_s \propto \tilde{n}^0$, i.e. independent of $\tilde{n}$. Thus for very large charge carrier densities $\tilde{n}$ where $\sigma_l > \sigma_s$ the resistivity is dominated by the constant short range scattering.

The total conductivity $\sigma$ is given by the contributions of all scattering mechanisms. Using Matthiessen’s rule, the total scattering time $\tau^{-1} = \tau_l^{-1} + \tau_s^{-1}$ is calculated from the scattering times due to long range scattering $\tau_l$ and short range scattering $\tau_s$.

Since $\sigma$ is related to the scattering time according to Eqn. (4.11) the conductivity $\sigma = \rho^{-1}$ can be written as (Hwang et al., 2007a; Dean et al., 2010):

$$\sigma = \frac{1}{(\tilde{n}e\mu + \sigma_{\text{min}})^{-1} + \rho_s}$$ \hspace{1cm} (4.15)

Here $\rho_s = \sigma_s^{-1}$ is the resistivity due to short range scattering.

The minimum conductivity $\sigma_{\text{min}}$ received large attention due to mismatch of its theoretically predicted value and experimental observations. Several different values for $\sigma_{\text{min}}$ have been predicted depending on the theoretical models and approximation schemes (Das Sarma, 2011). The universal theoretical limit $\sigma_{\text{min}} \sim 4e^2/\pi\hbar$ is only achieved for ballistic transport on undoped graphene. Indeed this has been experimentally realized on short devices where boundary effects are negligible (Miao et al., 2007) and ballistic transport is achieved for small aspect ratios $L/W$ of the device. In most real world devices $\sigma_{\text{min}}$ is found to be larger than the theoretical minimum due to the larger aspect ratios $L/W$ (Miao et al., 2007) and the presence of electron-hole puddles at very low charge densities (Das Sarma, 2011).

In Fig. (4-12)(c) we summarize fit results from transport measurement on our device as a function of time (throughout the sample life time). The bright red line in the graph marks the universal value $\sigma_{\text{min}} \sim 4e^2/\pi\hbar$ and the blue diamonds are results from fitting the diffusive transport model of Eqn. (4.15). The fit values are close but slightly above the universal value. The fit results for $\sigma_{\text{min}}$ are underestimating the ac-
Figure 4-9: (a) Conductivity of single layer graphene as a function of charge carrier density. Red solid line is a fit to the data using diffusive transport. Dotted line is a fit using ballistic transport. (b) Zoom into region around the Dirac point.

tual measured $\sigma_{\text{min}}$ shown as red diamonds by a factor $\sigma_{\text{real}}/\sigma_{\text{min}} > 4$. The difference between fit and data in the low density regime can be well seen in Fig. (4-9)(b). Our experimental results are in agreement with the observations on samples with similar aspect ratios (For our sample $L = 17 \mu m$ and $W = 4 \mu m$ so $L/W = 4.25$) (Miao et al., 2007).

Many details of the scattering mechanism such as the dependence on temperature and impurity density are implied within $\rho_s$ and $\mu$ and must be obtained from theoretical models. While scattering by lattice vibrations and phonons sets a fundamental limit to transport in graphene, it has been shown to only play a minor role and we did not include scattering from phonons in our analysis.

We observe sublinear behavior in high mobility transport in our sample shown in Fig. (4-9)(a). We find that the data is well described by Eqn. (4.15) (shown by the solid red line) using $\mu \sim 16000 \ cm^2/Vs$ and $\rho_s \sim 30 \ \Omega$.

The quality of the fit obtained by Eqn. (4.15) is illustrated well when compared with a model for ballistic transport. Ballistic transport can be observed on ultra high
quality samples showing mean free paths > 1 µm (Du et al., 2008; Mayorov et al., 2011). The difference to diffusive transport is the dependence on the charge carrier density: \( \sigma_{bal} \propto \sqrt{n} \) (Bolotin et al., 2008a). Fitting our data, shown in Fig. (4·9) (a) (dotted line), shows that our observations are not in the ballistic regime.

4.4.3 Experimental transport data

By monitoring the transport parameters as a function of time, we detect changes in sample quality due to external processes such as evacuation of the probe chamber, cooling and annealing steps. In addition by simultaneous measurement of transport during Raman gatesweeps we correlate the mobility to the broadening observed in Raman.

Monitor of sample quality vs. time

To demonstrate how we monitor the sample quality we look at initial evacuation and cooling once the sample was mounted on the microscope. The experiments on this sample lasted about 3-4 weeks with the sample in the vacuum chamber of our Raman microscope. About of the total time we cooled to \( T = 77 \, K \) using liquid nitrogen. We performed 2 cooling cycles between low and room temperatures and attempted various efforts of annealing and cleaning. While at atmospheric pressure the sample was kept on ground reference, transport measurements were only started after pressure dropped below \( p < 10^{-3}torr \).

In Fig. (4·10)(a) we show the resistance as a function of gate voltage during pump down of the sample. At \( t = 0h \) the resistance (blue curve) shows strong hysteresis when the sweep direction is reversed and the resistance peak is rather broad. After \( t = 39h \) in vacuum with \( p \sim 10^{-6} \, torr \), the hysteresis is reduced, the Dirac point shifted towards \( V_g = 0 \) and the width of the resistance peak decreased. Experiments show that the Dirac point position and width of resistance peak correlate with a higher
Effects of Pump down

(a) (b) Effects of Pump down Hysteresis and cooling

Figure 4-10: Gate voltage dependent resistance (a) during initial evacuation of the microscope chamber immediately after pump start (blue curve) and after 39h in vacuum (red curve). (b) Resistance after first cooldown (red curve) and after current annealing (black curve). Solid were obtained sweeping from negative to positive voltages, dashed lines from positive to negative voltages.

sample mobility (Tan et al., 2007; Chen et al., 2008). In the present experiment we believe that the sample quality improved by desorption of impurity molecules and residues in the vacuum of the microscope chamber.

We also observed significant changes in transport during cooldown shown in Fig. (4-10)(b). At $T = 77 \, K$ the symmetric resistance curve became distorted and asymmetric (red curve in the figure), probably due to freezing of residual gas on the sample while filling the He exchange gas (Jang et al., 2008). Current annealing has been shown to be able to clean graphene from residues and improve the sample mobility (Moser et al., 2007). We applied a current of $I = 1.88 \, mA$ for 12h and eventually we were able to recover a symmetric resistance with negligible hysteresis at $T = 77 \, K$.

At all points in time we acquired the parameters of the diffusive transport by Eqn. (4.15), for example in Fig. (4-11)(a) we show the conductivity at RT in vacuum
Figure 4.11: (a) Conductivity at RT after pump down (grey dots). Red curve is a fit of diffusive transport to the data. (b) Fits to the conductivity at RT in vacuum (red curve), after first cooldown and annealing (green curve) and after temperature cycle and further cleaning (blue curve)

and the best fit showing a mobility $\mu = 16100 \text{ cm}^2/\text{Vs}$.

The development of $\sigma$ is clearly sublinear indicating the influence of short range scattering at larger charge carrier density. We compare $\sigma(\bar{n})$ at different points of the experiment in Fig. (4.11)(b).

- Red curve: $\sigma$ at RT in vacuum, same data as in Fig. (4.11)(a)
- Green curve: $\sigma$ at $T = 77 \text{ K}$ after the annealing procedure described before. Mobility dropped to $\mu \sim 4900 - 6000 \text{ cm}^2/\text{Vs}$
- Blue curve: After a series of Raman measurements the sample was temperature cycled to RT to further remove frozen molecules and impurities. Data taken after re-cool shows slightly increased $\mu \sim 8000 - 9000 \text{ cm}^2/\text{Vs}$.
Discussion of the observed transport behavior

In Fig. (4·12) we summarize the transport parameters measured on our sample over time. We identify 3 regions of different sample quality which we marked in the figure: Region I contains all data points taken before the first cool down of the sample. Data in region II was acquired after the first cool down to $T = 77K$ and annealing was performed. Finally region III contains low temperature data after temperature cycling. Raman gatesweeps presented in Sec. (4.3) were taken in region II and III.

We already discussed the behavior of the mobility that drops between regions I and II and slightly increases in region III. The minimum conductivity shows similar behavior. Short range scattering $\rho_s$ remained fairly constant with somewhat large fluctuations. The error in measuring $\rho_s$ might be quite large. Due to the low $\mu$ values the conductivity is mostly linear so the fits are insensitive to changes in $\rho_s$. Finally the Dirac point is shifted towards $0 V$ between regions I and II and remains constant throughout regions II and III.

The behavior of $\mu$ and $V_d$ is somewhat peculiar. Experiments have demonstrated a connection between $\mu$ and $V_d$ on pristine samples and by charge impurity doping using potassium ions (Tan et al., 2007; Chen et al., 2008). The experiments are well described by diffusive transport (Das Sarma, 2011; Hwang et al., 2007a) where the mobility $\mu \propto n_i^{-1}$ with $n_i$ being the density of charged impurities. $V_d$ is located closer to $0 V$ for lower impurity densities.

The decrease in $\mu$ suggests that $n_i$ should increase by a factor of 2.5 between region I and II. The Dirac point located around $12 V$ in region I should shift to $V_d = 30 V$, but instead drops to $6 - 8 V$. We think the observation is explained by introduction of charged dopants of opposite sign to the initially present impurities so the scattering increases while Dirac point shifts towards $0 V$.

