MASTER

A study on hydrogenated epitaxial graphene

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A Study on Hydrogenated Epitaxial Graphene

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Abstract

Hydrogenated epitaxial graphene on silicon carbide (SiC) is potentially an interesting system, where defects play a crucial role in the emergence of exciting and new physical phenomena. One of them being the presence of pseudo-magnetic fields, which can exceed hundreds of Tesla, much larger than any external magnetic field that can be realised in the laboratory. In this work we present the remarkable appearance of fractal shapes on the hydrogenated epitaxial graphene surface, observed by the atomic force microscope. We believe that these fractal shapes directly reveal the presence of inhomogeneous pseudo-magnetic fields. Moreover our observations suggest that hydrogenated epitaxial graphene is a quantum Hall system at room temperature and zero magnetic field. This opens a new world of possibilities to study (fractional) quantum Hall effects and strongly correlated electron systems.
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1. Introduction

Epitaxial graphene on silicon carbide (SiC) is an extremely exciting material for the study of exotic physical phenomena in two-dimensional systems. This material simply consists of graphene, a flat monolayer of carbon atoms packed in a honeycomb lattice, grown on SiC. Graphene itself has been studied intensively after its experimental discovery in 2004 [1][2]. The fascinating electronic properties of graphene, such as exceptionally high mobilities (exceeding 100000 cm$^2$/Vs at room temperature) and relativistic behaviour of its charge carriers, has been the reason for the enormous amount of interest in this material [3]. In contrary to the exfoliated graphene flakes, high quality epitaxial graphene on SiC can be grown on relatively large areas allowing integration in device technology [4]. Hence graphene-based electronics and spintronics are feasible with epitaxially grown graphene.

In this report we present a variety of methods to study epitaxial graphene for fundamental purposes as well as practical applications such as graphene-based gas sensors. The main topic however, will be hydrogenated epitaxial graphene, which is epitaxial graphene with atomic hydrogen adsorbed on the carbon layer. The presence of defects in the SiC substrate has proven to be responsible for establishing ripples and curving in the graphene layer [5]. As a consequence the hydrogen atoms preferentially reside on these curved regions where a defect is located underneath [6]. This could potentially lead to the breaking of the graphene sublattice symmetry (imbalance in sublattice occupation) [7][8], giving rise to numerous exotic electronic and magnetic properties in this material. One of them being the emergence of ferromagnetism, which has been recently experimentally observed by Xie et al. and Giesbers et al. [9][10]. Because of its interesting (ferro-)magnetic behaviour we could think of applications in spintronic devices [11]. Secondly, density functional calculations (DFT) show the presence of so-called pseudo-magnetic fields (exceeding several hundreds of Tesla), forcing the electrons near the Fermi-level to strongly localise [12]. These strongly localised states can induce strong charge instabilities and large frustration in the kinetic energy, which is a key ingredient for strongly correlated electron systems.

We will show remarkable observations which support the latter, which is the appearance of cauliflower-like shapes on the surface of hydrogenated epitaxial graphene. We believe that these shapes, imaged by an atomic force microscope (AFM) at room temperature, appear because of the aforementioned strong charge instabilities. These electronic instabilities could be responsible for mesoscopic electronic phase separation. By changing the flow of hydrogen and by tuning the hydrogen exposure time we investigate the formation of these peculiar shapes and its fractal behaviour. With simple phenomenological models we aim to simulate these fractal shapes and make an attempt to understand the underlying growth mechanism. We propose that the growth is possibly governed by a Laplace-type fingering process. Analogous to viscous fingering of two fluids in a thin cell geometry (Hele-Shaw cell), an electron liquid can show fingering as well, in the presence
of a strong inhomogeneous magnetic field [13][14]. This strong inhomogeneity is realised in our system by non-uniform pseudo-magnetic fields, which arise because of a non-uniform distribution of hydrogen atoms on the epitaxial graphene surface.

Our observation of the viscous fingers suggests that hydrogenated epitaxial graphene is a quantum Hall system at room temperature and zero applied magnetic field. To gain experimental evidence to prove the latter we investigate the transport properties of hydrogenated epitaxial graphene in a Hall setup. In this thesis we present our pursuit to observe exotic (fractional) quantum Hall effects and phenomena that resemble the physics of high-temperature superconductors [15][16][17].
2. An introduction to hydrogenated epitaxial graphene

In this chapter we present a broad overview of the exciting properties of hydrogenated epitaxial graphene, some topics will be discussed in more detail in the following chapters. We will describe the preparation method of our samples followed by a brief discussion of the exotic physical phenomena that could arise from this material. However, firstly we introduce the physics of pristine graphene and its remarkable energy dispersion, which is important for many of its interesting electronic properties.

2.1 A brief summary on pristine graphene

The exotic properties of graphene, a two-dimensional layer of carbon atoms packed in a honeycomb lattice, can be partially attributed to its remarkable energy dispersion \[1\][2]. With a simple calculation we show the presence of the Dirac-cones and briefly discuss the consequences of the appearance of the two valleys, at the so-called \(K\) and \(K'\) points. The concepts and background introduced this section will be relevant for understanding the physical properties of hydrogenated epitaxial graphene, which will be discussed later on. For intrinsic pristine graphene, the carbon atoms are arranged in a hexagonal lattice, illustrated in figure 2.1. We can define the real lattice vectors \(\mathbf{a}_{\pm, -}\) and reciprocal lattice vectors \(\mathbf{b}_{\pm, -}\) as:

\[
a_{\pm, -} = \left( \frac{3a}{2}, \pm \frac{\sqrt{3}a}{2} \right), \quad b_{\pm, -} = \left( \frac{2\pi}{3}, \pm \frac{2\pi}{\sqrt{3}a} \right), \quad (2.1)
\]

here \(a\) represents the distance between two in-plane carbon atoms \((a = 0.142\ \text{nm})\), the real space lattice vectors are shown in figure 2.1. Also we see that the unit cell consists of two inequivalent carbon atoms, each belonging to its own triangular sublattice, say sublattice A and sublattice B. To find the energy dispersion we make use of the tight-binding model. This method is suitable for graphene since all the interactions are 'directional' (carbon atoms are covalently bond) and only include the neighbouring atoms. Therefore we describe the total wavefunction \(\Psi\) of the graphene system as a superposition of the Bloch functions on sublattice A and sublattice B:

\[
\Psi(\mathbf{k}, \mathbf{r}) = c_A u_A(\mathbf{k}, \mathbf{r}) + c_B u_B(\mathbf{k}, \mathbf{r}) \quad (2.2)
\]

Here \(u_{A,B} = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_{A,B}} e^{-i\mathbf{k}\cdot \mathbf{R}_{A,B}} \phi_{A,B}(\mathbf{r} - \mathbf{R}_{A,B})\) are the Bloch functions for sublattice A and B. Where \(\mathbf{R} = n_1 \mathbf{a}_+ + n_2 \mathbf{a}_-\) is the Bravais lattice vector and \(N\) the number of unit cells. The coordinates in real space and reciprocal space are \(\mathbf{r}\) and \(\mathbf{k}\) respectively. Note that only the \(p_z\) orbitals
of the carbon atoms are included in the calculation, since those orbitals describe the electrons that are able to delocalise and essentially determine the electronic properties of graphene. To find the energy dispersion \((E \text{ versus } k)\), we solve the Schrödinger equation for this system:

\[
\hat{H}\Psi(k, r) = E\Psi(k, r).
\] (2.3)

![Figure 2.1: Schematic representation of graphene and its carbon honeycomb lattice. The unit cell consists of two inequivalent carbon atoms (black and grey solid circles), forming two triangular sublattice which establishes the hexagonal lattice. The lattice vectors \(a_+\) reveal the contour of the unit cell.](image)

Multiplying both sides of equation 2.3 with the complex conjugates \(u_A^*\) and \(u_B^*\) and performing the spatial integral, we obtain, after substituting equation 2.2, the following set of equations:

\[
\int c_A u_A^* \hat{H} u_A dr + \int c_B u_A^* \hat{H} u_B dr = E\int c_A u_A^* u_A dr + \int c_A u_A^* u_B dr
\]

\[
\int c_A u_B^* \hat{H} u_A dr + \int c_B u_B^* \hat{H} u_B dr = E\int c_B u_A^* u_A dr + \int c_B u_B^* u_B dr.
\] (2.4)

Now considering the fact that the overlap between two carbon atoms is negligible \(\int u^*_A u_B dr = 0\) and representing \(\int u^*_A \hat{H} u_B dr\) as \(H(A,B),(A,B)\), we can rewrite equation 2.3 as a matrix equation:

\[
\begin{pmatrix}
H_{AA} & H_{AB} \\
H_{BA} & H_{BB}
\end{pmatrix}
\begin{pmatrix}
c_A \\
c_B
\end{pmatrix} = E
\begin{pmatrix}
c_A \\
c_B
\end{pmatrix}.
\] (2.5)

Where for \(H_{AA}\) and \(H_{BB}\) we find:

\[
H_{AA} = \frac{1}{N} \sum_{R_A} \sum_{R'_A} e^{-i k \cdot (R_A - R'_A)} \int \phi^*_A(r - R_A) \hat{H} \phi_A(r - R_A) dr
\]

\[
= \int \phi^*_A(r - R_A) \hat{H} \phi_A(r - R_A) dr
\]

\[
= E_0 = H_{BB}.
\] (2.6)
2.1. A BRIEF SUMMARY ON PRISTINE GRAPHENE

Here $E_0$ is defined as the energy of the $\pi$-electron on its carbon atom. The $H_{AB}$ terms in equation 2.5 describe the interaction between a single carbon atom with its three neighbours. Note here that the three neighbouring carbon atoms are positioned at the same sublattice, see figure 2.1. Therefore we find for $H_{AB}$:

$$H_{AB} = \frac{1}{N} \sum_{R_A} \sum_{R_B} e^{-i\mathbf{k} \cdot (\mathbf{R}_A - \mathbf{R}_B)} \int \phi_B^*(\mathbf{r} - \mathbf{R}_B) \hat{H} \phi_A(\mathbf{r} - \mathbf{R}_A) d\mathbf{r}$$

$$= (1 + e^{-i\mathbf{k} \cdot \mathbf{a} -} + e^{-i\mathbf{k} \cdot \mathbf{a} +}) \int \phi_B^*(\mathbf{r} - \mathbf{R}_B) \hat{H} \phi_A(\mathbf{r} - \mathbf{R}_A) d\mathbf{r}$$

$$= (1 + e^{-i\mathbf{k} \cdot \mathbf{a} -} + e^{-i\mathbf{k} \cdot \mathbf{a} +}) \cdot t, \quad (2.7)$$

where we define $t$ as the energy corresponding to the hopping integral. As a result we can now find the energy dispersion (after going through some algebra) by solving the determinant of equation 2.5 which yields:

$$E(k_x, k_y) = E_0 \pm t \cdot \sqrt{1 + 4 \cos^2 \frac{3k_x a}{2} \cos \sqrt{3} k_y a \frac{\sqrt{3} k_y a}{2}}. \quad (2.8)$$

Figure 2.2: The energy dispersion of pristine graphene, by plotting the result obtained in equation 2.8. The Fermi level is located at 0 eV and the following parameter values are chosen: $t = -1$ eV and $a = 0.25$ nm. It is clearly visible that in the vicinity of the $K$ and $K'$ points (black and red circle), the dispersion is linear, and we see the two Dirac cones touch. The Fermi velocity, $v_F$, remains constant in the low energy regime and is typically $10^6$ m/s ($\frac{v_F}{c} \approx \frac{1}{300}$). The Fermi level is exactly situated in the point where the two Dirac cones meet, here the electrons behave as massless particles, which gives rise to relativistic properties of the charge carriers in graphene \[3\].
The energy dispersion is shown in figure 2.2 for the case $t = -1$ eV, $a = 0.25$ nm and $E_0 = 0$ eV, the $K$ and $K'$ points are highlighted by the black and red circle. Because of the valley degeneracy and the spin degeneracy, each state is fourfold degenerate in graphene. Note that the other electron states in the system (corresponding to the in-plane orbitals) are filled and not shown in the figure. Also it should be mentioned that the electrical conductivity is expected to be low for intrinsic graphene, because the density of electron states approaches zero near the Dirac point. However, due to relativistic nature of the electrons, electrical conductivity is preserved [18]. Furthermore, by calculating the density of states (DOS), we know that the amount of charge carriers at the Fermi level $n(E_F)$ can be approximated by [19]:

$$n(E_F) = \frac{1}{\pi} \frac{(E_F - E_D)^2}{\hbar^2 v_F^2}.$$  \hspace{1cm} (2.9) 

Where $E_D$ is the energy at the Dirac point, also called the charge neutrality point (CNP) and $v_F$ is the Fermi velocity. Therefore it is possible to approximate the Fermi energy by determining the charge carrier density experimentally, with for example a Hall measurement. From equation 2.9 we can understand that, when pristine graphene is doped, the conductivity can be increased significantly. In chapter 6 we utilise this by using epitaxial graphene samples as a gas sensor. The gas molecules (NO$_2$) extrinsically dope the epitaxial graphene, which will result in a change in electrical resistance. This resistance change can be used as a measure of the amount of NO$_2$ molecules in the gas phase.
2.2 Step towards epitaxial graphene on SiC

The graphene samples, which are used in the experiments throughout this thesis, are epitaxially grown on a silicon carbide (6H-SiC(0001)) substrate. Since the graphene layer weakly interacts with the substrate, the electronic properties are slightly different from pristine graphene. Figure 2.3 shows a schematic picture (side-view) of the monolayer graphene grown on SiC. The size of the substrates are 4 mm × 4 mm and are highly n-doped with nitrogen atoms. We make use of the growth recipe proposed by Riedl et al. [4][20][21], which is based on thermal decomposition of the substrate. This recipe makes use of the difference in evaporation temperature between silicon and carbon atoms. By heating the substrate at the right temperature, the silicon atoms evaporate, leaving a layer of carbon atoms on top. A concise description of the fabrication procedure and some features of the epitaxial graphene on SiC is included in the paragraph below.

![Figure 2.3](image.png)

Figure 2.3: A schematic side-view of the mono layer, buffer layer and intercalated buffer layer grown on a 6H-SiC substrate with underneath the corresponding energy dispersion diagrams. The solid circles in blue, grey and orange represent the hydrogen, carbon and silicon atoms respectively. Note that the Si dangling bonds disappear after intercalation of the buffer layer (also called quasi free standing epitaxial graphene). The Fermi level in each case is illustrated by the red dashed line. The monolayer epitaxial graphene is initially n-doped, the buffer layer is insulating while the quasi free standing graphene restores the linear dispersion and is slightly n-doped.

The fabrication of epitaxial graphene consists of two main steps: etching and growing. Prior to the etching and growing the 6H-SiC(0001) samples are cleaned in the ultrasonic bath with acetone, followed by iso-propanol. Hereafter the samples are placed in a graphite susceptor inside an oven. The etching procedure starts immediately after degassing at 825°C. During etching in hydrogen atmosphere, surface defects and impurities on the SiC surface are removed. This provides a smooth
surface, containing terrace-like structures [20] with a typical width of 1 µm. The above mentioned etching procedure takes 40 minutes at a temperature of 1550°C and a hydrogen flow of 3 slm.

The etching step is followed by degassing and the growth procedure. The growth of epitaxial graphene is carried out by thermal decomposition in an argon atmosphere, which initiates Si atoms to sublime, leaving a layer of carbon atoms on top of the substrate. This process creates a buffer layer, often called the zero/interface layer graphene. This layer of carbon atoms is formed above the SiC substrate and has a $6\sqrt{3} \times 6\sqrt{3}R30^\circ$ reconstruction, see figure 2.3. However, not all the carbon atoms of the buffer layer are bond to a silicon atom of the substrate, which gives rise to the presence of silicon dangling bonds, see figure 2.4. Approximately 1 out of 3 silicon atoms at the interface is actually a dangling bond [5]. The other two silicon atoms are covalently bond to the carbon atom of the zero layer graphene. Recent experiments show indications that these dangling bonds are possibly crucial in establishing ferromagnetism in hydrogenated graphene [10]. The role of these Si dangling bonds in relation to the adsorption of atomic hydrogen will be discussed in more detail in chapter 3.

The monolayer graphene is grown on top of the aforementioned buffer layer, as shown in figure 2.4. The growth step is carried out at a temperature of 1650°C and an argon flow of 0.1 slm for 13 minutes. Subsequent to this step is the cooling down phase in a low pressure climate ($2 \times 10^{-5}$ mbar) with a cooling rate of roughly 90°C per minute. The fabricated graphene samples typically show (1 - 5)µm size terraces. An example of morphology of the clean epitaxial graphene surface is shown in figure 2.3. Furthermore the epitaxial graphene samples grown on SiC are initially n-doped, with its Dirac point shifted approximately 0.42 eV below the Fermi level and an intrinsic doping of $n_{EG} = 2 \cdot 10^{13}$ cm$^{-2}$ [4, 22].

Alternatively, it is also possible to only grow the buffer layer, this can be realised by setting a lower growth temperature, 1450°C instead of 1650°C. The buffer layer behaves as an insulator, due to its strong coupling with the SiC substrate. Therefore this carbon layer does not show the linear dispersion and the Dirac point. However, applying the intercalation described by Riedl et al., the buffer layer can be decoupled from the substrate by breaking the silicon-carbon bonds with hydrogen [4]. The decoupled layer, also called quasi free standing epitaxial graphene (QFEG), is conductive with typical mobilities in the order of 800 cm$^2$/Vs and an intrinsic doping of $n_{QFEG} = 1.5 \cdot 10^{12}$ cm$^{-2}$ at room temperature[22].
2.2. STEP TOWARDS EPITAXIAL GRAPHENE ON SiC

Figure 2.4: Left: low energy electron diffraction (LEED) image of the buffer layer on SiC. The white arrows point towards the bright spots, which can be attributed to the $6\sqrt{3} \times 6\sqrt{3}R30^\circ$ surface reconstruction of the buffer layer. The red arrow indicates the presence of SiC substrate. The energy of the electrons is approximately 150 eV. Right: an atomic force microscope image (AFM) of clean epitaxial graphene. The terraces are clearly visible and are typically 3-5 µm in width. The step edges are approximately 10-15 nm in height. The scan size is $13\mu m \times 13\mu m$. 
2.3 Hydrogenated epitaxial graphene

Hydrogenated epitaxial graphene caught recent attention due to its surprising ferromagnetic properties [9][10]. In this section we shortly touch upon the interesting electronic and magnetic properties of hydrogenated epitaxial graphene, after we briefly describe our experimental hydrogenation treatment. For the hydrogen treatment of the epitaxial graphene surface we use atomic hydrogen which is produced by cracking molecular hydrogen gas at elevated temperatures ($\geq 800 \text{ K}$). This is realised by letting molecular hydrogen gas flow through a heated capillary tube in which the $\text{H}_2$ molecules dissociate into $\text{H}$ atoms. The surface of the sample is placed directly in front of the capillary. A flow meter is able to control the hydrogen gas flow, alternatively we make use of a needle valve to dose the amount of hydrogen gas. A schematic illustration of the hydrogen treatment is shown in figure 2.5. The treatment takes place in UHV conditions, where the base pressure of the chamber is typically $10^{-8}$-$10^{-9}$ mbar. Note that the sample itself is at room temperature and the distance between the tube and the sample is fixed. By varying the flow, the temperature of the capillary tube and the hydrogen treatment time (exposure time) we are able to tune the amount of hydrogen adsorbed on the graphene surface.

![Diagram of hydrogen treatment process](image)

Figure 2.5: Hydrogen gas flowing in from the left will dissociate in the hot capillary tube. Atomic hydrogen will exit the tube and part of the total output flux adsorbs on the graphene surface.

For a ‘low’ flow of atomic hydrogen, we make use of a needle valve. When opening the valve, the pressure in the chamber increases to $10^{-6}$ mbar due to the incoming hydrogen atoms. During the treatment we keep the pressure at a constant level. An AFM image of hydrogenated epitaxial graphene at a low hydrogen flow at 720 K (this is the temperature close to the capillary tube, not at the sample) for 3 minutes, is shown in figure 2.6. The bright coloured features correspond to the hydrogenated graphene areas (increasing the treatment time results in larger amount of these bright features). After heating up the sample to 1100 K we clearly see the hydrogenated areas
2.3. HYDROGENATED EPITAXIAL GRAPHENE

disappear. This is in agreement with the results presented by Goler et al. where the desorption of hydrogen is observed by STM above 900 K. We are able to increase the hydrogen flow by using a flow meter instead of the manually controlled needle valve. The morphology turns out to be completely different, fractal like shapes appear in the AFM, as will be discussed in more detail in chapter 4.

![AFM images](image)

Figure 2.6: AFM topography images of a) hydrogenated epitaxial graphene and b) the same sample after heating up to 1100 K. The bright areas observed in the topography map are related to hydrogenated graphene. It is clear that after the heating step the amount of bright structures decreased significantly. The image size is 700 nm × 700 nm.

Reports from literature also show that atomic hydrogen do not reside randomly on the graphene surface, but rather adsorb on curved areas of the graphene sheet. The curvature, can be induced by the presence of the Si dangling bonds in the underlying SiC substrate. Figure 2.7 shows a DFT result of the relaxed epitaxial graphene layer on top of the buffer layer and the SiC. We can clearly see the curvature induced by the Si dangling bonds of the substrate. Furthermore, scanning tunnelling microscope (STM) experiments show that the hydrogen atoms preferentially adsorb in a periodic fashion on the graphene surface where a Si dangling bond is underneath. The periodicity of the superstructure, which is the (6 × 6), has a typical dimension of 2 nm as shown in figure 2.7 as a diamond shaped unit cell. When a hydrogen atom binds to a carbon atom, the in-plane carbon atom has to change from an sp² to an sp³ (out-of plane) configuration. The energy barrier for hydrogen adsorption can significantly reduced where the carbon sheet is initially curved, since less energy is needed to pull the carbon atoms in the curved regions out of the plane. Since the Si dangling bonds appear periodically below the graphene surface, it turns out that one of the two sublattices of graphene is preferential for hydrogen to adsorb on. The latter leads to the opening of a bandgap, ferromagnetic behaviour, and the origin for many exotic physical phenomena. Before getting into the details of the exotic properties, we first briefly discuss the energy dispersion of hydrogenated epitaxial graphene.

The latest electronic structure calculations, which take into account that hydrogen atoms adsorb on the surface in a periodic fashion, as depicted in figure 2.7, show some unusual features in the
electronic dispersion. For a hydrogen coverage of less than 1%, the linear dispersion, as seen in pristine graphene, completely disappears. As an example, figure 2.8 shows the calculated electronic band structure and the density of states of hydrogenated epitaxial graphene. Here we clearly see the opening of a ≥1 eV bandgap at the K point, as well as extremely flat bands in between the gap. In the density of states we observe highly degenerate states, in correspondence with the observed dispersionless bands near the Fermi level, which can be attributed to the emergence of so-called pseudo Landau levels. Similar to Landau levels, which arise from a magnetic field applied to a two dimensional electron gas (2DEG), pseudo Landau levels give rise to highly degenerate and very localised electron states. The difference is that, for pseudo Landau levels to arise, the electrons need to experience an ‘effective’ magnetic field (pseudo-magnetic field), not a real magnetic field. Sensibly, we should ask ourselves what is responsible for the pseudo-magnetic field in hydrogenated epitaxial graphene. Intuitively the latter can be understood as follows [26]: the chemical interaction between the hydrogen and carbon atom and the induced strain induced by the hydrogen adsorption affects the nearest neighbour hopping parameter $t$ by a small perturbation $\delta t$. As a result the energies of the eigenstates of the system change, such that the wave vector $\vec{k} \rightarrow \vec{k} + \delta\vec{k}$. We notice here the similarity with a 2DEG submitted to a perpendicular magnetic field, where the momenta of the electrons are shifted by a term proportional to the vector potential $\vec{A}$, such that $\vec{k} \rightarrow \vec{k} + \frac{e}{\hbar}\vec{A}$. It becomes clear now that a perturbation or modulation in the hopping parameter $t$ induces an effective vector potential (pseudo-vector potential) and hence a pseudo-magnetic field. The strength of this pseudo-magnetic field can exceed hundreds of Tesla, much larger than any external field that can be realised in an experiment [27][12].

In figure 2.8 we also see that the majority of electrons is spin up. The spin splitting of the (zeroth) pseudo Landau level (the localised states near the Fermi level) is induced by the exchange interaction between the hydrogen and carbon atom. Therefore the pseudo Landau level is half-filled at the Fermi energy. This phenomenon could possibly explain the experimental observation of ferromagnetism in hydrogenated epitaxial graphene [9][10][12]. Here we want to underline that the hydrogen adsorbate is responsible for opening the gap, generating a pseudo-magnetic field as well as...
inducing the spin polarisation. In chapter 5, we describe the transport properties of hydrogenated epitaxial graphene in more detail, also the appearance of (pseudo) Landau levels in graphene will be discussed more carefully. Regarding the flat bands observed in figure 2.8, we note that it shows great similarities with so-called Chern insulators. These insulators, until now only described theoretically, have nearly dispersionless energy bands, even when no external magnetic field is applied. It has been shown that the filling of the flat bands, also called Chern bands, is analogous to the filling of the Landau levels in the quantum Hall effect. The latter raises the question whether fractionally filled Chern bands can be seen as an equivalent to the fractional quantum Hall effect. If this is true, Chern insulators would be very interesting for the study fractional quantum Hall effects, which is fundamentally not well understood yet. An experimental realisation remains elusive, but an interesting candidate would be the hydrogenated epitaxial graphene system. Especially because of its large intrinsic magnetic field in the order of hundreds of Tesla, it would be extremely appealing to study quantum Hall phenomena at room temperature without applying a real magnetic field.

![Graphene Band Structure and Density of States](image)

Figure 2.8: Left: the electronic band structure of hydrogenated epitaxial graphene obtained by spin-polarised DFT calculations considering the periodic distribution of hydrogen atoms shown in figure 2.7b. Note that at the K point the linear dispersion has disappeared and a gap $\geq 1$ eV has opened up. In between the gap we observe extremely flat bands, which can be attributed to the presence of so-called pseudo Landau levels. Right: the density of states (DOS) calculated from the electronic structure calculations. Here we observe peaks appearing on top of the original DOS of clean graphene, these peaks correspond to the highly degenerate pseudo Landau levels. Due to exchange interactions the pseudo Landau levels are spin split (red and blue graphs). Source: Ridene et al. [12].
2.3. HYDROGENATED EPITAXIAL GRAPHENE

Preliminary results of ARPES on hydrogenated epitaxial graphene

As a first experiment to verify the DFT results shown in figure 2.8, we perform an angle-resolved photoemission spectroscopy (ARPES) measurement on a hydrogenated epitaxial graphene sample. Without going into the technical details of the technique, we show here a preliminary result. In the ARPES experiment, we use a He2 light source that produces 40.8 eV photons. These photons excite the electrons in the hydrogenated graphene sample to the vacuum state (photoelectric effect) and are detected by an analyser. By measuring the kinetic energy and the momentum of the outgoing electron, it is possible to determine the energy and momentum of the electron in the solid. Therefore, the band structure of the material can be probed, this result is shown in figure 2.9. Here we see the measured energy dispersion for the hydrogenated epitaxial graphene sample, the centre of the momentum is positioned at the K point.

Firstly, we see a p-doping effect, the Fermi level is shifted to the Dirac point (from approximately -0.5 eV to -0.1 eV). This implies that the hydrogen atoms act as p-dopants as it saturates the pz electrons of graphene. This was not clearly observed in the hydrogenated epitaxial graphene spectra shown by Bostwick et al., 2.9b. Secondly, we believe to observe two contributions in the band structure, the first contribution originating from the clean graphene and the second contribution from the hydrogenated parts. This is plausible since the photoemission experiment measures the band structure over an average of several square millimetres. From the AFM topography, figure 2.9d, we do observe dark regions between the bright spots. These dark areas could possibly correspond to clean epitaxial graphene patches, which result in the observation of a linear dispersion feature in the measured band structure. The bright spots corresponding to the hydrogenated areas have a typical size of 20 nm. The small size of the features could introduce incoherence in the ARPES spectrum and lead to broadening of the measured intensities. Hence, the parabolic band that we observe in the DFT result at the K point close to $E - E_f = -0.8$ eV, figure 2.8, can only be weakly observed in the experimentally obtained ARPES spectrum. Note however that the cut in momentum space, shown in figure 2.9a, is not along the $\Gamma - K - M$ direction, so a direct comparison to figure 2.8 cannot be made. However, we do expect the dispersion near the K point to be paraboloid-like.

A final remark we place on the high intensity measured close to the Fermi energy and the indication of the presence of the pseudo Landau levels. The high intensity near the Fermi energy could be an indication of the localised states or pseudo Landau levels appearing in the gap as predicted by the DFT calculations. In figure 2.9a, the $n = 0$ and $n = -1$ pseudo Landau levels are highlighted, which is in agreement with the density of states obtained by DFT shown in figure 2.9c. The non spin-polarised DFT makes use of a 1% hydrogen coverage, modifying the coverage could lead to different positions of the pseudo Landau levels. Therefore more extensive study in terms of different hydrogen coverages is required to conclude whether the DFT calculations match the experimental results obtained by ARPES. Also for supporting evidence of the ferromagnetic behaviour of hydrogenated epitaxial graphene, spin polarised ARPES could be performed to observe the spin up/down bands separately.
2.3. HYDROGENATED EPITAXIAL GRAPHENE

Figure 2.9: a) The obtained experimental band structure for hydrogenated epitaxial graphene. The energy with respect to the Fermi level is shown as a function of the reciprocal distance $1/\Angstrom$. The zero is located at the K point. The high intensity regions are shown in (dark)red while the low intensity areas are blue coloured. The Dirac cone can be clearly observed with the Dirac point located at approximately -0.1 eV, see the dashed lines as a guide for the eye. The dashed parabola reveals the parabolic dispersion also observed in the theoretical result 2.8. The energy resolution is 5 meV. b) The ARPES of hydrogenated epitaxial graphene with the Dirac point at -0.5 eV, adapted from Bostwick et al. [30]. c) The density of states of hydrogenated epitaxial graphene. The black arrows indicate the pseudo Landau levels $n=\pm 3$, adapted from Ridene et al. [12]. d) The corresponding AFM image of the hydrogenated graphene sample measured in a).
2.4 Characterisation of samples with Raman Spectroscopy

To check the quality and characterise our graphene samples we make use of Raman spectroscopy with a pump laser wavelength $\lambda = 514$ nm. Typical spectra for the buffer layer (BL), intercalated buffer layer (IBL) (quasi free standing graphene) before and after hydrogenation (HBL and IHBL respectively) are shown in figure 2.10. For pristine graphene it is known that the Raman spectrum contains two distinct peaks, the G and the 2D peak positioned at approximately $1580$ cm$^{-1}$ and $2670$ cm$^{-1}$ respectively [31]. The G peak can be assigned to an in-plane vibrational mode near the center of the Brillouin zone while the 2D peak is related to intervalley resonance scattering of two optical phonons near the edge of the Brillouin zone [17]. For the intercalated buffer layer, blue spectrum in figure 2.10, the G and 2D peaks are clearly visible and located at $1584 \pm 9$ cm$^{-1}$ and $2679 \pm 27$ cm$^{-1}$. The latter is in agreement with results obtained in the references [17][31][32].

Moreover, the spectrum of the intercalated buffer layer reveals a peak positioned at roughly $1340$ cm$^{-1}$. This peak, labeled with D, is referred to as the defect peak and can be ascribed to a phonon scattering process induced by the presence of a defect [17]. A measure for the amount of defects in pristine graphene is the ratio between the intensity of the D peak and the intensity of the G peak ($I_D/I_G$). Consequent to hydrogenation of the intercalated buffer layer, we observe that the D peak grows with respect to the G peak, as expected. After hydrogenation, 30 minute atomic hydrogen exposure at approximately $1000$ K, the ratio $I_D/I_G$ increases from 0.14 to 0.36. Hydrogenation of the buffer layer also leads to a significant increase in the ratio $I_D/I_G$ as can be observed in figure 2.10.