When moving from II to III, equal amounts of positively and negatively charged
Figure 4.12: Transport parameters during the sample lifetime. Blue diamonds are determined from fitting Eqn. (4.15) to the measured, charge carrier density dependent conductivity. Data in region I was recorded at room temperature before the first cooldown of the sample. Data in regions II and III was recorded at $T = 77$K. The sample was annealed at room temperature in between regions II and III. Red diamonds mark the actual measured minimum conductivity $\sigma_{\text{min}}$. The red line marks the position of the "universal" value $4e^2/\pi\hbar$. 
dopands were removed, $V_d$ stayed $\mu$ recovered modestly.

4.5 Correlation of transport and Raman measurements

Our observations from Raman measurements show that increasing $\delta$ seems to be related to the quality of transport. Here we propose the idea that the correlation between the G-band and transport behavior is due to a connection of scattering times that are related to the respective observations. According to a study by Hwang and das Sarma (Hwang and Sarma, 2008) there exist two different scattering times in disordered conducting materials that describe relaxation of electron band states. The transport scattering time $\tau_t$ determines the conductivity according to Eqn. (4.13). The second timescale is referred to as the single particle relaxation time $\tau_q$ which specifically determines the quantum mechanical broadening of the electronic momentum eigenstates by $\delta_q = \hbar/\tau_q$. $\tau_q$ can be measured from the oscillation amplitude of the Shubnikov-de Haas effect (Hong et al., 2009). We argue that the relationship between $\tau_t$ and $\tau_q$ obtained by Hwang and das Sarma can be used to explain the correlations between our observations in Raman and transport measurements.

4.5.1 Relationship of transport and relaxation times

In the theory the transport scattering time $\tau_t$ is evaluated by solving the Boltzmann transport equation in the relaxation time approximation and $\tau_q$ is given by the Self energy of the electron propagator (Hwang et al., 2007b). Coulomb and short range scattering are considered as the most important scattering mechanisms in graphene (Hwang et al., 2007b; Das Sarma, 2011). The total scattering time is given by the contributions from long and short range scattering

$$\frac{1}{\tau_t} = \frac{1}{\tau_{t,l}} + \frac{1}{\tau_{t,s}}$$

(4.16)
The index $i$ stands for transport or quantum lifetime respectively. The scattering times are related to an energy scale by $\delta_i = \hbar / \tau_i$.

Hwang and das Sarma show that there exists a well defined relationship between $\tau_t$ and $\tau_q$. The ratio $\tau_t / \tau_q$ between the scattering times is independent of the charge carrier density and changes as a function of the dielectric screening properties of the substrate and (in the case of charged impurities) by the distance of the impurities to the graphene sheet. The screening due to the substrate is described by the parameter $r_s$ (Hwang et al., 2007b):

$$r_s = \frac{e^2}{4\pi \varepsilon_0 \hbar \nu_F \kappa} = \frac{\alpha}{\kappa} \left( \frac{c \nu_F}{v_F} \right)$$  \hspace{1cm} (4.17)

$\alpha \sim 1/137$ is the fine structure constant and $\kappa$ is the static permittivity of the substrate, making $r_s$ the effective fine structure constant.

The difference between the transport and quantum scattering times arises from the directional dependencies of the scattering cross sections (Hwang et al., 2007b). The scattering times are given by the equation (Hong et al., 2009):

$$\frac{1}{\tau_q} = \int_0^\pi Q(\theta)(1 + \cos \theta) d\theta$$

$$\frac{1}{\tau_t} = \int_0^\pi Q(\theta)(1 + \cos \theta)(1 - \cos \theta) d\theta$$  \hspace{1cm} (4.18)

$\theta$ is the scattering angle and $Q(\theta)$ contains the details of the scattering mechanism, e.g. for charged impurity scattering $Q(\theta)$ would be related to the Coulomb potential. Surprisingly the only difference between the calculation of $\tau_t$ and $\tau_q$ is angular dependence which is shown in Fig. (4.13)(a). For transport in graphene small angle and large angle scattering are strongly suppressed, while only large backscattering angles are suppressed for $\tau_q$. 
The $r_s$ dependence of $\tau_t/\tau_q$ (copied from (Hwang et al., 2007b)) is shown in Fig. (4.13)(b): The figure shows results for both graphene and conventional 2D materials as shown by the labels in the figure. $\tau_t/\tau_q$ are plotted separately for pure Coulomb and pure short range scattering. While for the former it is found that $\tau_{t,l}/\tau_{q,l} > 2$, one finds $\tau_{t,s}/\tau_{q,s} < 2$ in the latter case. The index $l,s$ specifies that the respective value is due to only long range or short range scatterers. Experimental observations (Hong et al., 2009) confirm the independence of $\tau_t/\tau_q$ from the charge carrier density. They find results similar to theoretical studies (Hwang et al., 2007b) but slightly larger values of $\tau_t/\tau_q$ than we mentioned above probably because the charged impurities are located some distance away from the graphene sheet $\sim 2 \, \text{nm}$.

### 4.5.2 Measurement of relaxation times from transport and Raman

We want to connect the single particle lifetime $\tau_q$ to Raman measurements. Let’s consider the electron momentum states at energies $\pm \hbar \omega_G/2$ around the Dirac point
that are connected by G-band phonon decay into electron hole pairs. When the Fermi energy is increased the electron states of width $\delta_q = \hbar/\tau_q$ are occupied and the coupling to the optical phonon is blocked as seen in Sec. (4.2.3). Here our naive point of view is that the width of the transition between blocked and unblocked states corresponds to the transition width $\delta$ observed in the FWHM of the G-band. Therefore $\delta$ should be determined by the width (lifetime) of the optical phonon as well as the width of the electron states involved in phonon decay. However we already showed that the width of the phonon $\delta_G \sim 1 \text{ meV}$ is one order of magnitude smaller than $\delta$ found by fitting the G-band position and FWHM. We conclude that the phenomenological broadening $\delta$ is then essentially equal to $\delta_q$.

We extract the total transport scattering time $\tau_t$ from the conductivity using Eqn. (4.13). In particular we evaluate $\tau_t$ at the charge density $\bar{n}$ such that $E_F = \hbar \omega_G/2$, where the phonon decay into electron-hole pairs is activated. We use the transport parameters obtained during two Raman gatesweeps labeled A and B shown in Fig. (4.7). We emphasize that $\tau_t$ includes the effects of long and short range scattering, while $\mu$ describes only the scattering due to charged impurities. We find:

$$A: \quad \mu = 4900 \text{cm}^2/\text{Vs}; \rho_s = 4.1 \Omega \rightarrow \tau_t = 52 \text{ fs} \rightarrow \delta_t = 13 \text{ meV}$$
$$B: \quad \mu = 7800 \text{cm}^2/\text{Vs}; \rho_s = 22.1 \Omega \rightarrow \tau_t = 70 \text{ fs} \rightarrow \delta_t = 9 \text{ meV}$$

(4.19)

To compare with the theory of Hwang and das Sarma we determine the screening parameter $r_s$ for the dielectric constant of the SiO$_2$ substrate, $\kappa = 3.9$. We find $r_s = 0.5$. From Fig. (4.13) we find for Coulomb scattering that $\tau_t/\tau_q(0.5) \sim 3$ for long
range scattering. While fitting Raman data we found Sec. (4.3.3)

\[ A: \delta_q = 60 \text{meV} \]
\[ B: \delta_q = 20 \text{meV} \]

using the values of \( \delta_t \) from Eqn. (4.19) we find for \( \tau_t/\tau_q \):

\[ A: \frac{\tau_t}{\tau_q} = 4.6 \]
\[ B: \frac{\tau_t}{\tau_q} = 2.2 \]

(4.21)

Hong et al. (Hong et al., 2009) find values of \( \tau_t/\tau_q \sim 3.5 \) when Coulomb scattering dominates and \( \tau_t/\tau_q < 3 \) in samples with strong contribution of short range scattering. Moreover using magneto-transport the charge carrier dependence of \( \tau_t/\tau_q \) can be measured, whereas our Raman experiment only determines \( \tau_t/\tau_q \) at one particular \( E_F = \hbar\omega_G/2 \). We find larger \( \tau_t/\tau_q \) in experiment A, where short range scattering was weaker compared to measurement B. In contrast to the experiments by Hong et al. (Hong et al., 2009) we did not use magnetic fields in our measurements instead measuring \( \tau_q \) using optical methods.

The major source of error in our experiment is the influence of charge inhomogeneities making exact determination of \( \delta \) challenging. Spatial scans might be able to identify regions of low charge inhomogeneity that could provide higher quality data. Further measurements on graphene on hBN where lower \( \tilde{n} \) values are expected should allow for more accurate measurements as well. In addition, high quality samples with large electron mobility would allow for more precise measurement of the relative contributions due to long and short range scattering.
In summary, we performed gate voltage dependent Raman and transport measurements on single layer GFETs. We determine the electron-phonon coupling strength $\lambda$ and phenomenological broadening $\delta$ according to the model by Ando. Most importantly we have to include the effect of inhomogeneous line broadening assuming a normally distributed charge carrier density distribution within the probe volume. We propose that the broadening $\delta$ is equal to the single particle lifetime of the electron momentum states that are connect by G-band phonon decay. Raman and transport measurements are then related by a relationship between transport and quantum lifetimes that is given by the screening properties of the substrate. Such a mechanism would explain the correlation that is observed between Raman gatesweeps on samples of different transport mobilities. Further measurements on devices of various mobilities have to be performed to confirm these ideas. In addition a better understanding of the effects of inhomogeneous broadening would enable a more precise determination of $\delta$. 
Chapter 5

Charge tuning of magneto-exciton phonon interactions

5.1 Introduction

In this chapter we describe Raman measurements on single layer graphene in high magnetic fields. In magnetic fields one mechanism that can excite electrons between the discrete level transitions is the e-ph interaction. Coherent superpositions of inter-LL magneto-excitons and phonons occur when the magnetic field is tuned to resonance between LL transition and optical phonons (Ando, 2007; Goerbig et al., 2007; Goerbig, 2011). Systems where the electronic and phonon dephasing is smaller than the electron-phonon interaction strength show pronounced anti-crossings of the energy of the phonon and magneto-exciton states (Ando, 2007; Goerbig et al., 2007; Goerbig, 2011; Kossacki et al., 2011; Kim et al., 2012; Yan et al., 2010; Kühne et al., 2012; Faugeras et al., 2011; Yan et al., 2010).

Here we discuss theory and experiments that explore the magneto-exciton phonon coupling. We perform charge carrier density dependent magneto-Raman measurements on single layer GFETs at constant magnetic fields to control the filling factor \( \nu \). Contrary to previous magneto-phonon studies, we explore the Raman response in a magnetic field far from magneto-phonon resonance conditions. We predict a linear dependence on \( \nu \) in the non-resonant regime, rather than \( \sqrt{\nu} \) behavior predicted for the on-resonance response. Notably we observe pronounced splittings and slope
changes of the G-band phonon energy as a function of \( \nu \). We show that the structure in the e-ph coupling is due to the occupancy of Landau level magneto-exciton transitions coupled to the phonon. In contrast to on-resonance measurements, no single transition dominates the coupling, and several inter and intra-band transitions have to be included to account for the experimental observations. We will show that the observed splitting is due to the different filling factor dependent response to left and right hand polarized light.

### 5.2 Electron-phonon coupling in magnetic fields

#### 5.2.1 Two-level model, anticrossings

We extend the discussion of e-ph coupling from chapter 4 to magnetic fields where the continuous band structure is replaced by discrete energy levels (Sec. (2.2.2)). As a simple text book model for gaining qualitative understanding of the behavior of the e-ph coupling we consider a coupled two-level system following (Cohen-Tannoudji et al., 2006).

We label the two coupled states as \( |\varphi_1\rangle \) and \( |\varphi_2\rangle \) with energies \( E_1 \) and \( E_2 \). \( |\varphi_1\rangle \) shall represent an optical phonon so \( E_1 = \hbar \omega_G \), whereas \( |\varphi_2\rangle \) represents a magneto-exciton created by inter Landau level excitation of electrons with energy given by Eqn.2.37. The coupling is represented by off-diagonal terms in the hamiltonian matrix of the system:

\[
H_c = \begin{pmatrix} E_1 & W_{12} \\ W_{12} & E_2 \end{pmatrix}
\]

(5.1)

with the detuning \( \Delta = 1/2(E_1 - E_2) \) and the mean energy \( E_m = (E_1 + E_2)/2 \). The eigenvalues are:

\[
E_\pm = E_m \pm \sqrt{\Delta^2 + |W_{12}|^2}
\]

(5.2)

The eigen-states of Eqn. (5.1) are combinations of unperturbed states and can be
Figure 5.1: (a) Anticrossing of coupled phonon magneto-exciton state within the approximation of a two-level model. (b) Mixing of the state $|\Psi_\pm\rangle$. Red line is the magnitude of the phonon part, green line of the magneto-exciton part $\propto \sin \theta/2$. Dashed grey line marks the energy of the unperturbed states written in terms of the mixing angle $\theta = 2|W_{12}|/(E_1 - E_2)$:

$$
|\Psi_+\rangle = \cos \frac{\theta}{2} |\varphi_1\rangle + \sin \frac{\theta}{2} |\varphi_2\rangle \\
|\Psi_-\rangle = -\sin \frac{\theta}{2} |\varphi_1\rangle + \cos \frac{\theta}{2} |\varphi_2\rangle
$$

We show the energy of the coupled eigen-states in Fig.5.1(a) as a function of the applied magnetic field and coupling strength $W = 20\ cm^{-1}$. The anticrossing of the mixed states are clearly visible. The size of the gap between the states is determined by the coupling strength.

It is also interesting to look at the detailed character of the mixed eigen-states. In Fig. (5.1) we illustrate the amount of phonon and magneto-exciton character for the
state $|\Psi_+\rangle$. The magnitude of the phonon part is $\propto \cos \theta/2$, whereas the magnitude of the magneto-exciton part is $\propto \sin \theta/2$. Only in a narrow range around resonance does a significant mixing between the states exist. Naturally, far away from resonance, where our experiments are focused, the states have mostly phonon or exciton character and little mixing occurs.

5.2.2 Observations of resonances in the electron-phonon coupling in magnetic fields

The first observation of strong electron-phonon coupling at resonance conditions was made by Raman spectroscopy of magneto-phonons in multi-layer graphene on SiC (Faugeras et al., 2009). However the sample was not pristine enough to exhibit coherent phonon magneto-exciton states (Faugeras et al., 2009). For low coherence of the quantum mechanical process no clear overlap of the coupled magneto-exciton phonon modes are visible. However a strong shift of the energies is still observed. Coherent magneto-phonon Raman response, showing clear anticrossings with overlap of the eigenstates, has since been observed in graphite (Kossacki et al., 2011; Kim et al., 2012; Yan et al., 2010) and decoupled surface layers of graphene on graphite crystals (Kühne et al., 2012; Faugeras et al., 2011; Yan et al., 2010). Recently, magneto-phonon resonances have also been observed on single layer graphene exfoliated on SiO$_2$ (Kim et al., 2013; Kossacki et al., 2012).

5.2.3 Selection rules for magneto-exciton phonon coupling

A more general theory of the electron-phonon interactions in magnetic fields has to to take the full quantum mechanical description of graphene into account. Ando and Goerbig (Goerbig et al., 2007; Ando, 2007) extended the many body theory of electron-phonon coupling in graphene described in chapter 4 to magnetic fields. While the phonon and interaction hamiltonian keeps the same form, the electronic hamilto-
nian has to be replaced by Eqn. (2.38) to take account of the discrete level structure. The interaction can then be treated as a perturbation coupling the degenerate Landau level states.

**Coupling to orthogonal phonon states**

The longitudinal and transverse optical phonon branches of the phonon dispersion are degenerate at the Γ point. The displacement due to the zero momentum optical phonons can then be written as a linear combination of the transverse polarized phonons $u_x$ and $u_y$ as

$$u_{\sigma^+} = u_x + i u_y$$
$$u_{\sigma^-} = u_x - i u_y$$

This notation is formally equivalent to circular polarized waves. Writing the interaction Hamiltonian $H_{e-ph}$ in term of $u_{\sigma^+}$ and $u_{\sigma^-}$ gives:

$$H_{e-ph} = g\sqrt{\frac{2M\omega}{\hbar}} i \left[ \sigma_x \frac{u_{\sigma^-} - u_{\sigma^+}}{2} + i \sigma_y \frac{u_{\sigma^-} + u_{\sigma^+}}{2} \right]$$

In chapter 2.2.3 we described a simple model for inter Landau level transitions due to a circular polarized electro-magnetic waves. By comparison with Eqn. (2.50) we see formal equivalence between $H_{pert}$ and $H_{e-ph}$. Therefore the same selection rules apply for phonon induced transitions namely $\Delta |n| = \pm 1$. The LL transitions coupling to the orthogonal phonons have equal energy, but originate from different LL. For example, the interband transitions involving the $n$-th LL are $-n \rightarrow n + 1$ and $-n - 1 \rightarrow n$. Their energy $T_n$ follows immediately from Eqn.2.37:

$$T_n = T_0 \left( \sqrt{n + 1} + \sqrt{n} \right)$$

Similarly for the intraband transitions $S_n$ between $-n - 1 \rightarrow -n$ and $n \rightarrow n + 1$ the
Table 5.1: Resonant magnetic field in Tesla for the first inter and intraband transitions for 3 different values of the Fermi velocity

<table>
<thead>
<tr>
<th></th>
<th>$v_F = 1.13 \times 10^6 ms^{-1}$</th>
<th>$v_F = 1.10 \times 10^6 ms^{-1}$</th>
<th>$v_F = 1.05 \times 10^6 ms^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_0$</td>
<td>22.9</td>
<td>24.1</td>
<td>26.5</td>
</tr>
<tr>
<td>$T_1$</td>
<td>3.9</td>
<td>4.1</td>
<td>4.5</td>
</tr>
<tr>
<td>$T_2$</td>
<td>2.3</td>
<td>2.4</td>
<td>2.7</td>
</tr>
<tr>
<td>$T_3$</td>
<td>-1.6</td>
<td>1.7</td>
<td>1.9</td>
</tr>
<tr>
<td>$S_0$</td>
<td>22.9</td>
<td>24.1</td>
<td>26.5</td>
</tr>
<tr>
<td>$S_1$</td>
<td>133.2</td>
<td>140.6</td>
<td>154.3</td>
</tr>
<tr>
<td>$S_2$</td>
<td>226.2</td>
<td>238.7</td>
<td>262.0</td>
</tr>
<tr>
<td>$S_3$</td>
<td>318.3</td>
<td>335.9</td>
<td>368.7</td>
</tr>
</tbody>
</table>

Energy is given by:

$$S_n = T_0 \left( \sqrt{n+1} - \sqrt{n} \right)$$

with $T_0 = v_F \sqrt{2e\hbar B}$. In our main experiment the magnetic field strength was set to $B = 12.6 \, T$, so $T_0 \approx 140 \, meV$, much smaller than the G-band energy $\sim 196 \, meV$.