Figure 2.10: Raman spectra of the buffer layer (BL), intercalated buffer layer (IBL), before and after hydrogenation (HBL and IHBL respectively). The characteristic peaks are labeled with D, G and 2D. The corresponding peak ratios are listed on the right.
2.4. CHARACTERISATION OF SAMPLES WITH RAMAN SPECTROSCOPY

Raman spectra of clean epitaxial graphene (monolayer) and hydrogenated epitaxial graphene is shown in figure 2.11. Similar to figure 2.10 we see the D, G and 2D peaks appearing in the spectra. A clear rise in the D peak is observed after the hydrogen treatment as well as a significant change in the intensity of the 2D peak can be seen. The 2D peak becomes smaller and more broadened after hydrogenating the surface. This indicates loss of in-plane phonon modes which can be understood since the hydrogen adsorbates will destroy the sp2 in-plane carbon bonds, which suppresses the 2D peak. An in-depth study of the Raman spectra for hydrogenated epitaxial graphene is presented by Giesbers et al. [10].

Figure 2.11: Raman spectra of clean epitaxial graphene (EG) and hydrogenated epitaxial graphene (HEG). The hydrogen treatment was approximately 30 minutes. The defect peak rises significantly, as well as a clear broadening and decrease in the intensity of the 2D peak can be observed. The 2D peak is positioned at approximately 2725 cm$^{-1}$, which is blue shifted compared to the intercalated buffer layer, this shift can be attributed to strain arising from the interaction with the SiC substrate.
3. The role of Si dangling bonds on the morphology of hydrogenated buffer layer studied by AFM

When growing the buffer layer (or zero-layer) graphene, as described in the previous chapter, half-filled silicon dangling bonds from the SiC substrate interact strongly with the carbon layer above. As a result the presence of Si dangling bonds induces local curvatures in the carbon layer which significantly influences the morphology of epitaxial zero-layer graphene (buffer layer) as shown by Varchon et al. Therefore it is expected that these Si dangling bonds also affect the surface morphology of hydrogenated graphene as observed by the atomic force microscope (AFM). The role of these Si dangling bonds is studied by hydrogenation of both intercalated and non-intercalated buffer layer samples. The intercalation procedure, as described previously in chapter 2, saturates the dangling bonds and breaks the Si-C bonds. As a consequence the buffer layer becomes electronically decoupled from the SiC substrate, leaving us so-called quasi free standing epitaxial graphene. To understand the role of the Si dangling bonds we compare the AFM topography of the following samples: 1) hydrogenation of the buffer layer (HBL), 2) hydrogenation of intercalated buffer layer (HIBL) and 3) intercalation of hydrogenated buffer layer (IHBL). Note here that we do not hydrogenate epitaxial monolayer graphene.

3.1 Imaging with the atomic force microscope (AFM): tip-sample interactions

As mentioned in the introduction of this chapter, the topography of the hydrogenated graphene samples are investigated by room-temperature AFM. The AFM results are obtained in intermittent-contact mode, also known as tapping mode. Here the oscillation amplitude of the cantilever is the feedback parameter. Keeping the tip-sample force constant gives information about the morphology of the surface, without damaging the surface. The tip-sample interaction, in tapping mode, is mainly dominated by short range exchange repulsion and long ranged Coulomb repulsion and attractive Van der Waals forces. The strong repulsion occurs at short tip-sample distances, typically a few angstroms, when electronic orbitals start to overlap. Due to Coulomb repulsion the AFM can be very sensitive to charge density gradients. The characteristic force-distance curve is shown in figure 3.1. Note that the actual tip-sample force can be strongly affected by the geometry of the tip. In reality the tip apex has a radius of approximately 10 nm, which leads to tip-sample convolution when small features are present on the surface. In case the typical feature size on the surface is of
3.1. IMAGING WITH THE ATOMIC FORCE MICROSCOPE (AFM): TIP-SAMPLE INTERACTIONS

Figure 3.1: Force-distance diagram corresponding to a Lennard-Jones-like potential. The red coloured section of the curve illustrates the relevant force region for tapping mode AFM. The oscillating tip pushes repeatedly into the repulsive region to probe the surface.

the same order of magnitude as the tip radius, as illustrated in figure 3.2, it can be easily shown from a geometrical calculation that:

\[ \rho_c = \sqrt{(R + r)^2 - (R - r)^2} = 2\sqrt{Rr}. \]  

(3.1)

Here \( r \) is the radius of a 'spherical' feature on the sample surface, \( R \) the radius of the tip and \( \rho_c \) the radius of the observed feature by AFM (curvature radius). The tip radius \( R \) is approximately 10 nm. Therefore, invoking equation 3.1, 1 nm size surface features will appear in the AFM image as 6 nm size features. Note that the latter also holds when the surface contains charge gradients, features due to strong localization of charge may appear larger in the AFM topography image because of tip-sample convolution.

Figure 3.2: Tip of radius \( R \) probing a sphere on a surface with radius \( r \). The red dashed curve indicates the appearance of the surface feature in an AFM image.
The surface morphology of hydrogenated buffer layer with and without the presence of Si dangling bonds

In this section we focus on the morphology as observed by the AFM of the hydrogenated buffer layer surface with and without the Si dangling bonds. To study the role of the Si dangling bonds we compare the AFM topography of the following samples: 1) hydrogenation of the buffer layer (HBL), 2) hydrogenation of intercalated buffer layer (HIBL) and 3) intercalation of hydrogenated buffer layer (IHBL). A scheme of the different investigated samples is presented in figure 3.3. The presence of Si dangling bonds induces locally curved areas in the carbon layer as shown by Varchon et al. [5]. These curved regions, also schematically drawn in figure 3.3, are the preferential regions for the hydrogen atoms to reside when exposing the surface to atomic hydrogen [23]. Therefore it is expected to observe different morphologies for the buffer layer (with curved regions due to Si dangling bonds) and the intercalated buffer layer (no Si dangling bonds, no curved areas). However it is noteworthy that hydrogen itself, when it adsorbs on the surface, can cause a local curvature [24]. This can be understood by the fact that the hydrogen atom induces a transition from an in-plane C=C sp\(^2\) bond to an out-of-plane C-H sp\(^3\) bond.

In figure 3.4 the three different samples are compared side by side. Significant changes can be observed in the AFM topography, depending on the presence of the Si dangling bonds. At this point it is important to discuss what exactly can be observed in the AFM image. The measured height, typically in the order of a nanometer, is significantly larger than expected for a ‘physical’ protrusion as a result of hydrogen sitting on top of the carbon layer, which is typically sub-Angstrom [34]. It is therefore reasonable that the features observed in the AFM images are related to inhomogeneous charge distributions on the surface and do not solely reflect the geometrical curvature. The latter is not surprising since upon adsorption of a single hydrogen atom, a region of localised states will be established in the vicinity of the adsorbate as discussed in the introduction chapter [35]. These localised states are likely to increase the Coulomb repulsion between the sample and the tip.
resulting in the observed height as shown in figure 3.4. Therefore an inhomogeneous distribution of hydrogen adsorbates could be responsible for charge density gradients, which will be mapped by the AFM as height gradients.

The first observation we make is that the surface of the hydrogenated buffer layer is largely covered by small droplets (bright circular shapes), typically 8 nm in size, while the intercalated buffer layer samples show a smaller amount of larger sized droplets. Secondly, the height observed for the HBL in AFM ($\approx 0.4$ nm) is much smaller than the IHBL and HIBL ($\geq 1$ nm). Starting from a mechanical and electrostatic point of view, the results shown in figure 3.4 can be understood in two different ways. The buffer layer contains preferential sites (curved and convex regions due to the Si dangling bonds) for hydrogen to adsorb to, on the other hand the non preferential sites (concave regions) become harder to attach to. This is because the carbon layer is strongly bound to the substrate (Si-C bonds), which prevents hydrogen atoms to bind to these carbon atoms and ‘pull’ up the surface upon adsorption. Therefore the size of the clusters are limited by the fact that the buffer layer is anchored to the substrate by the Si-C bonds, as illustrated in figure 3.5. For the HIBL sample, we observe larger droplets corresponding to larger clusters of aggregated hydrogen atoms. The latter is viable since the carbon layer is now electronically decoupled from the substrate, so the carbon layer is not anchored and thus does not obstruct hydrogen atoms to form larger size agglomerates, see figure 3.5. This explanation is purely based on the geometrical and mechanical effects, but it does effectively explain the discrepancy observed in the height of the AFM topography (figure 3.4). Since the hydrogen clusters are smaller in the HBL, the amount of
localised states is less compared to the larger hydrogen clusters observed in the HIBL. Hence the (electrostatic) Coulomb repulsion is smaller for the small hydrogen clusters and larger for the large hydrogen clusters, which elucidates the height difference observed in the AFM for the HBL and the HIBL.

However to understand the AFM topography of the IHBL (intercalation after hydrogenating the buffer layer) sample, figure 3.4b, more careful thought is required. The significant change in morphology after intercalation, compare figure 3.4a and 3.4b, could be an indication that hydrogen atoms have rearranged themselves during the intercalation procedure. The intercalation temperature is approximately 550 °C, which is roughly 100 degrees lower than the expected hydrogen desorption temperature [23]. Therefore we cannot exclude any diffusion related processes of the hydrogen atoms on the surface during the intercalation step.

The second explanation is based on the electrostatic screening in case free electrons are available in the carbon layer for the different samples. The buffer layer is an insulator, due to the strong coupling with the substrate. Therefore nearly no free electrons are available that could screen the electrostatic interactions to reduce the local charge gradients induced by adsorbed hydrogen atoms. As a consequence of the ineffective screening of the localised electrons, the clusters cannot grow into larger sizes. So the Coulomb repulsion makes it unfavourable to have locally high densities of hydrogen atoms. The latter will give rise to the formation of small clusters of hydrogen atoms, as can be seen in 3.4a. This is in contrast to the intercalated samples, where free electrons in the carbon layer are present to screen the localised states induced by the adsorbed hydrogen atoms (sheet carrier density is approximately 10^{11} cm^{-2}). The effective screening allows hydrogen atoms to form larger clusters. This could possibly explain why the AFM images of the IHBL and the HIBL show larger features (≥ 20 nm) with a clear edge, while the features observed on the HBL appear much less pronounced and are smaller in size (≤ 8 nm).

If we now assume that the adsorbed hydrogen atoms do not diffuse in the intercalation procedure (intercalation after hydrogenating the buffer layer). It would contradict the first explanation which...
only takes into account the geometrical changes. It cannot explain why the distribution of bright features on the buffer layer is more or less homogeneous in the beginning, while after intercalation we observe separated clumps with a significantly larger size. On the other hand, considering the electronic screening, it is likely that the small hydrogen clusters are fully screened. Only the larger clusters are not sufficiently screened. This would imply that the dark areas, in between the bright clumps, do contain hydrogen atoms but are not visible due to the electrostatic screening. As reported by Guinea et al. [36] phase separation can occur when the long range Coulomb interaction cannot be sufficiently screened, as a result charge puddles can be formed in a strongly localised electron system. We would like to note here that this phase separation could be present in this system, reflected by the bright and the dark regions. In the following chapter we continue with hydrogenated epitaxial graphene samples. There we deposit hydrogen on top of the monolayer graphene, which is on top of the buffer layer and substrate (see figure 2.3). This, surprisingly, shows fractal like shapes on the surface when imaged by the AFM.
4. Viscous fingers on hydrogenated epitaxial graphene

The observation of fractal-like structures on hydrogenated epitaxial graphene with an AFM, as shown in figure 4.1, is entirely different than observed in the previous chapter for the hydrogenated buffer layer samples. The important difference is that epitaxial graphene is a monolayer of graphene on top of the buffer layer. The latter significantly changes the electronic properties of the system as mentioned in chapter 2. The typically electron density of epitaxial graphene is \( n_{EG} = 2 \times 10^{13} \text{ cm}^{-2} \) which is roughly ten times larger than the intercalated buffer layer (quasi free standing) sample. Also the Si dangling bonds are present here, which could play an important role in the adsorption process of hydrogen on the surface of epitaxial graphene as shown in the previous chapter. The emergence of the peculiar fractal shapes is motivating us to investigate the underlying growth mechanism in more detail. In this chapter we simulate these shapes and compare it to the experimental observations. We present an extensive discussion in understanding the mechanism that possibly establishes such shapes in our AFM experiments. Moreover we show that the underlying mechanism could be strongly related to the fact that the electrons are strongly localised because they experience a strong pseudo-magnetic field, which is induced by the adsorbed hydrogen atoms.

4.1 Viscous fingering of the electron droplet

The appearance of fractals is very common in nature, for instance the structure of snowflakes (crystallised water), the shape of a tree and the British coastline are some stereotypical examples [37]. Several other examples of radially grown fractal like structures are shown in figure 4.1. A specific type of fractal, called a brownian tree, emerges when fractals are formed by Laplacian growth, which is in 2D governed by the Laplace equation:

\[
\nabla^2 u(x, y) = 0. \tag{4.1}
\]

The equation above shows that the frequent appearance of fractals is not surprising because of its close relation to physical laws in for example electrostatics and fluid dynamics. In equation (4.1) \( u(x, y) \) is a scalar potential which is analogous to the electrostatic potential in electrostatics or the pressure field in fluid dynamics. In the case of fluid dynamics, the local fluid velocity is directly proportional to the local pressure gradient \( (v \propto \nabla p) \), also called D’Arcy’s law. Assuming that the fluid is incompressible \( (\nabla \cdot v = 0) \) we can easily see that this problem should satisfy the Laplace equation (4.1). A famous and intensively studied example of Laplacian growth can be experimentally carried out in a Hele-Shaw cell, in which a low viscosity fluid is injected into
4.1. VISCOUS FINGERING OF THE ELECTRON DROplet

a highly viscous fluid in a narrow gap between the two parallel plates [38][39]. The characteristic patterns of this type of growth is shown in figure 4.1. Finger like structures form at sites in which the pressure gradient (arising from local instabilities) is significantly larger compared to its surrounding. Note that in these experiments the growth is almost two dimensional, in the limit of the distance between the two parallel plates going to zero. It has been noticed by Agam et al. that similar phenomena take place in 2D semiconductor nano structures [14]. We recall that they described an incompressible two dimensional electron droplet in a strong inhomogeneous magnetic field. The growth of such an electron droplet is then described by:

\[ \hbar \partial_t \rho(z) \approx \rho_{N+1} - \rho_N \approx |\psi_N|^2 \approx \frac{1}{2\pi} |w'(z)| \delta_C(z). \]  

(4.2)

Where the left hand side simply represents the change of the charge density distribution \( \rho(z) \), which is approximated by the probability of adding the \( N^{th} \) particle to the droplet \( |\psi_N|^2 \). This process is then proportional to the harmonic measure \( |w'(z)| \), similar to D’Arcy’s law in fluid dynamics[14] and \( \delta_C(z) \) is a delta function localised on the position \( z \).

Figure 4.1: a) AFM image of fractal observed on hydrogenated epitaxial graphene surface, the size is approximately 80 nm. b) A dark-coloured low-viscosity fluid (water) injected into a light-coloured high-viscosity hydrophobic fluid, in a Hele-Shaw cell, gives rise to a so-called viscous fingers. Adapted from Zhao et al. [38]. c) Fractal created by a DLA simulation, adapted from Witten and Sander [40].

We propose here that a comparable situation arises in our hydrogenated epitaxial graphene system. Upon adsorption of a hydrogen atom on epitaxial graphene, an area of localised charges will be induced in the (nearly) two dimensional carbon layer, for a critical amount of hydrogen adsorbates it will establish our 2D electron droplet [8][35]. The size of the electron droplet grows as the number of adsorbed hydrogen atoms increases. This droplet can become much larger than the droplets observed in the previous chapter, where the (intercalated) buffer layer was hydrogenated, because of the larger screening. The more efficient screening of the localised charges is provided by the larger amount of free electrons in epitaxial graphene compared to the (intercalated) buffer layer, see figure 2.3. This indicates that ingredients for the formation of the fractal shapes could be related to the amount of charge carriers in the system.