Resonances occur where $T_n(S_n) = \hbar \omega_G$. Table 5.1 lists the resonant B-field for a few inter and intraband transitions.

**Experimental Observation**

Experimentally the coupling of the magneto-exciton transitions to the orthogonal states of the degenerate modes of the G-band phonon is closely related to the polarization of the excitation light and signal in Raman scattering experiments (Kossacki et al., 2011). Selective excitation of the orthogonal states can be achieved using cross circular polarized optical excitation and detection channels. In the following we label an observation that is excited with $\sigma^+$ polarized light and probed as $\sigma^-$ polarized light simply by writing $\sigma^+/\sigma^-$. In a $\sigma^+/\sigma^-$ configuration, only states coupling to $\Delta n = +1$ transitions can be observed, while only states coupling to $\Delta n = -1$ transitions are observed in $\sigma^-/\sigma^+$ polarization configuration (Kossacki et al., 2012; Kim
et al., 2013; Kossacki et al., 2011; Kühne et al., 2012). In the following discussion we show that these selection rules create optical dichroism for doped graphene (Goerbig et al., 2007; Ando, 2007). This effect has been observed in graphene on SiO$_2$ due to partial Pauli blocking of the initial or final Landau level states (Kim et al., 2013; Kossacki et al., 2012).

Only high quality graphene on SiC or on graphite can be considered charge neutral, while the abundantly used exfoliated graphene on SiO$_2$ typically shows accidental doping from sample preparation and impurities in the substrate. Experiments on magneto-exciton phonon coupling so far achieved only limited control of the doping level $\tilde{n}$ by annealing and gas exposure in between scanned B-field measurements (Kim et al., 2013). However, for constant $\tilde{n}$ the filling factor $\nu$ varies with the B-field strength. By using GFETs we gain full control of the charge density and decouple the effects of magnetic field and filling factor dependence.

### 5.2.4 General description of the G-band energy shift

The complete description of the e-ph interaction involves the solution of the quantum mechanical many body problem using the discrete electron structure. Following (Goerbig et al., 2007; Ando, 2007; Kossacki et al., 2012) we are interested in the phonon energy $\varepsilon_A$ from Eqn. (5.8), where the index $A$ denotes the two orthogonal circularly polarized phonon states accessed by $\sigma^+$ or $\sigma^-$ circularly polarized light. The renormalized phonon energy is given by the poles of the phonon Greens function:

$$
\varepsilon_A^2 - \varepsilon_0^2 = 2\varepsilon_0\lambda T_0^2 \left[ \sum_{n=0}^{N} \left( \frac{f_{\lambda,n}(\nu) T_n}{(\varepsilon_A + i\delta)^2 - T_n^2} - \frac{1}{T_n} \right) + \sum_{n=1}^{N} \frac{f_{\lambda,n}(\nu) S_n}{(\varepsilon_A + i\delta)^2 - S_n^2} \right] \tag{5.8}
$$

Here $\varepsilon_0$ is the unperturbed phonon energy, $\lambda$ is the dimensionless electron-phonon
coupling parameter and $\delta$ is the phenomenological broadening introduced by Ando (Ando, 2007). The two sums are the contribution from all the interband and intraband asymmetric transitions (see Fig. 5·8(a)). The filling factor dependence of the coupling to the highly degenerate Landau level states is described by the factor $f_{A,n}$. For interband transitions $f_{A,n}$ is defined by

\begin{align}
    f_{\sigma^+,n} &= (1 + \delta_{n,0})(\bar{\nu}_n - \bar{\nu}_{(n+1)}) \\
    f_{\sigma^-,n} &= (1 + \delta_{n,0})(\bar{\nu}_{-(n+1)} - \bar{\nu}_n)
\end{align}

(5.9)

Here $\bar{\nu}_n$ is the normalized filling factor describing the fraction of filling of the $n$th Landau level. It is related to the filling factor $\nu$ by $\bar{\nu}_{\pm n} = [\nu - (4(\pm n) - 2)]/4$ since each Landau level state is fourfold degenerate. Hence $0 < \bar{\nu}_n < 1$. The definition of $f_{A,n}$ for intraband transition is easily obtained by replacing the index $\mp n$ by $\pm n$. For convenience we show plots of the transitions weights $f$ in chapter 5.6.1, that illustrate the linear increase and decrease as a function of $\nu$.

Eqn. (5.8) is valid for all $B$ fields and charge states, although it is cumbersome to use. Near resonance, a single resonant term dominates, so other terms can be neglected in solving Eqn. (5.8). The solution is described by a two-level coupled mode model (Yan et al., 2010; Kim et al., 2013)

\begin{align}
    \varepsilon_{A}^{\pm} = \frac{T_n + \varepsilon_0}{2} \pm \sqrt{\left(\frac{T_n - \varepsilon_0}{2}\right)^2 + \frac{\lambda T_0^2}{2} f_{A,n}}
\end{align}

(5.10)

Eqn. (5.10) describes the anticrossing between the coherent coupled states $\varepsilon_{A}^{\pm}$. The index $\pm$ refers to the upper and lower branches of the anticrossing.

In the non-resonant regime, where our experiment is performed, the approximation leading to Eqn. (5.10) is not valid. Since $\Delta \varepsilon_A = \varepsilon_A - \varepsilon_0$ is small, Eqn. (5.8) can be linearized by noting that $\varepsilon_{A}^{2} - \varepsilon_{0}^{2} \approx (\varepsilon_{A} - \varepsilon_{0})2\varepsilon_{0}$, and replacing the $\varepsilon_A$ in the
denominator by the unperturbed phonon frequency $\varepsilon_0$ (Ando, 2007). The shift of the G-band in the non-resonant regime is then given by

$$
\Delta\varepsilon_A = \text{Re} \left\{ \lambda T_0^2 \left[ \sum_{n=0}^{N} \left( \frac{f_{A,n} (\nu) T_n}{(\varepsilon_0 + i\delta)^2 - T_n^2} - \frac{1}{T_n} \right) \right] 
+ \sum_{n=1}^{N} \frac{f_{A,n} (\nu) S_n}{(\varepsilon_0 + i\delta)^2 - S_n^2} \right\}
$$

(5.11)

The expressions Eqn. (5.10) and Eqn. (5.11) are distinguished by the numbers of terms needed, and by their different filling factor dependence. In the resonance approximation Eqn. (5.10) the shift is proportional to $\sqrt{\nu}$ while in the non-resonant case Eqn. (5.11) is linear in the filling factor $\nu$.

5.3 Experimental setup and samples

In the following sections we discuss our experimental observations in the context of the model of magneto-exciton phonon interactions.

5.3.1 Sample Preparation

GFETs were prepared by standard micro fabrication processes following the process described in chapter 3.1.3. We produce single layer graphene by scotch tape exfoliation from crystals of natural graphite. We exfoliate on degenerately doped Si (n-type, $\rho < 0.005 \, \Omega cm$) wafers covered with thermally grown SiO$_2$ of thickness $d_{SiO_2} = 300 \, nm$. We identify single layer graphene samples by measurements of optical contrast and Raman measurements. Next we spin a double layer Poly(methyl methacrylate). To facilitate liftoff we spin a bilayer of PMMA495 followed by PMMA950. Afterwards we define contacts on top of graphene using standard electron beam lithography and evaporate Cr/Au contacts. Once the sample was in vacuum in the cryostat
we performed a series of in situ current annealing steps in order to clean the sample from fabrication residues. The maximum current applied was $I = 1.5 \ mA$ for $\sim 4 \ h$.

### 5.3.2 Experimental setup

Raman measurements are performed at 4K in a He bath cryostat, schematically drawn in Fig. 5-2(a).

The sample is mounted on a piezoelectric x-y-z stage at the focus of a confocal, free-space microscope cooled with He exchange gas and placed in the center of a superconducting magnet with an accessible range of $B = \{0 \ T, 12.6 \ T\}$. The Raman response is excited using a HeNe Laser at $\lambda = 632.8 \ nm$ with a diffraction limited spot.
size $\sim 1 \mu m$. The excitation laser is linearly polarized, although we do not monitor or optimize the polarization. Since our experiment uses linear polarized light without an analyzer, we measure both $\sigma^+/\sigma^-$ and $\sigma^-/\sigma^+$ transitions, i.e. both $\Delta|n| = \pm 1$ transitions are detected simultaneously. Scattered light is filtered by a long pass filter to remove the laser light, collected by a single mode fiber and analyzed using a conventional grating spectrometer.

Fig. 5·2(b) illustrates the effect of applying a backgate voltage $V_{bg}$ at finite magnetic field of $B = 12.6\, T$. For $\nu = -4.7$ ($V_{bg} = -20\, V$) the G-band is symmetric with a single peak (black line), but splits into 2 peaks for $\nu = -1.8$ ($V_{bg} = -8\, V$) due to the interaction of the optical phonons with the discrete Landau levels \footnote{This was presented by S. Rémi, M. Liu, A. K. Swan and B.B. Goldberg at the 2009 KIAS Graphene meeting (but not published) and cited in Ref. (Faugeras et al., 2009; Goler et al., 2012)}.

5.4 Gatesweep measurements at B=0T

Characterization of the phonon response versus charge density was performed by Raman spectroscopy while sweeping the backgate in the range $V_{bg} = \{-40\, V, 40\, V\}$ both at $B = 0\, T$ as well as $B = 12.6\, T$.

Fig. 5·3 shows a Raman intensity map of the observed spectra as a function of $V_{bg}$. We extract the position of the G-band by fitting the spectra with single ($B = 0\, T$) and double lorentzian ($B = 12.6\, T$) functions shown in Fig. 5·3(c) and (d).

5.4.1 Measurements at $B = 0\, T$

Measurements results at $B = 0\, T$ are shown in Fig. 5·3(a) and (c). Using the methods from Sec. (4) we fit the model of (Ando, 2006) to the data, and include the effects of inhomogeneous broadening due to charge carrier density fluctuations (Yan et al., 2007b). In Fig. 5·3(c) we plot the fit results (red dashed line) as a function of $V_{bg}$, and extract the following system parameters: The electron-phonon coupling strength
\[ \lambda = 4.8 \times 10^{-3}, \] the phenomenological broadening parameter (Ando, 2006) \( \delta = 10 \text{meV} \), the unperturbed phonon energy at \( B = 0 \text{T} \), \( \varepsilon = 1582.0 \text{ cm}^{-1} \), the inhomogeneous broadening \( \delta \tilde{n} = 0.3 \times 10^{12} \text{ cm}^{-2} \) (standard deviation of a Gaussian distribution) and finally the Fermi velocity \( v_F = 1.10 \times 10^6 \text{ ms}^{-1} \). The qualitative and quantitative analysis at \( B = 0 \text{T} \) is described in the following section.

**Figure 5.3:** Raman intensity map of the G-band Raman spectra as a function of applied backgate voltage. The charge density and filling factor are indicated on top of the figures. a) Measurements for \( B = 0 \text{T} \). b) \( B = 12.6 \text{T} \). A clear splitting is visible for voltages \( |V| \leq 20 \text{ V} \). c) and d) show phonon energies from Lorentzian fits in a) and b). Dashed red line is a fit using a model of the phonon anomaly in graphene (Ando, 2006).
5.4.2 Fitting of spectra at B=0T

We initially extract the position and width of the G-band by fitting the raw data to a single Lorentzian peak (Fig. 5.4(a)). We find that all spectra have a pronounced low energy shoulder, so fitting with a single peak does not always describe the spectra well. In the vicinity of $V_{bg} = 0 \ V$, the G-band overlaps with this peak and spectra still appear as a single Lorentzian. For larger value of $V_{bg}$, strong deviations from the single Lorentzian lineshape occur, and the position and width of the G-band are not described accurately. We find that the low energy shoulder seems to be of equal size and position for all values of $V_{bg}$, and might be caused by a spectral ghost created by the grating of our spectrometer.

To achieve a better fit, we use two Lorentzian peaks where the low energy peak is kept fixed in position, width and amplitude. This model results in very acceptable fits to the data (Fig. 5.4(b)).

For evaluation of our measurement results as a function of the Fermi energy $E_F(V_{bg})$ we first calculated the charge carrier density $\tilde{n}$ in the standard way from a simple capacitive model (Novoselov et al., 2004):

$$\tilde{n} = C \frac{V_{bg}}{e} = \frac{\varepsilon_{SiO_2} \varepsilon_0 V_{bg}}{d_{SiO_2}} \frac{V_{bg}}{e} \approx 7.18 \times 10^{10} cm^{-2} V V_{bg}$$

(5.12)

with the dielectric constant of SiO$_2$, $\varepsilon_{SiO_2} = 3.9$ and thickness of SiO$_2$, $d_{SiO_2} = 300 \ nm$. $\varepsilon_0$ is the permittivity of free space. The Fermi energy is then calculated as:

$$E_F = \hbar v_F \sqrt{\pi n}$$

(5.13)

In Fig. 5-5 we show the fit results as a function of $E_F$. We obtained $v_F = 1.10 \times 10^6 ms^{-1}$ by the method discussed in Sec. (5.4.3). Black lines are the result from single Lorentzian fits and grey from double Lorentzian fits. We observe a local dip in the G-band position around $E_F = \hbar \omega_G/2$ (grey vertical lines) which is especially visible in the data extracted from double Lorentzian fit results. This might be an
Figure 5.4: Fitting of raw spectral data (blue dots) by single Lorentzian peak (a) or two Lorentzian peaks (b) where the low energy peak is kept fixed in position, width and amplitude. Spectra are taken at different gate voltages.
Figure 5.5: Combined fit results for single and double Lorentzian fits. Black lines are results of single Lorentzian fit, grey lines are results from double Lorentzian fit and red dots mark the selected data points for further analysis.

indication of the logarithmic divergent e-ph coupling (Ando, 2006) at this level $E_F$, but as in Sec. (4) a considerable amount of broadening is present in the sample.

The linewidth is unusually large as measured by double Lorentzian fits when compared to other experiments (Yan et al., 2007b). We therefore choose to use data from single Lorentzian fits for $E_F < |\hbar\omega_G|$ where the fit describes the data well, and we use data from double Lorentzian fits for all other regions. The data choice is illustrated in Fig. 5.5 where we marked the data points selected for further analysis by red dots.

5.4.3 Quantitative Description at $B = 0T$

To achieve a quantitative description of the data we describe the gate-voltage dependent energy and FWHM in terms of the Fermi level by the model Sec.4.2.1. We adjust the scale of the Fermi energy by selecting an appropriate Fermi velocity that fits to the qualitative features of the measurement results. Fig. 5.6 illustrates the scaling of the data due to different selections of $v_F$. Selecting a larger $v_F$ places data points at higher energies than lower Fermi velocity values. Using the structure of the phonon response at $B = 0T$ given by Eqn. (4.3) the Fermi velocity can be estimated. While
the theoretically calculated shift and FWHM does not depend on $v_F$, the data has to be scaled by $v_F$ to accomplish a good fit to Eqn. (4.3). Selecting $v_F$ in the range $v_F = \{1.00 \times 10^6 \text{ ms}^{-1}, 1.20 \times 10^6 \text{ ms}^{-1}\}$ can used for acceptable fits to the data. We select $v_F = 1.10 \times 10^6 \text{ ms}^{-1}$ for best fit results.

Next we extract the system parameters $\lambda, \delta, \varepsilon_0$ and $\delta_0$ ($\delta_0$ being the unperturbed phonon linewidth) in complete analogy to Sec. (4), including inhomogeneous broadening.

The procedure for calculation of inhomogeneous broadening is numerically extensive and time intensive. Likewise, the large parameter space makes it difficult to select the optimal choice of fitting values for a global fit, e.g. by $\chi^2$ minimization. Consequently we chose to adjust parameters by eye instead. Each parameter has a characteristic influence on the energy and FWHM calculated using Eqn. (4.1).

We present fit results in Fig. 5·7(a). The fit parameters are: $\lambda = 4.8 \times 10^{-3}$, $\delta = 10\text{ meV}$, $\delta_0 = 5.5 \text{ cm}^{-1}$, $\varepsilon_0 = 1582 \text{ cm}^{-1}$, $\delta n = 0.3 \times 10^{12} \text{ cm}^{-2}$. We show both numerical results not-including (solid black lines) and results including inhomogeneous broadening (red dashed lines). Comparing the black and red line of the FWHM in Fig. 5·7(a) shows that in our model inhomogeneous broadening reduces FWHM$_{\text{max}}$. The distribution $\delta n = 0.3 \times 10^{12} \text{ cm}^{-2}$ corresponds to a distribution

**Figure 5·6:** Effect of changing the Fermi velocity on the position of data points after conversion $V_{bg} \rightarrow E_F$. 

Figure 5·6: Effect of changing the Fermi velocity on the position of data points after conversion $V_{bg} \rightarrow E_F$. 

The figure shows the effect of changing the Fermi velocity on the position of data points after conversion $V_{bg} \rightarrow E_F$. The theoretically calculated shift and FWHM does not depend on $v_F$, the data has to be scaled by $v_F$ to accomplish a good fit to Eqn. (4.3). Selecting $v_F$ in the range $v_F = \{1.00 \times 10^6 \text{ ms}^{-1}, 1.20 \times 10^6 \text{ ms}^{-1}\}$ can used for acceptable fits to the data. We select $v_F = 1.10 \times 10^6 \text{ ms}^{-1}$ for best fit results.

Next we extract the system parameters $\lambda, \delta, \varepsilon_0$ and $\delta_0$ ($\delta_0$ being the unperturbed phonon linewidth) in complete analogy to Sec. (4), including inhomogeneous broadening.

The procedure for calculation of inhomogeneous broadening is numerically extensive and time intensive. Likewise, the large parameter space makes it difficult to select the optimal choice of fitting values for a global fit, e.g. by $\chi^2$ minimization. Consequently we chose to adjust parameters by eye instead. Each parameter has a characteristic influence on the energy and FWHM calculated using Eqn. (4.1).