Now, the inhomogeneity in hydrogen adsorbates on the epitaxial graphene surface gives rise to strong inhomogeneous pseudo-magnetic fields as introduced in chapter 1. This is analogous to what is described by Agam et al. [14], instead of inhomogeneous magnetic fields we have inhomogeneous \textit{pseudo-magnetic} fields present in our hydrogenated epitaxial graphene system. As a reminder: the
presence of the pseudo-magnetic field is provided by the chemical interaction of the hydrogen-carbon bond and its induced strain in the graphene sheet. This shifts the eigenenergies of the system and therefore effectively generates a pseudo-vector potential in our 2D system [26][27][30], see chapter 1. Therefore we believe that the fractal like shapes we observe on hydrogenated epitaxial graphene, as shown in figure 4.1a, are related to the viscous fingering phenomenon of electron droplets in inhomogeneous magnetic fields [13][14].

In the cartoon shown in figure 4.2 the proposed idea is illustrated. In the initial stages of the hydrogen treatment, the hydrogen atoms, will stick to the preferential sites on the epitaxial graphene. These preferential sites are the curved regions induced by the Si dangling bonds in the substrate [5][23]. Hydrogen atoms are able aggregate on the convex areas, forming clumps. The region in between, we believe, still contains hydrogen adsorbates, but in much lower concentration. The hydrogen agglomerates establish the charge ‘puddles’ of strongly localised electrons (electron droplet). The charge distribution then forms, in presence of a strong inhomogeneous field, the fractal shapes/viscous fingers. Therefore we underline that the features observed in AFM, should not be attributed to the positions of the hydrogen atoms but to the underlying induced charge density distribution. In the following of this chapter, we show that the observed fractals, indeed share the same fractal behaviour as viscous fingers. Also we present a phenomenological model, based on diffusion limited aggregation, and a Monte Carlo simulation, which both show qualitative similarities with the experimentally observed fractal shapes.

Figure 4.2: Artist’s impression of the curved graphene landscape with on top atomic hydrogen adsorbed (blue spheres).
4.2 Laplacian growth, simulated by diffusion limited aggregation

From literature we know that fractal-like patterns grown by diffusion limited aggregation (DLA) appear to be very much alike structures arising from Laplacian growth [41]. Furthermore experimental research has been done on this matter in the past, for instance by Daccord et al. [39]. In their work they find both a quantitative and qualitative agreement between DLA and viscous fingering in Hele-Shaw cell. To intuitively understand why the two growth modes are comparable we first briefly describe the DLA algorithm. The growth of fractals, seen in figure 4.1c, can be simulated with a relatively simple algorithm proposed by Witten and Sander [40] [42]. A discussion of simulation results will be presented in the next section, however a brief introduction to the algorithm will be given here. The DLA algorithm basically starts with the initialisation of one seed (nucleation site) in the centre of a square lattice which consists of $L \times L$ lattice points. As the simulation starts, a particle is injected from a distance which is sufficiently far from the seed. This injected particle performs a random walk until it meets an adjacent particle (a neighbouring cell which is occupied, which is for the first particle obviously the seed in the centre) and then becomes part of the cluster. After that, a new particle is placed on the lattice and that particle performs again a random walk until it eventually sticks to the cluster. An illustration of this algorithm is presented in figure 4.3 and the source code is listed in Appendix A. If we assume that the walker sticks always to an occupied neighbour cell, it can be intuitively understood that because of this, the cluster mainly grows mostly on the perimeter. In other words as the size of the cluster grows, it becomes very hard for the next random walker to reach the centre of the fractal, since the outer branches ‘screen’ the inner part of the fractal. This is analogous to Laplacian growth where the formation of cusps occurs at the ‘tip’ of the branch. The latter is crucial for the formation of these fractal-like patterns. Please keep in mind that the particles in this simulation represent the position of the electrons. By adding new particles, the number of electrons is increasing which leads to the growth of an electron droplet. Note for now that the algorithm allows only one particle on the entire lattice to move, and the time it needs to stick to the cluster is arbitrary since it performs a random walk. The probability $P(i, j)$ of finding a particle on lattice site $(i, j)$ is of course determined by the probabilities of the neighbouring sites and can be written as [41]:

$$P(i, j) = \frac{1}{4} [P(i - 1, j) + P(i + 1, j) + P(i, j - 1) + P(i, j + 1)].$$

Furthermore the lattice random walk satisfies the diffusion equation:

$$\frac{\partial \rho(x, t)}{\partial t} = D \nabla^2 \rho(x, t),$$

(4.4)

here $\rho(x, t)$ describes the total particle distribution as a function of the position $x$ on the lattice and time $t$, the diffusion constant is the parameter $D$. As a consequence of one single particle moving at a time, it becomes clear that $\frac{\partial \rho}{\partial t} \rightarrow 0$ [43]. Since the left-hand side approaches zero, it is now evident from equation 4.3 that the diffusion equation reduces to a Laplace-like equation, shown earlier on in equation 4.1. To underline the likeness of the analytic Laplace equation and the discrete DLA model even more, we discretise the Laplace operator in 2D from equation 4.1 this yields:
4.2. LAPLACIAN GROWTH, SIMULATED BY DIFFUSION LIMITED AGGREGATION

\[ \nabla^2 u(x, y) = \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \]

\[ \approx \frac{u(x - dx, y) - 2u(x, y) + u(x + dx, y)}{dx^2} + \frac{u(x, y - dy) - 2u(x, y) + u(x, y + dy)}{dy^2} = 0, \]

making use of the latter and substituting \( dx = dy \), it follows that:

\[ u(x, y) = \frac{1}{4} [u(x - dx, y) + u(x + dx, y) + u(x, y - dy) + u(x, y + dy)]. \]

It was Witten and Sander, who pointed out the similarity between equation 4.6 and the probability \( P(i, j) \) of finding a random walker on site \((i, j)\) on a lattice \([42]\) shown in equation 4.3. This means that the scalar field \( u(x, y) \) can be statistically sampled by a random walk, where we observe that the probability \( P(i, j) \) is proportional to \( u(x, y) \). We note here that the comparison between DLA and Laplacian growth given in this section only gives an intuitive comparison. The main difference that should be stressed, is that DLA is grown serially with constant particle size, while Laplacian patterns are grown by advancing each boundary point in parallel, proportionally to the gradient of the Laplacian field \([41][44]\), which implies that the two growth processes are fundamentally different. On the other hand, both quantitative and qualitative similarities have been found between DLA simulations and experiments with Laplacian growth (viscous fingers) \([39][41][45]\).

Figure 4.3: Simple scheme of the DLA algorithm, a seed is planted in the center of the lattice \((L \times L)\) and particles are injected from a distance \(3 \geq R_g\) where \(R_g\) is the radius of gyration of the fractal. When the particle moves too far away from the seed (say distances larger than \(6R_g\)) the particle will be destroyed and a new particle will be injected.
4.3. THE DLA ALGORITHM: COMPARING SIMULATIONS WITH EXPERIMENTAL OBSERVATIONS

4.3 The DLA algorithm: comparing simulations with experimental observations

As mentioned in the introduction of this chapter, we are highly interested in the growth mechanism of fractals observed on the surface of hydrogenated epitaxial graphene with the atomic force microscope (AFM). We propose that diffusion limited aggregation simulations could help us reveal whether the observed patterns, as shown in figure 4.1a, are indeed related to viscous fingering of an electron droplet in an inhomogeneous magnetic field. To do this we assume that the fractals observed by AFM are directly related to the presence of hydrogen atoms, and that the localised charges (charge density gradients) are imaged by the AFM. Thus, the hydrogen atoms are not specifically arranged in a fractal shape, it is rather the underlying charge density distribution. In addition we assume that the electron droplet grows when a hydrogen atom adsorbs in its surrounding area. For all of this to happen, hydrogen atoms should be able to diffuse and have a slight tendency to cluster. Moreover it is known, see chapter 3, that hydrogen atoms prefer to reside on curved regions which could explain a local aggregation of hydrogen atoms [6].

To find out whether the growth of the fractals on epitaxial graphene can be modelled by DLA we compare the fractal dimension, $D_f$, between the simulations and the experimental results. This parameter is a measure of the space-filling of the fractal and differs between distinct types of fractals. Similar work is conducted by Brune et al., where they studied fractal growth of silver on Pt(111) [46]. A drastic change in the morphology of the silver fractals could be realised by increasing the flux rate of the silver atom deposition. At relatively high fluxes they reported that the fractal growth is strongly affected by the anisotropy induced by the substrate, which results in so-called dendritic fractals. At low fluxes however, the branches of the cluster frequently alter their direction and do not show any long range order. Very much alike the work of Brune et al. we vary the deposition time and compare the observed fractals with the DLA simulations [46].

To study and understand the shape and fractal dimension of fractals we firstly review the DLA algorithm more carefully. A step-by-step description of the DLA algorithm is summarised below in a flow chart shown in figure 4.4, the complete source code, written in MATLAB, can be found in Appendix A.

1. Define 2D lattice and set the seed in the centre of the grid (so this is a zero matrix with in the centre an ‘1’, which defines an occupied site, the zeros resemble the empty lattice sites).
2. Define a injection square around the seed (initially 30 grid points/lattice units), this is where a new particle is placed in at the start of the random walk. When the simulation proceeds, the size of the square grows with the size of the fractal (characterised by its radius of gyration, $R_G$), to make sure that each particle is injected from a distance which is sufficiently far from the cluster, this is to preserve the randomness in approaching the cluster [43].
3. Pick a random site (i,j) on the square lattice and set it to ‘1’.
4. Pick a random number $\in [0,1]$, and make a move: left/right/up/down. The four directions are equally probable, which reflects the concept of a random walk.
5. Check if particle moves too far away from the cluster, if the distance between the particle and the seed is larger than $6R_G$, the particle will be removed and a new particle will be injected. This feature prevents the random walkers to spend long time on the lattice without ever attaching to the cluster, as a result the simulation time is significantly reduced.
4.3. THE DLA ALGORITHM: COMPARING SIMULATIONS WITH EXPERIMENTAL OBSERVATIONS

6. Check if any neighbouring cells are occupied. If yes, the particle has a probability $\sigma$ of sticking to the cluster. If all neighbour sites are empty, the algorithm continues with step 4.

7. If the particle is stuck the matrix will be updated and the radius of gyration, $R_G$, will be calculated.

8. Return to step 3, the simulation stops when $N$ lattice sites are occupied.

9. Plot the lattice, also the radius of gyration as a function of the number of occupied cells (area/volume of the fractal) can be plotted.

Figure 4.4: Flow chart of the DLA algorithm. The simulation ends when the size of the cluster equals $N$.

The size of the fractal is characterised by the radius of gyration $R_G$, in the algorithm the radius of gyration is defined as:

$$ R_G = \sqrt{\frac{1}{N} \sum_i |\mathbf{r}_i - \mathbf{r}_{\text{seed}}|^2}. $$

(4.7)

As the number attached particles to the cluster increases, also the size and hence the radius of gyration of the fractal grows. To describe the scaling between volume of the fractal and its size we define:

$$ S \propto R_G^{D_f}, $$

(4.8)

Where $S$ is the volume of the fractal (which is proportional to the number of particles), $R_G$ the radius of gyration and $D_f$ the fractal dimension as mentioned earlier. To obtain a slightly better
understanding of $D_f$ we can look at the situation when $D_f \to 2$. This would imply that the cluster would appear circular shaped (in two dimensions), because the volume $S$ (this is the surface area in 2D) of the cluster scales with its squared radius. If $D_f \to 1$ the cluster would be more linear shaped. Therefore, in general, the fractal dimension is a measure of the space filling (the amount of space it fills in relation to its size).

4.3.1 Simulated DLA fractals and their fractal dimension

To determine the fractal dimension $D_f$ we calculate $R_G$ (equation 4.7) as a function of the volume of the fractal $S$. Then, making use of equation 4.8 the fractal dimension can be estimated. The simulation results for fractals with a size of $N = 3000$ and different sticking probabilities are presented in figure 4.5. In figure 4.5a $\ln(S)$ is shown as a function of $\ln(R_G)$, the proportionality constant, which is the fractal dimension $D_f$, is extracted from a linear fit. The inset shows the final shape of the fractal for $N = 3000$ and sticking probability $\sigma = 1$. Note that the fit significantly deviates from the simulation data for $\ln(R_G) \leq 1.5$, this is related to the fact that the statistics are not well evolved in this regime. Figure 4.5b shows the fractal dimension for different values of the sticking probability $\sigma$, $D_f$ is an average over five simulations, the error bars show the statistical uncertainty in the simulation. At $\sigma = 1$, implying that the walking particle always sticks to the cluster, we find $D_f = 1.74 \pm 0.05$, which is in agreement with the literature [42][43][41][39]. For decreasing values of $\sigma$, the geometrical ‘screening’ by the outer branches of the fractal will be less effective, because the walker does not immediately stick to the first occupied cell it encounters. As a result, walking particles get more opportunities to move into the core (closer to the seed) of the fractal. For this reason the fractal becomes denser (like a solid disk) and thus the fractal dimension increases, which can be observed in figure 4.5b. In the limit of $\sigma \to 0$ we naturally expect that $D_f \to 2$. Simulated fractals for different values of $\sigma$ and $N = 3000$ are shown in figure 4.6. We clearly see from the simulations that the fractals become denser as $\sigma$ becomes smaller which is expected and in agreement with the results shown in figure 4.5. From the experimental point of view this parameter $\sigma$ could describe the strength of inhomogeneities, such as the pseudo-magnetic fields. For a uniform magnetic field the growth will be uniform, this is, more or less circular shaped, therefore $D_f \to 2$. For large and strongly non-uniform pseudo-magnetic fields it is expected that the 'fractality' increases.
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Figure 4.5: a) The fractal dimension $D_f$ extracted by a linear fit from the $\ln(S)$ versus $\ln(R_G)$ plot for a fractal grown with $\sigma = 1$ and $N = 3000$. The inset in the lower right corner shows the shape of the fractal at the end of the simulation. b) The fractal dimension for varying sticking probability, each point is averaged over five simulations, the error bars show the statistical uncertainty of the DLA simulation.

Figure 4.6: Three simulated fractals for $N = 3000$ and $\sigma = 0.2$, 0.6 and 1, it is clearly visible that the fractal becomes more dense when lowering the sticking probability $\sigma$. 
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4.3.2 The fractal dimension of the experimentally observed fractals

The method to calculate the fractal dimension $D_{f,\text{box}}$ of the fractals observed by AFM, as pictured in figure 4.7, differs slightly from the method to determine $D_f$ in the simulations since we are not able to image the fractals in successive stages of the growth during the hydrogenation procedure. Instead of measuring the radius of the fractal as a function of its volume, we divide the image of a single fractal in square boxes with size $\epsilon \times \epsilon$ and count the number of boxes $K$ required to fully cover the surface of the fractal. Note that the scaling between $\epsilon$ and $K$, given by $\epsilon \propto K^{D_{f,\text{box}}}$, works only at a limited scale. This is due to the fact that the minimum size of the features of the fractal electron droplet is determined by the finite sharpness of the AFM tip and the maximum size is of course limited since the cluster size is finite. By averaging the $D_{f,\text{box}}$ for an ensemble of individual fractals on the same sample surface we are able to approximate the fractal dimension. Figure 4.7 shows the hydrogenated epitaxial graphene surface (for 3 minutes of hydrogen treatment time and at a cracker temperature of 1000 K) with a scan size of 700 nm by 700 nm. We can clearly see the fractal shapes with a typical size of slightly less than 100 nm. Ten different electron droplets have been analysed and we find that $D_{f,\text{box}} = 1.69 \pm 0.05$ for this particular sample. This result is in agreement with the value of the fractal dimension obtained with DLA simulations with a sticking probability close to unity, where we found $D_f = 1.74 \pm 0.05$.