We present fit results in Fig. 5·7(a). The fit parameters are: $\lambda = 4.8 \times 10^{-3}$, $\delta = 10\text{ meV}$, $\delta_0 = 5.5 \text{ cm}^{-1}$, $\varepsilon_0 = 1582 \text{ cm}^{-1}$, $\delta n = 0.3 \times 10^{12} \text{ cm}^{-2}$. We show both numerical results not-including (solid black lines) and results including inhomogeneous broadening (red dashed lines). Comparing the black and red line of the FWHM in Fig. 5·7(a) shows that in our model inhomogeneous broadening reduces FWHM$_{\text{max}}$. The distribution $\delta n = 0.3 \times 10^{12} \text{ cm}^{-2}$ corresponds to a distribution
Figure 5.7: G-band position and FWHM and fit results using the Ando model Eqn. (4.3). (a) $B = 0 \, T$. Black line: no inhomogeneous broadening. Red line: $\delta n = 0.3 \times 10^{12} \, cm^{-1}$. (b) $B = 0 \, T$ for different parameter values (see text). (c) $B = 12.6 \, T$ with same parameter values as in (b). Thick blue and red lines are the numerical solutions for $\sigma^-$ and $\sigma^+$ transitions including the effects of symmetric transitions. Shaded blue and red regions illustrate shift when not including symmetric transitions.
of charge carriers in energy for $\delta E_{\delta n} \approx 70 meV$. We expect that the reduction of FWHM$_{\text{max}}$ is significant once $\delta E_{\delta n} \simeq \varepsilon_G$.

Due to the large number of parameters, other choices of their values can be found for acceptable fits to the data. For instance in Fig. 5.7(b,c) we chose: $\lambda = 4.2 \times 10^{-3}$, $\delta = 10 \ meV$, $\varepsilon_0 = 1582 \ cm^{-1}$, $\delta_0 = 5.5 \ cm^{-1}$ and $v_F = 1.18 \times 10^6 \ ms^{-1}$. To describe data in magnetic fields (Fig. 5.7(c)) we include the effect of symmetric transitions with coupling strength $\lambda_s = 0.2 \lambda$ (thick solid lines).

The alternative parameter values describe the energy splitting of the orthogonal phonon channels better than the values initial chosen and produce a reasonable fit to $\varepsilon_G(B = 0 T)$. However FWHM$_{\text{max}}$ is reduced compared to the fit in Fig. 5.7(a). Since FWHM$_{\text{max}} \propto \lambda$ suggests $\lambda$ points towards a too small choice of $\lambda$. At the same time selecting $v_F = 1.18 \times 10^6 \ ms^{-1}$ appears as an unnatural large choice given that $v_F$ has been determined to be around $v_F = 1.10 \times 10^6 \ ms^{-1}$ by measuring the position of magneto-phonon resonances (Kossacki et al., 2012; Kim et al., 2013).

The precision in measuring the system parameters could be increased by higher S/N measurements and at higher Fermi energies. Since $E_F \propto \sqrt{V_{bg}}$ the Fermi energy increases only slowly at higher gate voltages. Even at $V_{bg} = 100V$ on standard $d_{SiO_2} = 300 \ nm$ oxide $E_F = 340meV$. Higher $E_F$ could be achieved on thin gate dielectrics, e.g. thin layers of hBN.

5.5 Gatesweep measurements at B=12.6T

5.5.1 Filling factor dependent splitting

Fig. 5.3(b) and (d) shows a very different behavior for $B = 12.6 \ T$. G-band splitting starts around $\nu=-6 \ (V_{bg} \approx -25 V)$ then reaches a maximum at $\nu=-2 \ (V_{bg} \approx -9 V)$, disappears at $\nu=0 \ (V_{bg} = 0 \ V)$ and repeats symmetrically for $\nu > 0$. The largest magnitude of the splitting is $\sim 12 \ cm^{-1}$. At $B = 12.6 \ T$, the nearest magneto-phonon
Figure 5.8: a) Schematic view of the Landau level spectrum at $B = 12.6\, T$, filling factor $\nu = 2$ and the lowest Landau level transitions participating in magneto-phonon coupling. Filled electronic states are highlighted using orange color. Red and blue arrows show transitions allowed by the selection rule $\Delta |n| = \pm 1$. Dashed arrows mark Pauli blocked transitions. Circular arrows represent the angular momentum involved in the transitions b) Relative strength and filling factor dependence of individual terms of the phonon self energy for $\sigma^+$-transitions. Terms describing interband transitions are shaded red, intraband transitions are shaded green. c) Phonon energy as a function of the filling factor at $B = 12.6\, T$. Vertical orange lines mark specific filling factors at $\nu = -6, -2, 0, 2, 6$ where the $n = -1, 0, 1$ levels are completely filled/depleted with charge carriers ($\nu = 0$ corresponds to half filling of $n = 0$ level). The calculated magneto-phonon energies according to Eqn. (5.11) are plotted as solid red ($\Delta n = +1$) and solid blue ($\Delta n = -1$) lines.

resonances are the transitions between $|n| = 0$ and $|n| = 1$ at $B = 25\, T$ and $|n| = 1$ and $|n| = 2$ at $B = 4.1\, T$. In the next sections we are going to describe in detail the phonon interaction with the discrete Landau levels that lead to the interesting structure of the G-band.

The filling factor dependence is obtained from the analysis of the transition weights $f_{A,n}$ in Eqn.5.9 To illustrate $\nu$ dependence we show in Fig.5.8(a) the level occupation for a filling factor $\nu = 2$, i.e. the $n = 0$ level is completely filled (partial filling factor $\bar{\nu}_0 = 1$). Hence, the transition between $n = -1$ and $n = 0$ is Pauli blocked (dashed
lines in figure) and \( f_{\sigma^-,0} = 0 \), while all transitions originating from the \( n=0 \) level have maximum strength due to the high density of occupied states that can be excited, with \( f_{\sigma^+,0} = 1 \).

### 5.5.2 Calculation of the coupling strength

We now consider the effect of the charge tuning in Eqn. (5.11) with fixed \( B \) field. In order to evaluate the contributions from participating inter- and intra-band transitions, we calculate the individual contribution to the phonon energy shift \( \Delta \varepsilon_n \) from each term in Eqn. (5.11) evaluated at \( B = 12.6 \ T \). Shown in Fig. 5·8(b) are the \( \Delta \varepsilon_n \) for the lowest lying inter- and intra-band transitions for \( \sigma^+ \) polarization, i.e. transitions with \( \Delta n = +1 \). We use the values for \( \varepsilon_0, \lambda, v_F \) and \( \delta \) from the \( B = 0 \ T \) fit. Curves are labeled as \( T_n \) (red shaded) for inter-band and \( S_n \) (green shaded) for intra-band transitions, normalized by \( \lambda T_0 \). The largest contribution is due to the \( T_0 \) term which shows a strong peak at \( \nu = 2 \). The contributions from the remaining inter-band transitions are strong as well. The shift due to the \( T_1 \) term is 28% and the \( T_2 \) term is still at 17.9% relative to the shift caused by the \( T_0 \) term. The action of intra-band terms are restricted to a smaller range of \( \nu \) values, but their strength can be significant nevertheless (\( S_1/T_0 \approx 10\% \)). The case of \( \sigma^- \) polarization is completely symmetric relative to the point \( \nu = 0 \).

Finally, we combine these contributions and compare to our experimental data (Fig. 5·8(c)). We only include the first 5 terms of Eqn. (5.11) in our calculation, since the neglected terms only cause a small overall downshift of \( \sim -1 \text{cm}^{-1} \) of the G-band energy in the range of our measurement (See Sec. (5.6.3)). The phonon energy is plotted versus filling factor rather than charge density to highlight the correspondence between the filled Landau levels and the extrema of kinks in the slope (orange lines). The solid red and blue lines are the numerical results for the energies \( \varepsilon_{\sigma^+} \) and \( \varepsilon_{\sigma^-} \). We emphasize that no adjustable parameters have been used to compare data and
theory at $B = 12.6 \, T$ - all parameters are determined from the $B = 0$ data. The splitting between $\varepsilon_{\sigma^+}$ and $\varepsilon_{\sigma^-}$ is maximal at $\nu = -2$ and $\nu = 2$ where the coupling strength to the $T_0$ transitions corresponding to $\Delta|n| = \pm 1$ respectively are strongest. Fig. 5.8(b) also explains the kink in slope $\nu = \pm 6$ due to Pauli blocking of $T_0$ and $T_1$ transitions. The upshift with increasing $|\nu|$ is caused by the linear decrease of the $T_1$ transition as the LL $n = \pm 1$ are filled or emptied, respectively. In principle scanning to larger absolute value $|\nu|$ will reveal higher and higher $n$ transitions. There is some evidence in the data of a small contribution from the symmetric transitions $\Delta n = 0$ (Kossacki et al., 2011) at the same reduced coupling strength seen by (Faugeras et al., 2011; Kühne et al., 2012), however, it is not conclusive (see Sec. (5.6.5)). We could not resolve the small splitting of $\sim 1 \, cm^{-1}$ between $\varepsilon_{\sigma^+}$ and $\varepsilon_{\sigma^-}$ for $|\nu| > 6$ predicted by the model.

The extracted values of Fermi velocity $v_F = 1.1 \times 10^6 \, m/s^{-1}$ and electron phonon coupling $\lambda = 4.8 \times 10^{-3}$ agree well with those determined in previous experiments on SiO$_2$ (Kim et al., 2013; Kossacki et al., 2012). However, for graphene on graphite, a lower $v_F$, and a 23% higher value of $\lambda$ is reported (Yan et al., 2010). (See Sec. (5.6.4)).
5.6 Details of the phonon magneto-exciton coupling

In this section we would like to present details of our description of the magneto-exciton phonon coupling that were not thoroughly described in the previous sections.

5.6.1 Inter LL transition weights vs. level filling

The filling factor dependence of the electron-phonon coupling strength related to a particular LL transition is described by the functions $f_{A,n}$ of Eqn.5.9 for both orthogonal circular polarized phonon channels $A = \sigma^-, \sigma^+$. For convenience we are presenting a graphical representation of $f_{A,n}$ in Fig. 5-9.

![Graphical representation of transition weights $f_{A,n}$ for $\Delta n = \pm 1$ inter (a,c) and intraband (b,d) transitions. (a,b) $\sigma^+$ polarization, (c,d) $\sigma^-$ polarization.](image)

**Figure 5-9:** Graphical representation of transition weights $f_{A,n}$ for $\Delta n = \pm 1$ inter (a,c) and intraband (b,d) transitions. (a,b) $\sigma^+$ polarization, (c,d) $\sigma^-$ polarization.

Most visibly the transition weights $f_{A,0}$ related to the transitions into and from the
n=0 Landau level have a maximum value twice as high as any other transitions. This phenomenon is related to the special structure of the n=0 LL presented in chapter 2.2.2. The n=0 eigenstates have non zero weight only on one of the two sublattices. The larger normalization factor compared to n > 0 states leads to apparent increase in coupling strength to the optical phonon states. Another point of view is that the transitions to the n = 0 level within the ∆n = ±1 selection rule have both interband and intraband character and appear therefore twice as strong.

5.6.2 Relative coupling to individual LL transitions

In the non-resonant coupling regime the effects of phonon coupling to many inter-LL transitions can be observed only if the partial interaction strength (that is the interaction strength neglecting coupling to all other transitions) is large enough to be observed within the experimental resolution. As a quick reference we calculated numerical values of the strength of electron-phonon coupling separately for asymmetric inter and intraband and symmetric transitions (λs = 0.2λ). For each transition we select the filling factor that maximizes the transition strength (e.g. by comparing to Fig. 5.9).

<table>
<thead>
<tr>
<th>n</th>
<th>$T_n (\Delta \varepsilon_G / \lambda T_0)$</th>
<th>$S_n (\Delta \varepsilon_G / \lambda T_0)$</th>
<th>$T_{-n \rightarrow n} (\lambda_s \Delta \varepsilon_G / \lambda T_0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.18</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>-0.62</td>
<td>0.24</td>
<td>-0.19</td>
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<tr>
<td>2</td>
<td>-0.39</td>
<td>0.17</td>
<td>-0.09</td>
</tr>
<tr>
<td>3</td>
<td>-0.31</td>
<td>0.15</td>
<td>-0.06</td>
</tr>
<tr>
<td>4</td>
<td>-0.26</td>
<td>0.13</td>
<td>-0.05</td>
</tr>
</tbody>
</table>
5.6.3 High Energy cutoff

The origin of kinks and splittings in the magnetic field data becomes easily understandable when looking separately at the contributions of individual transitions to the G-band shift. We found largely that within the range of filling factors we observe, kinks and splitting in the data are related to the lowest lying transitions. For this reason we typically only include the 5 lowest terms in calculating the G-band shift at $B = 12.6 T$ and find good agreement to our data. Theoretically the natural cutoff for transitions has to be selected where the actual dispersion of graphene deviates from the linear approximation around the K and K’ points of the Brillouin zone (Goerbig, 2011). The energy of the LL at the cutoff is approximately given by $E_{N_c} \sim t$ where $t \approx 3eV$ is the nearest neighbor hopping energy. For $B = 12.6 T$ we find $N_c \approx 450$. Fig. 5-10 shows the effect of including transitions up to $N_c$ using otherwise identical parameters. The effect is an overall downshift of $\sim -1 \text{ cm}^{-1}$.

![Figure 5-10](image)

**Figure 5-10**: G-band splitting in magnetic field $B = 12.6 T$. Experimental data: grey dots. Numerical simulation (red and blue lines) for high energy cutoff $N_c=5$ (a) and $N_c=450$ (b). Dashed lines are results including effects of symmetric transitions with $\lambda_s = 0.2 \lambda$. 
5.6.4 Coupling strength of previous studies

The parameter values determined from fitting to $B = 0 T$ data ($v_F = 1.1 \times 10^6 ms^{-1}$, $\lambda = 4.8 \times 10^{-3}$, neglecting charge inhomogeneous broadening) describe the $B = 12.6 T$ data well. In addition the parameter values agree with those determined in previous experiments. A high Fermi velocity has been observed on graphene on SiO$_2$ ($1.08 - 1.10 \times 10^6 m/s$) (Kim et al., 2013; Kossacki et al., 2012) while the Fermi velocity for graphene on graphite and SiC layers is in the range of $1.02 - 1.04 \times 10^6 m/s$ (Faugeras et al., 2009; Kühne et al., 2012). It has been suggested that the Fermi velocity depends strongly on screening due to electron-electron interactions (Hwang et al., 2012). This could explain the systematic difference in $v_F$ between graphene on different substrates, although (Hwang et al., 2012) predicts $v_F$ of graphene on SiO$_2$ to be smaller than $v_F$ of graphene on SiC.

To compare $\lambda$ with earlier work, we recall that $\lambda$ is related to the coupling factor $g$ used e.g. in (Yan et al., 2010; Kim et al., 2013) by $g^2 = (\lambda T_0^2/2) f_{A,n}$. We note that the value of $g$ will depend on both $v_F$ and the magneto-phonon resonance in question via $T_0$, as well as $\tilde{n}$ via $f_{A,n}$. The electron-phonon coupling strength $\lambda = 4.8 \times 10^{-3}$ determined by us, would result in $g = 78.8 \text{ cm}^{-1}$ ($g/\sqrt{B_{0,r}} = 15.8 \text{ cm}^{-1}/T^{1/2}$, $B_{n,r}$ being the resonant field for transition $T_n$) at the $T_0$ resonance, and $g = 32 \text{ cm}^{-1}$ ($g/\sqrt{B_{1,r}} = 15.8 \text{ cm}^{-1}/T^{1/2}$) at the $T_1$ resonance using $v_F = 1.1 \times 10^6 ms^{-1}$ for a charge neutral sample. For graphene on SiO$_2$ in (Kim et al., 2013), the reported value is nearly identical; $g = 17 \text{ cm}^{-1}/T^{1/2}$ ($\sigma^+$ polarization, $\tilde{n} = 0.4 \times 10^{12} cm^{-2}$). However for the more pristine sample of graphene on graphite (Yan et al., 2010) $\lambda = 6.2 \times 10^{-3}$, a 23% higher value. Again, the values seems to be affected by the substrate.
5.6.5 Coupling to symmetry forbidden transitions

The model calculations show a more shallow slope of the low energy magneto-phonon component than the data for $2 < |\nu| < 6$. A possible cause could be coupling to symmetric transitions $\Delta n = 0$ which are strongly suppressed due to the symmetry of the graphene lattice (Kossacki et al., 2011). Hybridization of $\Delta n = 0$ transition and optical phonons were observed in decoupled graphene layers on natural graphite (Faugeras et al., 2011; Kühne et al., 2012) with a coupling strength of almost 20% of $\lambda$. We include the effects of the first five $\Delta n = 0$ transitions by adding resonance terms with a similarly reduced coupling strength, $\lambda_{symm} = 0.2\lambda$. The results are shown as dashed lines in Fig. 5-10.

5.7 Conclusions

By focusing on the non-resonant regime we have discovered fine structure in the G-band optical phonon in single layer graphene at high magnetic fields as a function of charge density. The observed behavior is caused by coupling between the phonon and magneto-exciton far from resonance that results in a linear dependence on filling factor, in contrast to on-resonant coupling that leads to a square root dependence on filling factor. High magnetic field Raman scattering with electrostatic tuning of the charge carrier density allows us to explore the filling factor dependent coupling strength of orthogonal, non-resonant magneto-phonon states as they are being turned on and off. By including coupling to many Landau level transitions we show qualitative and quantitative agreement with numerical calculations of a linearized model of electron-phonon interactions in magnetic fields. The measured coupling strength, broadening and Fermi velocity is in good agreement with independent observations at $B = 0 \ T$ and earlier experiments.
Appendix A

Detailed procedure for GFET fabrication

- Materials
  - Natural graphite, for example NGS Naturgraphit at http://www.graphit.de, Graphenium flakes
  - Si substrate, Grade - prime, Orientation - 100, Doping - As or B, Resistivity < .005Ωcm, 285 nm thermally grown oxide
  - adhesive tape, Scotch brand tape works well due to high adhesion, but leaves many residues on the surface.