Figure 4.7: AFM image of hydrogenated epitaxial graphene (700 nm × 700 nm), 10 fractals individual fractals are used to estimate the fractal dimension. As an example, four fractals are zoomed in, the typical size is approximately 80 nm.

An interesting feature that can be observed in figure 4.7 is that the step edge seems to act like a nucleation line for the fractal growth. Since step edges and defects are more reactive sites for hydrogen to adsorb on, we expect to observe growth of viscous fingers near the edge. With a modest adjustment, we are able to simulate growth along such a step edge as well. The simulation result is shown in figure 4.8. The main difference in the simulation is that the seed is not a single particle in the center, but a line instead. Furthermore, periodic boundaries are applied in the direction perpendicular to the line. This simulation result clearly shows the alikeness with the
4.3. THE DLA ALGORITHM: COMPARING SIMULATIONS WITH EXPERIMENTAL OBSERVATIONS

Experimental observation, see figure 4.7. The qualitative similarities between the shapes, compare figures 4.6 and 4.8 with figure 4.7, and the quantitative agreement between their fractal dimension, suggest that the experimentally observed fractals could possibly be described by a phenomenological diffusion limited aggregation model and hence indicates Laplacian growth. This implies that the observed fractals could indeed be viscous fingers of 2D electron droplets, arising due to intrinsic inhomogeneous pseudo-magnetic fields of hydrogenated epitaxial graphene on SiC [14][27][13].

Figure 4.8: Diffusion limited aggregation starting with a vertical line in the center of the grid as the nucleation ‘line’. In the horizontal direction periodic boundary conditions are applied. The simulation is ran for \( N = 2000 \) and \( \sigma = 1 \).

By changing the treatment time and temperature, we obtain different sizes and amount of the electron droplets on the surface. For a quick and more accurate averaging over a larger ensemble of the observed fractals, we make use of the fractal analysis tool of the WSxM software [47]. The fractal dimension is determined by an analysis of its perimeter \( \Omega \) versus its surface area \( S \). For a perfect circle we know that \( \Omega \sim S^{\frac{1}{2}} \) while for a straight line we expect \( \Omega \sim S^{1} \). Therefore the fractal dimension is defined as \( \Omega \sim S^{1-D_{f,\Omega}} \), where \( 1 \leq D_{f,\Omega} \leq 2 \). The results of a collection of fractal shapes observed on different sample preparations are shown in figure 4.9. Starting from epitaxial graphene with a hydrogenation time of 3 minutes at approximately 1000 K (4.9 a) we increase the treatment time to 30 minutes at a temperature of 900 K and 1000 K (4.9 b and c respectively). The ensemble of analysed fractals for each sample is shown in the second row (the green coloured perimeter highlights the fractal shapes). The fractals at the edge are not taken into account in the analysis. Also, small electron droplets (\( \leq 1000 \) nm\(^2\)) are not included in the averaging process. The third row shows the \( \log(\Omega) \) versus \( \log(S) \) plot, where we use the slope to extract the fractal dimension \( D_{f,\Omega} \). Increasing the hydrogen treatment time from 3 to 30 minutes significantly increases the size of the observed fractal shapes by the AFM (compare figure 4.9 a and c). This can be understood since the number of hydrogen atoms adsorbed is increased and hence the electron droplet volume grows. Lowering the temperature of the cracker decreases the amount cracked molecular hydrogen, therefore the amount of atomic hydrogen coming out of the capillary is smaller than at higher temperature. The latter explains the difference between the sizes of the electron droplets observed in figure 4.9 b and c.
Figure 4.9: AFM images and the corresponding fractals for each sample that has been analysed. The samples are fabricated for different hydrogen treatment duration and cracking temperature. The first row shows the AFM topography (700 nm $\times$ 700 nm), the second row the fractal shapes that are included in the fractal analysis and the third row the diagrams which are used to determine $D_{f,\Omega}$. 
For the sample shown in figure 4.9 a, we find a fractal dimension \( D_{f,\Omega} = 1.68 \pm 0.03 \), this result is in agreement with the previously calculated fractal dimension \( D_{f,box} = 1.69 \pm 0.05 \) and the simulation result \( D_f = 1.74 \pm 0.05 \). However, when the amount of fractals increases or the sizes of the fractals become larger, individual fractals start to 'feel' each other. In contrast to the 3 minute hydrogenated sample, the 30 minute hydrogenated samples, contain fractals which possibly interact with fractals its surrounding. The growth of the hydrogen cluster (and hence its induced electron droplet) could therefore be influenced by neighbouring fractals, hence the obtained fractal dimensions for figure 4.9 b and c deviate from the previous samples and the simulation. For figure 4.9 b and c we find a fractal dimension of \( D_{f,\Omega} = 1.58 \pm 0.02 \) and \( D_{f,\Omega} = 1.62 \pm 0.03 \) respectively. The lower \( D_{f,\Omega} \) can be attributed to the fact that the electron droplet cannot grow radially since the growth is obstructed by a neighbour droplet. As a result the perimeter of the fractal (at the side facing the neighbour fractal) is reduced, leading to a lower fractal dimension. Note that even at the case where the electron droplets start to fully cover the surface, the droplets do not fuse or merge. A small quasi one-dimension channel, dark region (river like shape), is left. This could indicate that the observed electron droplets (\( \geq 100 \text{ nm} \)) have reached their maximum size. Larger structures cannot be formed due to insufficient amount of screening by the remaining free electrons in the sample.

\[
\text{a) } g=0.1 \quad \text{b) } g=0.2 \quad \text{c) } g=0.5
\]

Figure 4.10: Simulation with a phenomenological growth model based on classical DLA. Now the growth of multiple electron droplets can be simulated. The density or coverage \( g \) is varied from 0.1 to 0.5. A strong similarity can be noticed between these simulations and the AFM topography shown in figure 4.9. The lattice size is 200 by 200 grid points \( (L=200) \) and the number of moves per particle is \( M_{\text{max}} = 5000 = 25L \). The sticking probability is chosen to be unity.

By slightly modifying the original DLA simulation, we are able to simulate the growth of multiple fractals (or viscous fingering of multiple electron droplets) at the same time. The major difference is the implemented periodic boundary conditions and new injection/walking rules for new particles (‘volume’). Since the interactions in the simulation are only with the nearest neighbour we now define a lattice of \((L+2) \times (L+2)\) in size, when a volume of the particle enters the edges of the simulation grid, it will be mirrored to the other side of the grid. The particles in the lattice now perform a random walk, but the maximum number of moves it can make is limited \( (M_{\text{max}}) \). If the particle does not find a neighbour to attach to, within \( M_{\text{max}} \) steps, the particle will get stuck on the grid after the last movement. Therefore it is possible in this model to create multiple
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‘nucleation’ centres which can grow separately. Note that all injected particles, \( N \), or volume stay within the simulation ‘box’. Also, similar to the original DLA, only the injected particle is allowed to move, once a particle is stuck to the grid it will remain during the simulation. Injection of new particles now occur at random sites on the grid which are still unoccupied. Hence the growth does not follow the rules of the classical DLA simulation as presented in the beginning of the chapter. The result of the modified DLA, allowing multiple droplets to grow is shown in figure 4.10. Here we investigated the morphology for different densities (defined as \( g \) which is the ratio between the number of electrons \( N \) over the lattice area \( L^2 \)). We clearly see a qualitative correspondence between the experiment, figure 4.9, and the simulation 4.10. The lattice size is 200 by 200 grid points, for the sticking probability we choose \( \sigma = 1 \), as in the previous section and \( M_{\text{max}} = 5000 = 25L \). Lowering the ‘diffusion’ parameter \( M_{\text{max}} \) results in a larger number of smaller electron droplets, while increasing \( M_{\text{max}} \) gives rise to larger viscous fingers. Therefore we believe that the formation of hydrogen clusters and therefore establishing the fractal shaped electron droplets is highly dependent on the possibility for hydrogen atoms to ‘diffuse’ and adsorb on the energetically favourable sites. If atomic diffusion is suppressed, we expect that only the hydrogen atoms arriving in the vicinity of the cluster will adsorb. This would imply that a large amount of incoming atomic hydrogen is required to establish the fractal shapes. It is recommended to use a mass spectrometer in future experiments to quantify the number of hydrogen atoms, to which the sample surface is exposed. In Appendix B we have included a result showing the fractal shape depending on the ‘diffusion’ length of each injected particle. In the next section we describe the viscous fingers from a different perspective, where we use a Monte Carlo simulation to simulate the shape of electron droplets in an inhomogeneous magnetic field. In contrary to the DLA simulations, the Monte Carlo simulation includes ‘physical’ parameters describing electron-electron interactions within an inhomogeneous magnetic field.
4.4 Monte Carlo simulation of the quantum Hall droplet

Instead of a kinetic approach of simulating electron droplets, we now move on to a Monte Carlo type of simulation for electron droplets. In continuation of the study of quantum Hall droplets (electrons submitted to strong magnetic fields $\leq 10T$) by Agam et al. and Hughes et al. [13][14], we present here results of a simplified Monte Carlo (MC) model based on the same physical principals as brought forward in the works of the aforementioned authors. The remaining question in the review of Hughes et al. was how the quantum hall droplet simulations actually describe the growth of DLA fractals. As we have presented in the previous sections the growth of DLA fractals is intimately connected to viscous fingers and Laplacian growth. In this section we show results of the electron droplets in the presence of randomly distributed magnetic fluxes. The inhomogeneous distribution of the flux quanta should represent the inhomogeneous distribution of hydrogen atoms on the epitaxial graphene surface. The result of the simulations gives us an idea of the fractal dimension, which we can compare with the DLA simulations and the experimentally observed fractal shapes. Note that the Monte Carlo simulation only gives a final (ground) state of the system. The growth itself is a non-equilibrium process which is not described within this Monte Carlo Simulation. In Appendix C we make an attempt to include the kinetics in the Monte Carlo simulation in the form a Kinetic Monte Carlo simulation (KMC). Those preliminary results can be used in future research to better understand the growth process of the electron droplets.

The core of our equilibrium Monte Carlo simulation is based on the following fundamental assumptions:

1. The quantum Hall droplet can be described by the Laughlin wavefunction:
   \[ \psi(z_1, \ldots, z_N) = \prod_{i<j} \left| z_i - z_j \right|^{1/2} \exp\left(-\frac{1}{4l^2} \sum_{j=1}^{N_e} \left| z_j \right|^2 \right). \]

2. The inhomogeneity in the pseudo-magnetic field can be simulated with an inhomogeneous distribution of magnetic fluxes (in opposite directions) which interact with the electrons as impurity charges.

Therefore we make use of the Ansatz that the total energy of the system can be written as:

\[ E = -\sum_{i<j} \ln \left| z_i - z_j \right| + \frac{1}{4l^2} \sum_{j=1}^{N_e} \left| z_j \right|^2 + \sum_{a=1}^{N_i} \sum_{j=1}^{N_e} \Phi \ln \left| z_j - z_a \right| \]

(4.9)

The first assumption is plausible if we consider the system to be in the quantum Hall regime, when electrons become localised due to a large magnetic field. In this regime the Laughlin wavefunction give a description of the ensemble of strongly correlated electrons. Since we believe the pseudo-magnetic fields in the order of hundreds of Tesla to be present in our hydrogenated epitaxial graphene system, we assume the Laughlin wavefunction to be fair as first order approximation to describe the electrons in our system. The Laughlin wavefunction can be interpreted as the product of single electron wavefunctions which are Gaussian in the lowest Landau level. In fact the educated guess from Laughlin is a combination of Slater determinants satisfying the Pauli principle ($\psi(z_i, z_j) = -\psi(z_j, z_i)$) [?]. We note here that spin degeneracies are not treated in this description. The second assumption can be understood since a magnetic flux can be generated by an orbiting electron, therefore we describe the source of magnetic fluxes as a localised impurity charge. The total number of electrons and the number of impurity charges are named $N_e$ and

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respectively. From the first two terms in the energy we recognise the Laughlin wave function. The first term describes the effective Coulomb interaction between two electrons, while the second term describes the energy gain due to magnetic screening. The third term describes the interaction of the electrons with impurity charges, which represent the magnetic flux quanta. From equation 4.9 we can see that the electron-flux line interaction has the same form as the electron-electron interaction (first term). These magnetic flux quanta can also be interpreted as tiny solenoids, generating flux lines, such that \( \Phi = 0, \pm 1, \pm 2, \ldots \). The sign of \( \Phi \) determines whether the flux quanta point upwards or downwards, this reflects the two possible sublattices the hydrogen atoms can reside on. The position of the electrons and impurity charges (or solenoids) are described by the complex variable \( z_i \). The amount of flux quanta penetrating through surface (locally) is parameterised with \( \Phi \). To obtain equation 4.9 we make use of the fact that \( |\psi|^2 \sim \exp(-\beta U) \) and \( \psi(z_1, \ldots, z_N) = \exp\left[ \sum_{i<j} \ln|z_i - z_j| + \frac{1}{4\pi^2} \sum_{j=1}^{N_s} |z_j|^2 \right] \) and define \( \beta = 1/2 \). The positions of the charge impurities do no change during the simulation, only the electrons are allowed to move.

In the simulation we define a grid of \( L \times L \) lattice points, where we place \( N_e \) electrons and \( N_s \) charge impurities or solenoids at the start of the simulation. The electrons are positioned randomly on the grid and the position of the flux quanta are fixed and can be placed in a random or ordered fashion. The distribution of the electrons should give insight to the charge distribution in the inhomogeneous pseudo-magnetic field (simulated by the inhomogeneous distribution of the solenoids/charge impurities). For the Monte Carlo simulation we make use of the Metropolis algorithm [48]. In each simulation step we allow one electron to move one lattice unit in a random direction, by calculating the change in energy \( \Delta E \), we accept or reject this step. If \( \Delta E \leq 0 \) we accept the movement, while in the case \( \Delta E > 0 \) we invoke an acceptance rate of 0.5 [49].

Figure 4.11: a) The electron density distribution shows the circular shaped electron droplet resulting from the Monte Carlo simulation. b) The corresponding internal energy of the system. An equilibrium is reached within the 30000 simulation steps. The number of electrons is 100 and no magnetic fluxed are present in this simulation. The simulation grid is 50 \( \times \) 50 lattice points on a square lattice.

For \( N_e = 100, N_s = 0 \) and assuming \( l_b = 1 \) we expect to observe a circular shaped droplet [13],

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because the magnetic screening keeps the electrons together. The result of the simulation is shown in figure 4.11. We clearly observe the circular shape in the electron density distribution as expected. Since the electrons are initially randomly distributed over the grid, the initial energy is relatively high. As the amount of steps increases, the energy of the system decreases and eventually enters an equilibrium state. This equilibrium (or the ground state) is reached after approximately 10000 simulation steps. The amount of electrons and solenoids significantly influences the computation time, because each electron-electron and electron-flux interaction is calculated separately. Therefore we use a relatively small simulation box and a small ensemble of electrons to obtain only the qualitative behaviour. For a more detailed simulation we suggest to use a larger ensemble of electrons. The condition $l_b = 1$ can be satisfied in the high field limit, for a magnetic field of 300 T we find that the magnetic length $l_b \sim 1$nm.

To observe the fingering effect we add the flux quanta (solenoids) to the grid. By placing the flux lines in a triangular fashion we firstly reproduce similar results as presented by Hughes et al. [13], see figure 4.12. Note that the electrons cannot occupy the same sites as the pinned flux lines. As can be seen from figure 4.12 most electrons tend to stay in the middle, while the attractive solenoids are responsible for local electron accumulation. Decreasing the strength of the solenoids will result into a more circular shape of the electron distribution as shown in figure 4.11. On the other hand, increasing the strength of the solenoids will eventually break the droplet apart in three smaller droplets centred around the three solenoids.

Figure 4.12: a) The electron density distribution shows a triangular shape. The flux quanta act as positively charged charge impurities. b) The map indicating the positions of the solenoids (the blue dots), the strength here is $\Phi = -50$. c) The corresponding internal energy of the system. An equilibrium is reached within the 30000 simulation steps. The number of electrons is 100 in this simulation. The simulation grid is $50 \times 50$ lattice points.

Now by introducing a larger ensemble of electrons and a larger number of coils randomly distributed on the surface, we simulate fractal shapes of the electron droplet as we have observed experimentally. To estimate the fractal dimension $D_f$ of the obtained shapes we make use of the scaling relation introduced in section 5.3 [42]. There we found that the number of electrons (or surface area) is proportional to $R^{D_f}$, where $R$ is the radius of the fractal. An example of the electron distribution in an inhomogeneous field of flux quanta is shown in figure 4.13. Here we have used 500 particles and 500 randomly distributed solenoids with $\Phi = \pm 10$, furthermore the lattice size
here is increased to $100 \times 100$ lattice points. The increased number of electrons is required to determine the fractal dimension more accurately. The solenoids, now have both negative and positive sign, representing the attractive and repulsive electron-flux interactions respectively. Whether the solenoid is acting as an attractive or repulsive charge impurity depends in our real system on the adsorption of hydrogen atoms on one or the other sub lattice of the epitaxial graphene. If both sub lattices are equally occupied by hydrogen atoms, the net pseudo-magnetic field should equal to zero. As a result we take in our simulation that the sum of the fluxes, or solenoids, equals zero. So 250 solenoids have a strength $\Phi = -10$ while the other 250 solenoids are $\Phi = 10$. From figure 4.13 we can clearly see the viscous fingering behaviour as we have seen in the beginning of the chapter. The electrons initially prefer to stay clumped and form a circular droplet, however the inhomogeneous distribution of the solenoids tends to break the droplet apart, resulting in the fractal-like shape.

Figure 4.13: a) The distribution of 500 electrons on a square lattice in an inhomogeneous magnetic field due to the presence of 500 randomly distributed solenoids. The yellow tones correspond to higher electron densities while the blue tones reflect lower densities. b) The map illustrates the positions of the 500 solenoids. The yellow and blue dots correspond to the solenoids with strength $\Phi = 10$ and $\Phi = -10$ respectively. c) The corresponding internal energy of the system as the number of simulation steps increases. An equilibrium is reached within the 40000 simulation steps. The simulation grid is a square lattice of $100 \times 100$ lattice points.

Analogous to figure 4.5 the area of the fractal (or the number of electrons) $S$ is shown as a function of its radius for the Monte Carlo simulated electron droplets in figure 4.14. Two electron droplets are shown, each containing 500 electrons, however the underlying distribution of flux quanta is different. Hence the distribution of electrons is different in the two images. It’s interesting that the Monte Carlo simulations indeed give quantitatively and qualitatively similar results as DLA, as shortly mentioned by Hughes et al. [13]. We obtain a fractal dimension, averaged over 6 droplets consisting of 500 electrons, which is $D_f = 1.68 \pm 0.04$. This result is another indication (in addition to the DLA simulations) that the fractal shapes observed by the AFM of hydrogenated epitaxial graphene could indeed be a viscous fingered electron droplet. The electrons arrange themselves in such a shape that the energy, given in equation 4.9, is minimised. Hence only the final state is obtained with the Monte Carlo simulation and the growth of the droplet itself is not described. Therefore the interpretation of the shown result should be made carefully. Since the growth of the
droplet, as described by DLA or Laplacian growth, is a non-equilibrium process we could question whether the Monte Carlo simulation is accurate at all. The answer will mainly depend on the time scale of the events when droplet is growing. For the Boltzmann weights to be valid, we have assumed that in each simulation step, the particles are in a local equilibrium. As suggested in the beginning of this section, a kinetic Monte Carlo simulation could offer insight into the growth of the electron droplet within a Laughlin-like description of the electrons, equation 4.9. Preliminary results on the kinetic Monte Carlo simulation are shown in Appendix C.

Figure 4.14: The fractal dimension $D_f$ extracted from a linear fit of $\ln(S)$ versus $\ln(R_G)$. The inset images in the upper left and lower right corner show the shape of the corresponding fractal ($N = 500$). The fingering of the two electron droplets are different since the distribution of flux quanta is randomised. We find similar values of $D_f$ as with the fractal shapes obtained by DLA and the experimental results.

To conclude, we have shown in this chapter that the fractal like shapes observed with the atomic force microscope of hydrogenated epitaxial graphene are closely related to so-called viscous fingers of electron droplets (see figure 4.9). The viscous fingering should take place because of the inhomogeneous pseudo-magnetic generated by the adsorbed hydrogen atoms. We started by presenting the analogy between viscous fingers and diffusion limited aggregates. We compared the experimentally observed fractals with the simulated DLA fractals, because of its analogy with Laplacian growth and the formation of viscous fingers of an electron droplet. This phenomenological approach indicated that the observed fractals by AFM are of the same class as the DLA fractals and hence the viscous fingers. Furthermore, we continued with a more sophisticated Monte Carlo simulation, describing the ensemble of electrons as an electron droplet in an inhomogeneous pseudo-
magnetic field. The results support the findings presented by Agam et al. and Hughes et al. and show both quantitative and qualitative agreement with viscous fingers obtained by DLA\textsuperscript{[13][14]}. All our simulation results support the proposed idea that the observed fractal shapes on hydrogenated epitaxial graphene show the charge/electron distribution as a result of an inhomogeneous pseudo-magnetic field induced by the adsorbed hydrogen atoms. Furthermore, our findings give answer to the question brought forward by Hughes et al.\textsuperscript{[13]}: Can equilibrium Monte Carlo methods using a random potential be used to efficiently simulate non-equilibrium growth processes such as DLA; in other words, what can the quantum Hall effect tell us about DLA? A more detailed discussion on this matter is presented in appendix D, in a draft version of an article.
5. The quantum Hall effect (QHE) in hydrogenated epitaxial graphene

When at sufficiently low temperature an electron gas is confined in two dimensions, for example at the interface between two semiconductors (GaAs-AlGaAs) or graphene, a new state of matter can arise when a perpendicular magnetic field is applied \[50\]. In this state, the so-called quantum Hall state, the transport properties of charge carriers are quantised. This is called the integer quantum Hall effect (IQHE) and can be explained within the semi-classical picture of uncorrelated orbiting electrons\[51\][15][16]. A much more interesting effect sets in when electron-electron interactions start to become more dominant. In this regime, also called the fractional quantum Hall regime, the electrons are strongly correlated and show exotic physical phenomena such as charge fractionalisation. In this chapter we focus on the transport properties and we will show how the quantum Hall effect manifests in clean and hydrogenated epitaxial graphene.

5.1 An introduction to the quantum Hall effect

In 1980 von Klitzing et al. measured the quantisation of conductance in a 2 dimensional electron gas (2 DEG) at low temperatures (\(\sim 1.5\) K) and high magnetic fields (\(\sim 20\) T) \[52\]. For the experiment they prepared a Si MOSFET and confined the 2 DEG at the interface between SiO2 and Si. They found the universal quantisation of conductance \(\sigma_H\), given by:

\[
\sigma_H = n \frac{e^2}{h},
\]

where \(n\) is an integer number, \(e\) is the elementary charge and \(h\) is Planck’s constant. Two years after the discovery of the integer QHE by von Klitzing, experiments at even higher magnetic field strength and lower temperatures were carried out by Tsui et al. \[50\]. They found that the conductance is a fractional multiple of \(e^2/h\) (\(h/e^2 \approx 25812.8\)Ω, also called the Von Klitzing constant), revealing the existence of fractionally charged excitations\[53\]. While the integer QHE can be simply understood by edge currents and a single electron picture (which will be discussed in more detail in this section) the fractional effect emerges from strong electron-electron correlations in the 2 DEG. In this correlated system the electrons are described by collective excitations of the Laughlin ground state \[54\][55].

To understand the integer QHE we firstly start with a semi-classical description of electrons moving in a plane when exposed to a magnetic field perpendicular to that plane. The Hamiltonian of this system is then of the form:
5.1. AN INTRODUCTION TO THE QUANTUM HALL EFFECT

\[ H = \frac{1}{2m_e}(\hat{p} - q\hat{A}/c)^2. \]  

(5.2)

Here \( m \) is the electron mass, \( q \) the charge of the electron, \( c \) the speed of light, \( \hat{p} \) the momentum operator and \( \hat{A} \) the vector potential operator. When the magnetic field is directed in the z-direction with magnitude \( B_0 \), \( \mathbf{B} = B_0 \mathbf{z} \), the vector potential can be chosen such that we obtain the Hamiltonian of a quantum harmonic oscillator with a shift in the x-coordinate. The solutions of the Hamiltonian are the so-called Landau levels of a 2 DEG and the energy of each of the Landau levels is (equivalent to a harmonic oscillator) given by:

\[ E_n = \hbar \omega_c (n + \frac{1}{2}). \]  

(5.3)

Where \( n \) is an integer number (\( n = 0, 1, 2, ... \)) and \( \omega_c \) is the cyclotron frequency defined as \( \omega_c = eB_0/m_e \). Furthermore we can define a length scale which reflects the electron in the orbiting motion, which we call the magnetic length \( l_B = \sqrt{\hbar/eB_0} \). For \( B_0 = 1 \) T the typical energy is then in the order of several meV, in the case of GaAs \[56\], and the magnetic length is approximately 26 nm. As a result, the quantum Hall effect is usually only observed at low temperatures (~ 4 K), because at high temperatures the thermal energy \( k_B T \) will be larger than \( \hbar \omega_c \) and suppress the QHE.

An example of a quantum Hall measurement in a conventional semiconductor based 2DEG is shown in figure 5.1. The magnetotransport measurements are usually carried out in a Hall bar geometry, see figure 5.1a. The longitudinal resistance \( R_{xx} \) is obtained by measuring the potential difference along the applied current direction, this is the magnetoresistance. In the Hall bar geometry the magnetoresistance is defined as \( R_{xx} = \alpha V_{xx}/I_{xx} \), where \( \alpha \) is a geometrical factor determined by the ratio between the width and the length of the Hall bar. On the other hand, because the perpendicular magnetic field is responsible for a Lorenz force perpendicular to the current, which deflects the charge carriers in the system to the edges. Charge carriers will accumulate at the edges and a potential difference can be measured perpendicular to the current. We therefore define the Hall resistance \( R_{xy} = V_{xy}/I_{xx} = B_0 n_e e/e \), where \( n_e \) is the (sheet) carrier density. Note here that charge carriers will accumulate at the opposite side when the direction of the magnetic field is reversed, thus the Hall resistance switches its sign when the magnetic field is reversed.

In the case of graphene, where the electrons are considered to be massless and behave as relativistic particles with their Fermi velocity given by \( v_F \approx 10^6 \) m/s, the energy gaps can be much larger \[57\][2]. In addition, since graphene has two valleys (see chapter 2), the energy spectrum of the Landau level excitations is different from equation 5.3. The energy quantisation of pristine graphene is given by \[58\]:

\[ E_n = v_F \sqrt{2\hbar nB_0}. \]  

(5.4)

We can see from the above equation that the energy spacing between two Landau levels in graphene is not equidistant as in GaAs/AlGaAs 2D electron gases (equation 5.3, depicted in figure 5.1c). The other interesting feature that we can observe for graphene is that it contains a zero energy state, \( E_0 = 0 \). This explains the localised states near the Fermi level, observed in the band structure calculations of hydrogenated epitaxial graphene, figure 2.8. Now to intuitively understand the magnetotransport result which is shown in figure 5.1b, and 5.1d, we take a look at what happens to the electron density of states (DOS) and the energy spectrum in real space. Figure 5.2 shows the energy of the electron states across the sample in the case of graphene. At the edges of the graphene sample the energy levels rise due to the spatial confinement, while in the bulk the energy
5.1. AN INTRODUCTION TO THE QUANTUM HALL EFFECT

Figure 5.1: a) Illustration of the Hall bar, a commonly used geometry to perform magnetotransport measurements in 2DEG. The magnetic field is applied perpendicular to the 2DEG. b) The measured longitudinal and transversal resistance, given by \( R_{xx} \) and \( R_{xy} \) respectively, in a conventional semiconductor based 2D electron system. c) A comparison between the electron density of states for graphene and a conventional 2D system. d) The longitudinal \( R_{xx} \) and transversal \( R_{xy} \) resistances measured in graphene. Adapted from Janssen et al. [53].

states are given by the Landau levels, equation 5.4. By increasing the magnetic field the energy gap between the Landau levels will increase and move through the Fermi level. When the Fermi level lies in between two Landau levels, we can see that the conduction is then mainly carried by the electrons near the edges. The bulk behaves as an insulator. The states near the edges, often in literature referred to as ‘edge states’ [59], contain electrons similar to electrons in quasi one-dimensional channels. Hence the transport of these electrons close to the edge are nearly ballistic and backscattering is suppressed. Thus we expect a drop in the resistance when the Fermi level is aligned in between the Landau levels. In the case the Fermi level is aligned or close to \( E_n \) the electrons in the edge can scatter into the bulk states, hence transport will not be ballistically anymore and the resistance will rise. This behaviour in the magnetoresistance, \( R_{xx} \), can be seen in figures 5.1 and 5.2. We also see in figure 5.1 and 5.2 that the Landau levels are not infinitely sharp at \( E_n \), the broadening of the peaks in the DOS is caused by defects in the material.
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Figure 5.2: Illustration of the energy spectrum in real space (left) and the density of states (right) when a magnetic field is applied perpendicular to the graphene surface. Note that the energy of the electron states increases near the edges of the sample. The blue line indicates the Fermi energy, which lies in between the $n = 0$ and $n = 1$ Landau level.

To understand the steps and plateaus observed in the transversal (or Hall) resistance $R_{xy}$ we look at the number of filled Landau levels. As the electrons occupy the Landau levels, which are highly degenerate and localised states, they undergo a cyclotron motion and enclose a quantum of magnetic flux $\Phi_0 = \hbar/e$. Therefore we can define $n_{LL} = B_0/\Phi_0$ as the density of localised electrons in cyclotron orbits per unit area. The ratio between the electron sheet density $n_e$ and $n_{LL}$ is called the filling factor $\nu$:

$$\nu = n_e/n_{LL}. \quad (5.5)$$

We can see now if $n_e$ is an integer multiple of $n_{LL}$ the conductance is quantised. As a result the Hall resistance can be written as $R_{xy} = h/\nu e^2$. Each time a Landau level crosses the Fermi level, a step can be observed in $R_{xy}$. One can see in figure [5.1] that the filling factor $\nu$ for graphene differs from the conventional 2DEG. This is attributed to the fact that graphene has fourfold degenerate states, originating from the two valleys $K$ and $K'$ and the two-fold degenerate spin up/down states. Hence the filling factor for graphene is quantised as follows:

$$\nu = (4j + 2), \quad (5.6)$$

where $j = 0, 1, 2, ...$ is an integer number. Note that for $j = 0$ the filling factor $\nu = 2$, which implies that the zero energy state is only two-fold degenerate. By explicitly solving the Hamiltonian, invoking a linearisation around the Dirac-point, it can be shown that the zero energy state is only present in one of the two valleys of graphene [58][59]. Note here that the Zeeman splitting is in the order of meV, much smaller than the energy gaps of the Landau levels. In combination with the broadening of the Landau levels the Zeeman splitting can not be easily observed. An intriguing question now arises: what is the interplay between the real magnetic field and the intrinsic pseudo-magnetic field in hydrogenated epitaxial graphene? To answer this question we take a closer look
at the effect of the pseudo-magnetic field on the electronic structure. Guinea et al. have shown that the pseudo-magnetic field acts differently in the two valleys of graphene. The effective magnetic field is in opposite directions depending whether the electrons are in the K or K' valley. As a result, when we apply a real magnetic field, the effective magnetic field will be different in the K and K' point. This could lift the fourfold degeneracy as shown with scanning tunnelling spectroscopy by Li et al. [60]. One of the purposes of our magnetotransport measurement is to see the lift of the fourfold degeneracy by the appearance of Hall plateaus at even numbered filling factors \((2j+2)\).