- Fabrication of backgate contacts
  - Blow over new wafer with \( N_2 \) gas
  - Bake wafer on hotplate at \( T = 110^\circ C \) for 3 minutes
  - Cool by blowing \( N_2 \) gas
  - Spin coat wafer with Shipley S1813 photoresist: 4000rpm, 45s
  - Expose backgate pattern: 10mW, 8s
  - Development: M319 developer, 45s followed by DI water rinse and \( N_2 \) blow dry
  - Softbake: Hotplate \( T = 110^\circ C \) for 2 minutes
  - Etch: Buffered oxide Etch: 6:1 for 3 minutes (Rate 100 nm/min)
– Evaporation: E-beam evaporator, 5 nm Cr at 1 A/s and 50 nm Au at 1.5 A/s

– Liftoff: Acetone on hotplate at $T = 70^\circ C$ for 30 mins, followed by sonication if necessary

– Clean in acetone and isopropanol

• Fabrication of Alignment markers: Follow procedure for backgate fabrication but do not perform wet etch step

• Graphene exfoliation: Described in Sec. (3.1.1)

• Rinse sample immediately following exfoliation in isopropanol on hotplate at $T = 70^\circ C$ for 1 mins, and blow dry with $N_2$. This step will remove graphene sheets that are only weakly bound to the substrate surface and would not survive spin coating, a step that will save the sanity of the exfoliator and success rate of the whole process

• Take optical images of the sample at highest magnification that allows 2 alignment marks to be visible in the optical image. Also take an optical image at lower magnification and larger field of view. The high magnification image will be used to design the contact pattern on the graphene sheet, the low resolution image will be used to avoid overlap of contacts with large pieces of graphite in the vicinity of the sample that could destroy contacts during liftoff or create short circuits.

• Load the optical image into CAD software (e.g. Autodesk AutoCAD) and use the scale and rotation features to align the 2 alignment marks horizontally and spaced at their actual physical distance. The position and orientation of the graphene sheet is then exactly defined.
• Design EBL contact pattern avoiding overlap with graphite pieces

• EBL

  – Spin coat Copolymer resist (e.g. from Microchem Inc.) at 4000rpm for 45s
  – Bake on hotplate at $T = 150^\circ C$ for 60s
  – Spin coat PMMA resist (Microchem Inc.) at 4000rpm for 45s
  – Bake on hotplate at $T = 180^\circ C$ for 60s
  – Exposure: Use alignment features and SEM software to correctly align on sample
  – Development: MIBK/Isopropanol in ratio 1:3 for 30s
  – Evaporation: Evaporation: E-beam evaporator, 5 nm Cr at 1 A/s and 50 nm Au at 1.5 A/s
  – Lift off: Acetone on hotplate at $T = 70^\circ C$ for 30 mins or longer depending on progress. After 30mins use pipette to flow hot acetone over sample to facilitate lift off. Do not sonicate as this might destroy the sample
  – Clean in acetone and isopropanol, each at $T = 70^\circ C$ for 3 mins

• Optional annealing: Flow Ar/H$_2$ at atmospheric pressure 400sccm/100sccm at $T = 300^\circ C$
Appendix B

Fitting of Raman spectra

We obtained the position and FWHM of the G-band from fitting the spectral data. We show a selection of spectra and fits at different gate voltages in Fig. (B-1) for $\mu \sim 4900\text{cm}^2/V\text{s}$ and in Fig. (B-2) for $\mu \sim 7800\text{cm}^2/V\text{s}$. The fits were obtained by adjusting two lorentzian lines with free amplitudes, positions and FWHM. Typically the G-band has a highly symmetric lineshape that can be fitted with a single lorentzian curve as shown in many experimental studies (Stampfer et al., 2007; Ferrari et al., 2006; Yan et al., 2007b; Forster et al., 2013; Malard et al., 2009).

However the G-band obtained in our measurements is rather asymmetric with a shoulder at the low energy side of the main peak. Upon visual inspection a single lorentzian provides good fit results although the small deviations due to the low energy shoulder are visible. However upon analysis we measure the maximal FWHM of the G-band, obtained from the spectra around the Dirac point, to be $\Gamma_{FWHM}^G = 20\text{ cm}^{-1}$. Other experimental studies measure significantly smaller values $\sim 15 - 16\text{ cm}^{-1}$ (Yan et al., 2007b). The pixel limited resolution of our spectrometer is $\Delta\omega \sim 1.4\text{ cm}^{-1}$ and we should easily be able to measure the correct G-band linewidth.

We considered 3 different mechanisms for the creation of the asymmetric lines:

1. Light pollution due to intrusion of rest light into the spectrometer. The signature would be a stationary peak independent of gate voltage. However, we chose the Argon Ion $\lambda_{exc} = 488\text{ nm}$ to avoid light pollution at the expected position of the G-band. Background measurements on bare SiO$_2$ do not show
\[ \mu = 4900 \text{cm}^2/\text{Vs} \]

Figure B.1
$\mu = 7800 \text{cm}^2/\text{Vs}$

Figure B.2
any significant line or signal. Overall it seems unlikely that light pollution can account for the asymmetric G-band lineshape.

2. Spectral Ghosting due to a bad spectrometer grating

3. Distortion due to spectrometer optical elements

4. Distortion due to charge inhomogeneity

We try to get further insight by fitting with two lorentzian lines and comparing the properties of the low energy peak to the magnitude of asymmetry. In Fig. (B·3) we show the line properties obtained from the fit.

The position and FWHM behave similar to the G-band energy with $E_F$, indicating that this might be indeed a spectral ghost feature. In addition the difference in energy between high and low energy peak as well as the ratio of the FWHM are approximately constant as a function of the Fermi energy. However the amplitude of the low energy peak should increase for large $E_F$ whereas it decreases in the fit. The distortion of the Raman line seems also to be too large to be caused by charge inhomogeneity (see Sec. (4.3.3)) unless non-Gaussian distributions of charge carriers are considered. We do not observe this asymmetry in the 2D band Raman line where we achieve also higher S/N ratio in our measurement and single lorentzian fits describe the data very well.

Uniaxial strain could cause a splitting and distortion of the G-band as well and could be induced due to mismatch of the thermal expansion coefficients between graphene, substrate and contact materials. However cooling should produce biaxial strain that would not split the G-band. No other low temperature study of the G-band of graphene on SiO$_2$ has observed a strain splitting either.

While we are not able to identify the origin of the asymmetric G-band peak without further investigation, we extract the position of the main (high energy) peak
Figure B.3: Properties of the low energy shoulder as a function of $E_F$ obtained from the low energy peak of a double lorentzian fit. (a) Amplitude, (b) position, (c) FWHM, (d) Difference in position between high and low energy peak (blue line) and the ration of the FWHM (red line)
with good precision from double lorentzian fit and get reasonable measures for the FWHM. Future measurements of different samples under optimized conditions would most likely be able to obtain better line shapes. Moreover the main qualitative results presented in this chapter do not depend on the exact lineshape and are obtained for any form of fitting we performed on the data.
References


Kim, Y., Ma, Y., Imambekov, A., Kalugin, N. G., Lombardo, A., Ferrari, A. C.,
field raman measurements and electron-phonon coupling contributions. Physical

Kim, Y., Poumirol, J. M., Lombardo, A., Kalugin, N. G., Georgiou, T., Kim, Y. J.,
Novoselov, K. S., Ferrari, A. C., Kono, J., Kashuba, O., Fal’ko, V. I., and Smirnov,
D. (2013). Measurement of filling-factor-dependent magnetophonon resonances in

York, 8th edition.

Kobayashi, T., Bando, M., Kimura, N., Shimizu, K., Kadono, K., Umezu, N., Miya-
100-m-long high-quality graphene transparent conductive film by roll-to-roll chemi-
023112.

Review Letters, 2(9):393–394.

Kossacki, P., Faugeras, C., Kühne, M., Orlita, M., Mahmood, A., Dujardin, E., Nair,

Kossacki, P., Faugeras, C., Kühne, M., Orlita, M., Nicolet, A. A. L., Schneider, J. M.,
and electron-phonon coupling in bulk graphite through raman scattering in high

Kühne, M., Faugeras, C., Kossacki, P., Nicolet, A. A. L., Orlita, M., Latyshev,


Martin, J., Akerman, N., Ulbricht, G., Lohmann, T., Smet, J., Von Klitzing, K.,
and Yacoby, A. (2007). Observation of electron-hole puddles in graphene using a


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1. *Charge tuning of non-resonant magneto-exciton phonon interaction in graphene*
   S. Rémi, B. B. Goldberg, and A. K. Swan
   Submitted

2. *How Graphene Slides: Measurement and Theory of Strain-Dependent Frictional Forces between Graphene and SiO₂*
   Nano Letters, **13** 2605 (2013).

3. *Biaxial Strain in Graphene Adhered to Shallow Depressions*
   Nano Letters, **10** 6 (2007).

4. *The nonlinear Fano effect*

5. *Resonant saturation laser spectroscopy of a single self-assembled quantum dot*
   M. Kroner, S. Rémi, A. Högele, S. Seidl, A. W. Holleitner, R. J. Warburton, B. D. Gerardot, P. M. Petroff, and K. Karrai
   Physica E, **40** 1994 (2008).
Conference Papers & Presentations:

1. *Transport and Raman measurements in Graphene: Interaction strength and scattering mechanisms*
   Bulletin of APS Meeting 2013
   Baltimore, MD, USA, March 2013.

2. *Raman measurements of graphene in magnetic fields*
   Bulletin of APS Meeting 2011
   Dallas, TX, USA, March 2011.

3. *Pressure induced strain in circular, suspended graphene membranes*
   International Conference on Raman Spectroscopy, 2011
   Boston, MA, USA, August 2011.

4. *Micro Raman spectroscopy of graphene Hall Bars in the QHE regime*
   Bulletin of APS Meeting 2009
   Pittsburgh, PA, USA, March 2009.

5. *Micro Raman studies of 1st and 2nd order Raman scattering of Graphene*
   Bulletin of APS Meeting 2008

6. *Behavior of graphene under strain and in magnetic fields monitored by Raman spectroscopy*
   Recent Progress in Graphene Research Symposium, 2009
   Seoul, Korea, July 2009.