A second goal of the transport measurements is to observe fractional or non-integer filling factors. The above simplified description of electrons submitted to a magnetic field only holds for the integer QHE. For non-integer filling factors the mechanism can not be understood by the single electron picture. A well known example of a fractional QHE state is the so-called \(\nu = 1/3\) Laughlin state. The filling factor \(\nu = 1/3\) implies that each electron captures exactly 3 flux quanta in its ground state. In the case the electrons occupy one third of the lowest Landau level, which can be observed as a plateau in the Hall resistance at \(1/\nu \cdot h/e^2 \approx 75\ \text{k}\Omega\). These fractional excitations are carried by strong electron correlation effects. Because the theoretical results predict a strong effective magnetic field (\(\geq 300\ \text{T}\)) we believe that hydrogenated epitaxial graphene is a promising candidate for showing strongly electron correlated behaviour [12]. Hence the main purpose of our magnetotransport experiments on the hydrogenated epitaxial graphene is to observe these fractional excitations. By applying a real magnetic field we aim to tune the filling factor \(\nu\) and to find fractional excitations within the (lowest) Landau level.
5.2 Experimental: magnetotransport measurements

The transport properties of hydrogenated epitaxial graphene are investigated with magnetotransport measurements in a Van der Pauw geometry, shown in figure 5.3. The electrical contacts between the sample holder (an LLC chip carrier) and the graphene sample are manually fabricated with 200 \( \mu \text{m} \) (diameter) copper wire and droplets (\( \leq 500 \mu \text{m} \)) of silver paste, figure 5.3b. All the experimental results shown in this chapter are measured at 4.2 K, unless specified otherwise. Before we insert the sample into the cryostat we pump the sample space (chamber in which the sample is located) to \( 10^{-5} \text{ mbar} \). We then cool the sample down to approximately 200 K in 2 hours. This slow cool down step prevents the electrical contacts from breaking or disconnecting from the graphene sample due to thermal contraction. When 200 K is reached, we fill the sample space with helium gas (which serves as contact gas) to quickly cool down the sample to 4.2 K within 5 minutes. The external magnetic field is generated by a supermagnetic coil, with a coercivity of approximately 30 mT. The coil can produce a maximum field of 15 T. Furthermore we sweep the field at 1 T/min from positive to negative field or vice versa. The applied alternating current has an amplitude of 100 nA and a frequency of 11.73 Hz to avoid any interferences with surrounding electrical devices. Note the the Van der Pauw geometry is slightly different from the Hall bar drawn in figure 5.1. The current can be applied over different contacts and the longitudinal and transversal resistances are obtained by measuring the parallel and perpendicular voltages at the corners or sides of the sample.

Figure 5.3: a) Van der Pauw configuration, the contacts are placed on the corners and at the middle of the four sides of the sample. The red arrow indicates the direction of the applied current. The voltage can be measured parallel or perpendicular to the applied current. b) The sample is glued to the sample holder and mounted to the Hall probe in between the two screws.
5.2. EXPERIMENTAL: MAGNETOTRANSPORT MEASUREMENTS

5.2.1 Clean epitaxial graphene

The clean epitaxial graphene, see figure 2.4 for the AFM image, is measured to obtain an indication of the carrier concentration and the mobility of the sample. However, because of our large graphene sample size (sample dimensions are 4 mm by 4 mm), compared to the typical sizes of Hall bars (tens of microns), we observe so-called mixing of edge channels. This could possibly lead to a less accurate measurement in the magnetotransport since the path of the current through the sample is ill-defined on such a large sample. The latter is shown in figure 5.4 where $V_{xx}$ is measured as a function of the magnetic field for a clean epitaxial graphene sample. In this case we expect that $V_{xx}$ is symmetric in $B = 0$, since the magnetoresistance only depends on the magnitude of the field and not its direction. Nevertheless, an antisymmetric contribution in $V_{xx}$ can be seen in figure 5.4. Because the Hall resistance $R_{xy}$ is antisymmetric in $B = 0$, we believe that the observed antisymmetric contribution in $V_{xx}$ reveals the presence of $V_{xy}$ in the longitudinal measurement. No clear difference can be observed in the forward and backward sweep, only the hysteresis of the supermagnetic coil itself is visible at low fields ($\sim 30$ mT), see inset of figure 5.4. The origin of the peak near zero field will be discussed later on.

![Figure 5.4: The voltage $V_{xx}$ measured as a function of the magnetic field $B$ for two sweeps, from positive to negative field and vice versa. The inset shows a zoom-in for $-0.5 \ T \leq B \leq 0.5 \ T$. The peak observed close to zero magnetic field can be attributed to the weak localisation of electrons.](image)

To separate the mixing of $V_{xx}$ and $V_{xy}$, we apply a symmetrisation in the raw data, to extract the symmetric and antisymmetric components of the raw signal. The symmetrisation is applied to the result shown in figure 5.5, an example of $R_{xx}$ and $R_{xy}$ for the clean epitaxial graphene sample. From figure 5.5 we can distinguish two regimes in the magnetotransport: 1) for $B \leq 1T$ the classical regime, where the Hall resistance behaves linear with the magnetic field strength. From this region we extract the sheet carrier density $n_e$ and the mobility $\mu$. We find here for this clean...
epitaxial graphene sample $n_e \approx 1.8 \cdot 10^{11}$ cm$^{-2}$ and $\mu \approx 2.9 \cdot 10^4$ cm$^2$/Vs. The carrier density (the carriers are electrons) is lower than expected ($\sim 10^{13}$). This deviation could be caused by the presence of water on the surface [22], since the sample has been exposed to air between preparation and measurement. For $B > 1$ T we find the quantum Hall regime, where we observe a weak inflection in the slope of $R_{xy}$ and a clear plateau starting from $B \approx 4$ T. The plateau saturates at approximately 11.5 kΩ which presumably corresponds to the $n = 0$ ($\nu = 2$) plateau for graphene. Where the theory, equation 5.6, predicts the $\nu = 2$ plateau to establish at $B = 1/\nu \cdot \frac{2 e}{h} \approx 3.7$ T. The small deviation from the expected value of approximately 12.5 kΩ can be explained if we consider the effect of mixing. Also the possibility of currents running in bilayer stripes along the terrace edges of the epitaxial graphene could influence the measurement. This has been shown by Chua et al. where bilayer graphene patches acted as metallic shortcuts between the two edge channels [61]. The latter allows electrons to scatter from one to another side, which suppresses the ballistic transport and the quantum Hall effect. The inflection in the slope is located closely to 4 kΩ, where we expect to observe the plateau $n = 1$ ($\nu = 6$). This plateau, and also the plateaus corresponding to the higher Landau levels ($n \leq 2$) are not clearly visible. This is possibly related to the broadening of the Landau levels due to defects in the epitaxial graphene. In fact, higher Landau levels has not been observed yet in epitaxial graphene on SiC [62]. Therefore the overall behaviour for the Hall resistance is in agreement with experimental and theoretical results obtained for pristine and epitaxial graphene [53][63][64][65]. The magnetoresistance $R_{xx}$ shows however several peculiar features. First of all we observe a small peak close to $B = 0$, this is related to the weak localisation, which is a quantum interference phenomenon for conductive samples at low temperatures. In the case of graphene, the intervalley scattering of electrons enhances the backscattering (as a result of constructive interference) at zero magnetic field [66][67]. By applying a (small) magnetic field, the quantum interference effect can be lifted. This causes the drop in the magnetoresistance as observed in figure 5.5. An extensive discussion on the weak localisation is presented at the end of this chapter.

Secondly we see in figure 5.5 that $R_{xx}$ does not reach zero resistance when the Hall resistance shows a plateau. The resistance not dropping to zero indicates that the transport is not dissipationless. This observation can be explained in terms of the aforementioned mixing between the edge channels and the presence of bilayer epitaxial graphene. A last note we place on the effect of the step edges of epitaxial graphene. It has been shown by Schumann et al. that the direction of the step edges can significantly affect the magnetotransport measurements [63]. Electron transport perpendicular to the step edges could introduce scattering channels and suppress the visibility of quantum oscillations (Shubnikov-de Haas) at low magnetic fields. This possibly explains why $R_{xx}$ in figure 5.5 does not show any oscillations at low fields. It is recommended for future research to perform the transport measurements in a Hall bar geometry to control more accurately the injected current. Also it is of great importance to position the Hall bar parallel and between two step edges to avoid additional scattering effects at the edges of the terraces of the graphene (see figure 2.4).
5.2. EXPERIMENTAL: MAGNETOTRANSPORT MEASUREMENTS

Figure 5.5: The longitudinal $R_{xx}$ (black) and transversal $R_{xy}$ (red) resistance measured for clean epitaxial graphene, the magnetic field sweeps from 15 T to -15 T. For $R_{xy}$ we can clearly see the $\nu = 2$ plateau, a small inflection in the slope near 1 T probably reveals the presence of the $\nu = 6$ plateau.

5.2.2 Hydrogenated epitaxial graphene

The magnetotransport results for three different samples with different coverage of atomic hydrogen is shown in figure 5.6; the results are obtained in the same Van der Pauw geometry as for the clean sample. By increasing the dose of atomic hydrogen we see different morphologies appearing in the AFM, from tiny clusters ($\sim 20 \text{ nm}$) to fractal shapes ($\sim 100 \text{ nm}$). The first observation we make is that the slope of $R_{xy}$ of the hydrogenated graphene samples have a different sign compared to the clean samples. The negative slope in the Hall resistance suggests that the system becomes p-doped after the hydrogen treatment. Furthermore, by increasing the dose of hydrogen we see that the p-doping becomes larger. For the smallest dose, 5.6a), the hole density is $2.5 \times 10^{11} \text{ cm}^{-2}$ while at the highest dose we find $1.4 \times 10^{12} \text{ cm}^{-2}$. The result of this experiment demonstrates that the hydrogen adsorbates act as p-dopants on the epitaxial graphene layer, which is in agreement with our photo-emission experiments on hydrogenated graphene, presented in chapter 2. Furthermore it also supports the experimental work presented by Bostwick et al. [30][68] where they concluded that the hydrogen atoms saturate the $p_z$ orbitals and remove ‘free’ electrons from the graphene.

A significant rise in the longitudinal resistance is measured for the low and high coverage samples (figure 5.6k and c)), which can be understood since the presence of the hydrogen atoms will increase the amount of defect scattering [51]. Furthermore, looking at the band structure calculations shown in the introductory chapter (figure 2.8), we expect the opening of a band gap and vanishing of the linear dispersion of graphene. In the band gap we believe to get nearly dispersionless bands and hence strong electron localisation. The conduction is likely to be carried by the localised states.
near the Fermi level. Therefore the resistance of the hydrogenated epitaxial graphene is expected to increase. For the low and high hydrogen coverage samples we observe a tenfold increase in the longitudinal resistance compared to the clean epitaxial graphene sample. This in contrast to the intermediate covered sample, figure 5.6b), where we see no significant change in the resistance with respect to the clean sample. This could be explained considering that the hydrogen distribution is not totally homogeneous across the sample surface. As a consequence the conductance can be strongly influenced by non-hydrogenated graphene areas. The AFM pictures are taken near the centre of the 4 mm by 4 mm sample, at the edges however it is still possible that there are clean epitaxial graphene patches. This makes a quantitative study of the magnetoresistance as a function of hydrogen coverage challenging. As mentioned before, a more accurate and preferred experiment could be realised by fabricating Hall bars on the epitaxial graphene terraces.

Regarding the ferromagnetic properties of hydrogenated epitaxial graphene, no significant differences in the transport measurement has been observed for the forward and backward sweep in the magnetic field. This could be related to the relatively small net magnetisation of the epitaxial graphene sample [10]. To observe the ferromagnetic behaviour it is favoured to perform spin-dependent transport measurements, for example by utilising ferromagnetic contacts to inject spin polarised currents.

For $R_{xy}$ we observe well established plateaus for the low coverage sample, unlike the intermediate and high hydrogen coverage graphene. This can be understood if we call upon equation 5.6 where we see that the filling of the Landau levels depends on the carrier density. For increasing carrier density a larger magnetic field is required to reach the lower Landau levels (or equivalently lower filling factors). This explains why the $\nu = 2$ plateaus are possibly not well evolved for the intermediate and high coverage sample. A close examination of $R_{xy}$ for the high coverage sample reveals a discontinuity at $B = 0$, this is an numerical artefact arising from the antisymmetrisation of the dataset. Now if we recall the DFT calculations for hydrogenated epitaxial graphene, a logical question arises: why do we see the $\nu = 2$ plateau at all, if we may believe the band structure calculations shown in figure 2.8. The theoretical results predict a partial filling of the zeroth Landau level, hence the initial Hall resistance at zero field is expected to be non-zero. Turning on the external magnetic field should allow us to tune the filling within the Landau level. The observed similarities between hydrogenated and clean epitaxial graphene indicates however that this is not the case. An explanation could be that the hydrogen atoms in reality are not arranged in the periodic fashion as assumed in the theoretical calculation. Especially in the case of the high coverage sample it is plausible that not all the hydrogen atoms reside on the preferential sites on the epitaxial graphene surface. Moreover due to the presence of defects and step edges the theoretical model does not fully reflect the real sample. By decreasing the dimensions of the sample or fabricating Hall bar devices (in the order of 4 $\mu$m by 20 $\mu$m) on the graphene terraces we expect to obtain more conclusive results. From the magnetotransport results presented in figure 5.6 we can not conclude yet that we observe any exotic fractional excitations as described in the beginning of the chapter.
5.2. EXPERIMENTAL: MAGNETOTRANSPORT MEASUREMENTS

Figure 5.6: The obtained resistances of $R_{xx}$ and $R_{xy}$ of three different hydrogenated epitaxial samples shown in the left side figures. On the right side the corresponding AFM topography images of 700 nm × 700 nm. The sizes of the clusters and fractal shapes vary from approximately 20 nm up to 150 nm.
Although the Hall resistance does not show any conclusive results, we do notice an interesting feature in $R_{xx}$: the peak shape close to $B = 0$ becomes more pronounced as the hydrogen coverage increases. In the case of the high hydrogen coverage figure 5.6), the peak dominates in the measured magnetoresistance $R_{xx}$. Similar behaviour in the magnetoresistance has been observed for (highly) disordered epitaxial graphene [51] [69] [64]. The amount of disorder can be defined by a disorder parameter (Ioffe-Regel) defined as $k_F \lambda$. For low disorder systems the mean free path $\lambda$ is large compared to the Fermi wavelength $\lambda_F = 2\pi/k_F$, while strongly disordered systems show typically $k_F \lambda \ll 1$ which indicates an insulating system. The disorder parameter can be estimated by $k_F \lambda \approx h/2e^2 \cdot \frac{1}{R_{xx}(B=0)}$ [51]. As a result we find for the clean sample $k_F \lambda \approx 10$ and for the low and high hydrogen coverage respectively $k_F \lambda \approx 1$ and $k_F \lambda \approx 0.2$. To illustrate the difference between the low and high coverage sample, figures 5.6 a) and c), we look at the resistance at zero field $R_{xx}(B = 0)$ as a function of the temperature, shown in figure 5.7. We clearly see that the highly covered sample shows a insulating behaviour ($dR/dT < 0$) while the low coverage sample displays metallic-like temperature dependence in the resistance. The insulating behaviour is also expected since the hydrogen adsorbates open a bandgap. The low coverage sample is less disordered and possibly still contains clean patches of epitaxial graphene which explains the metallic behaviour.

The quantum interference effect that leads to the observation of the weak localisation peak can be understood as follows: in a conducting sample the electrons can form enclosed paths as illustrated in figure 5.8. This can result in constructive interference of the electrons and enhance the resistance at zero magnetic field. When a small magnetic field is applied, the electrons catch a phase factor which destroys the interference effects. The latter results in a drop in the resistance. An important requirement to observe this effect is that the sample behaves metallic, which is the case for the low coverage sample. A natural question that arises here is why we observe the quantum interference at all, if we assume the electrons in hydrogenated epitaxial graphene intrinsically feel an effective magnetic field. It has been theoretically shown for strained graphene that the weak localisation is suppressed by the presence of pseudo-magnetic fields [70]. The fact that we do observe the weak localisation in hydrogenated graphene contradicts with the picture of the hydrogen atoms inducing the pseudo-magnetic field when they adsorb on one particular sublattice as shown in figure 2.7. Therefore this result indicates that the sample also consists of non-hydrogenated graphene areas which we also observe in the AFM figures. We suggest for future research to study the weak localisation in more detail in the Hall bar geometry to exclude artefacts due to the large sample size. For the high coverage sample the negative magnetoresistance can be understood as an insulator to quantum Hall transition [51]. In this transition two length scales are in competition, being the magnetic length $l_b$ and typical distance between two hydrogen adsorbates $l_H$. $l_H$ we expect to be approximately 2 nm, recalling the presence of the preferential sites due the silicon dangling bonds. In the limit of low magnetic field the defects dominate the transport $l_H \ll l_b$ and the quantum Hall effect is suppressed. In the limit of high magnetic field $l_b \ll l_H$ the electrons are localised in ‘between’ the defects and the quantum Hall effect restores, hence the drop in the magnetoresistance can be explained.

It would be extremely interesting to continue the magnetotransport experiments in the Hall bar geometry placed on a single terrace. By reducing the sample size the experiment becomes better defined. We believe that those experiment could give a clear answer whether the hydrogenated epitaxial graphene system is indeed a (fractional) quantum Hall system at zero magnetic field.
5.2. EXPERIMENTAL: MAGNETOTRANSPORT MEASUREMENTS

Figure 5.7: The longitudinal resistance measured at zero magnetic field at different temperatures for the low and high hydrogen coverage sample. We clearly observe a metallic and insulating behaviour for the low and high coverage sample respectively. The dashed arrows serve as a guide for the eye.

Figure 5.8: Illustration of two electrons propagating along a closed path in opposite directions. Counter propagating electrons can interfere and enhance the scattering. The blue circles represent elastic scattering events that do not affect the phase coherence length. The dephasing rate which is inversely proportional to the coherence length is defined as $\tau_\phi^{-1}$. Figure adapted from [67].
6. Gas sensing with epitaxial graphene

In the previous chapters we have seen that the hydrogenated epitaxial graphene system is potentially a very exciting system to study fundamental physics. We recall that by transport and photoemission emission experiments we have observed the p-type doping effect of hydrogen on the epitaxial graphene layer. Atomic hydrogen is obviously not the only p-dopant for epitaxial graphene, another candidate for this chemical p-doping is nitrogen dioxide (NO$_2$). Due to the chemical doping, the resistance of the epitaxial graphene is expected to change, therefore epitaxial graphene would make an ideal nitrogen dioxide gas sensor. In this section we discuss a practical application of epitaxial graphene as a gas sensor which could answer the industrial need for a fast response, reversible and very sensitive nano-sensor [22][71][72]. In our experimental setup we expose the epitaxial graphene samples to different concentrations of nitrogen dioxide gas. With a Hall-setup we measure the sheet carrier density, mobility and the sheet resistance. The samples are prepared with the recipe as described in chapter 2. To remove the water from the sample, we heat the sample up to 425 K for a short period of time. After cool-down we expose the surface to NO$_2$ gas at various concentrations in the parts per billion (ppb) regime. In between two adsorption measurements we anneal the sample at 425 K for 30 minutes. Furthermore the experiments are performed in a dry nitrogen environment with a constant flow of nitrogen (3 slm). With a simple adsorption and desorption model we try to study the dynamics of this type of gas sensor.

6.1 Concept of epitaxial graphene based gas sensors

The idea of gas sensing with epitaxial graphene is purely based on effective doping upon adsorption of molecules such as NO$_2$. In the case of NO$_2$, the doping is p-type, due to the oxidising character of the oxygen atoms [22][73][74]. Since epitaxial graphene grown on silicon carbide (SiC) is initially n-doped (approximately 2·10$^{13}$ cm$^{-2}$) the amount of n-doping will decrease when NO$_2$ molecules adsorb on the graphene surface. The latter implies that the Fermi level shifts towards the charge neutrality point (or Dirac point) of graphene. In figure 6.1 this idea of the shift of the Fermi level is illustrated. When moving towards the Dirac point, the number of charge carriers becomes smaller, hence the resistance increases gradually when the surface is exposed to the nitrogen dioxide gas. By measuring the change in sheet carrier density and the change in sheet resistance we investigate the adsorption and desorption rates of the graphene gas sensor. It is expected that the dynamics of adsorption and desorption is strongly dependent on the concentration of NO$_2$ molecules in the gas phase. By determining the adsorption and desorption rate, we show that is possible to determine the concentration of NO$_2$ molecules in the gas phase. The results of this study could be extremely useful for calibrating epitaxial graphene gas sensors and improve the accuracy as well as increase the durability of the sensor.
6.1. CONCEPT OF EPITAXIAL GRAPHENE BASED GAS SENSORS

Figure 6.1: Illustration of the linear dispersion of graphene and the Fermi-level shift when nitrogen dioxide molecules adsorb on the surface. The carrier density, which is n-type initially, decreases significantly upon adsorption of NO$_2$ (the gas molecules act as an electron acceptor), therefore the epitaxial graphene becomes less n-doped and the resistance will increase. Note that the change in sheet carrier density $n_s$, shown at the right graph, has a positive sign. The change in the sheet carrier density is assumed to be proportional to the amount of adsorbed gas molecules.

The experimental setup consists of a Hall instrument. Through a Van der Pauw measurement we determine the sheet carrier density and the sheet resistance. We apply a constant magnetic field of $\pm 0.546$ T and 0.1 mA current over the sample when performing the transport measurements. A photograph of the experimental setup is shown in figure 6.2. The epitaxial graphene sample is mounted on top of a SiO$_2$ wafer plate. The silicon oxide plate, has platinum (Pt) covered patches which we use to contact 0.5 mm copper wires from the epitaxial graphene surface to the silicon oxide plate, as can been seen on the photo. These contacts are manually fabricated and connected through a small droplet of silver paste ($\leq 0.5$ mm). The two hoses, visible in figure 6.2 provide the nitrogen flow and the nitrogen dioxide to the chamber. Furthermore the sample space can be heated up to 425 K to anneal the epitaxial graphene surface between the cycles of adsorption measurements.
Figure 6.2: The Hall-setup, on epitaxial graphene sample can be measured at a time. The sample is glued with non-conductive epoxy on a SiO$_2$ substrate, the surface is electrically connected through the Pt patches with the Hall-probes.
6.2 The Langmuir adsorption model

The dynamics for species adsorbing on a surface, can be easily described by a Langmuir adsorption model. Since the epitaxial graphene surface is not perfectly homogeneous in its chemical reactivity, we propose that the graphene surface contains both reversible and irreversible sites for the gas molecules to adsorb on. The irreversible sites, when gas molecules are absorbed at these sites they cannot desorb, could be attributed to the presence of step edges at the terraces of epitaxial graphene. Because the step edges are more reactive, we expect these areas to be irreversible sites. The remaining majority part of the surface then acts as a reversible site for the gas molecules. For these reversible sites, where species can both adsorb and desorb, we make use of a simple linear differential equation which describes the time evolution of the amount of adsorbates on the surface:

$$\frac{dn_{\text{rev}}}{dt} = k_{\text{on,rev}}(1 - n_{\text{rev}}) - k_{\text{off,rev}}n_{\text{rev}}.$$  \hfill (6.1)

Here $n_{\text{rev}}$ is the fraction of the surface which is occupied by a certain gas molecule, say for instance NO$_2$. We assume that the reversible on/off rates, $k_{\text{on,rev}}$ and $k_{\text{off,rev}}$, do not change over time and do not depend on any other parameter such as $n_{\text{rev}}$. The solution of this simple first order linear differential equation is then given by:

$$n_{\text{rev}}(t) = \frac{k_{\text{on,rev}}}{k_{\text{on,rev}} + k_{\text{off,rev}}} [1 - \exp(-(k_{\text{on,rev}} + k_{\text{off,rev}})t)].$$  \hfill (6.2)

In the latter we invoke the initial condition $n_{\text{rev}}(0) = 0$, which implies that there are no adsorbates on the surface at the start of the experiment. For the irreversible sites we find, similar to the previous one, the following linear differential equation:

$$\frac{dn_{\text{irr}}}{dt} = k_{\text{on,irr}}(1 - n_{\text{irr}}).$$  \hfill (6.3)

Obviously, the irreversible sites do not have a desorption rate. The solution of the differential equation above, where $n_{\text{irr}}(0) = 0$, yields:

$$n_{\text{irr}}(t) = (1 - \exp(-k_{\text{on,irr}}t)).$$  \hfill (6.4)

To fully describe the dynamics of the gas adsorption and desorption we make use of the equations above. The next assumption we make is that the change in sheet resistance is proportional to the change in carrier density $n_s$ of epitaxial graphene. Also it is sensible that the sum of $n_{\text{rev}}$ and $n_{\text{irr}}$ is proportional to the carrier density, presuming each adsorbed molecule provides the same net charge transfer as described by Leenaerts et al. [73]. Therefore we obtain the following equations which will be used in the next paragraph to fit the model parameters:

$$R_{\text{rev}}(t) = R_{\text{rev,max}} \frac{k_{\text{on,rev}}}{k_{\text{on,rev}} + k_{\text{off,rev}}} [1 - \exp(-(k_{\text{on,rev}} + k_{\text{off,rev}})t)]$$  \hfill (6.5)

$$R_{\text{irr}}(t) = R_{\text{irr,max}}(1 - \exp(-k_{\text{on,irr}}t)), $$  \hfill (6.6)

where the total measured resistance is the sum of $R_{\text{rev}}(t)$ and $R_{\text{irr}}(t)$. 

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6.3 Calibration of an epitaxial graphene NO\textsubscript{2} gas sensor: resistance and carrier density measurements

To calibrate the epitaxial graphene gas sensor for NO\textsubscript{2}, we firstly have a look on the resistance change as a function of time for different levels of NO\textsubscript{2} concentration. The experimental result is shown in figure 6.3. Here the change in resistance is defined as \((R - R_0)/R_0\), where \(R\) is the sheet resistance (at time \(t\)) and \(R_0\) the initial sheet resistance at \(t = 0\). Note that the time is measured in minutes. The resistance is measured at different concentrations of NO\textsubscript{2}, varying from 15 ppb to 100 ppb. With the theoretical model proposed in the last section we will fit, later on, these curves to obtain the adsorption and desorption rates. Depending on the concentration of nitrogen dioxide in the gas phase we expect to find different values of the adsorption and desorption parameters. From figure 6.3 we clearly see a quick rise in resistance when the NO\textsubscript{2} valve is opened. This is the result of nitrogen dioxide molecules adsorbing to the surface, which lowers the number of charge carriers because of its p-doping effect (see figure 6.1). After 35 minutes the chamber is purged with nitrogen gas and a drop in the resistance can be observed, since some of the weakly adsorbed NO\textsubscript{2} molecules will desorb.

![Figure 6.3: The relative change in resistance as a function of time. The curves are obtained for different concentrations of NO\textsubscript{2} gas which the epitaxial graphene sample is exposed to.](image)

Before continuing with the results, we have to review our assumption that the rise in resistance of the sensor behaves proportionally with respect to the change in sheet carrier density. Figure 6.4 shows the resistance change, as a function of the change in sheet carrier concentrations \(n_s\).
For small changes in concentration the curve does not show the linear response in the resistance. Therefore the model might not hold for small concentration changes or small amount of adsorbates on the surface. However, for increasing amount of NO\(_2\) molecules adsorbed on the surface, the change in resistance evolves into a linear regime where the Langmuir adsorption model becomes more accurate. The non-linear part of the curve can be attributed to the fact that during the first few data points, the steady state concentration has not reached yet. From figure 6.4 we also obtain the slope of the four curves in the linear regime which is \(0.22 \pm 0.01 \cdot 10^{-12}\text{cm}^2\), we underline that the adsorption model breaks down for large shifts in the carrier concentration. This can be understood from the picture drawn in figure 6.1. Upon adsorption of the gas molecules, the Fermi level moves closer towards the Dirac point, which changes the sensitivity of the sensor significantly, hence the linear approximation will fail. At last we place a note on the curve observed for the 100 ppb NO\(_2\) where we clearly see no overlap with the other three curves at 15, 25 and 50 ppb. This could be explained if the annealing procedure was insufficient and did not recover the initial state of the sample.

Figure 6.4: The relative change in resistance as a function of the change in carrier concentration. The concentration NO\(_2\) to which the sample is exposed varies from 15 ppb to 100 ppb gas. The response in resistance becomes more linear as the the amount of NO\(_2\) adsorbates is increased.
6.3. CALIBRATION OF AN EPITAXIAL GRAPHENE NO\textsubscript{2} GAS SENSOR: RESISTANCE AND CARRIER DENSITY MEASUREMENTS

adsorption sites. The green curve is the sum of the irreversible and reversible contribution to the resistance change. The adsorption dynamics (before closing the valve) can be well fitted by the Langmuir model in figure 6.5. We clearly see that the red curve (the irreversible sites) shows saturation within 10 minutes. The initial adsorption and resistance change \((t \leq 4 \text{ minutes})\) is mainly determined by the irreversible sites. On the other hand, the blue curve (reversible sites) does not get saturated and mainly describes the slowly rising regime \((4 \leq t \leq 34 \text{ minutes})\). The shape of the blue curve is primarily determined by the ratio between \(k_{\text{on,rev}}\) and \(k_{\text{off,rev}}\). After approximately 94 minutes we close the NO\textsubscript{2} valve and pump out the NO\textsubscript{2} gas. The molecules on the irreversible sites are likely to stay adsorbed while the molecules on the reversible sites tend to desorb. Hence a drop in the resistance can be observed in \[6.5\]. From the fit (for \(t \leq 34 \text{ minutes}\)) we extract the adsorption and desorption parameters: \(k_{\text{on,irr}}, k_{\text{on,rev}}\) and \(k_{\text{off,rev}}\). The decrease in the resistance after closing the valve cannot be well described by the model, if we assume that the all the molecules on the reversible sites desorb. Apparently only a fraction of the molecules on the reversible sites desorbs, this can be understood since a new equilibrium will establish when the NO\textsubscript{2} is pumped out the chamber. Because of the latter and the fact that molecules reside on irreversible sites, the initial value of the resistance of the gas sensor cannot be restored, only after heating the sample the adsorbed species are removed.

Figure 6.5: The relative change in resistance as a function of exposure time of 100 ppb NO\textsubscript{2} gas. The red and the blue curve, show the contribution of the irreversible and reversible sites respectively. The green curve shows the sum of the contributions. The black solid circles belong to the measurement, it is clearly visible that the Langmuir model roughly fits the experimental data. Note that the blue curve does not go to zero after closing the NO\textsubscript{2} valve, this indicates that not all molecules on the reversible sites desorb.
The adsorption rate for the irreversible sites $k_{\text{on,irr}}$ is extracted from experiments for different background concentrations of nitrogen dioxide, presented in figure 6.6. From literature we expect a linear dependence between $k_{\text{on,irr}}$ and the NO$_2$ concentration, increasing the concentration therefore also increases the adsorption rate. From a linear fit we obtain an adsorption rate per ppb which is $(1.1 \pm 0.2) \cdot 10^{-3} \text{ min}^{-1}\text{ppb}^{-1}$. However, we strongly suggest to perform multiple experiments at higher concentrations of NO$_2$ in the ppm regime, to verify the linear behaviour. From figure 6.6 we see that the fit does not intercept at the origin, which indicates, that the behaviour at low concentration could be non-linear. Nonetheless, in the investigated domain of concentrations, we believe that our epitaxial gas sensor can measure NO$_2$ concentrations within an accuracy of 10-20 ppb.

![Figure 6.6: The adsorption rates for the irreversible sites $k_{\text{on,irr}}$ for different NO$_2$ concentrations, obtained from the fits of the Langmuir model. The slope of the fit is $(3.0 \pm 0.5) \cdot 10^{-3} \text{ min}^{-1}\text{ppb}^{-1}$.

Also the adsorption and desorption rates of the reversible sites $k_{\text{on,rev}}$ and $k_{\text{off,rev}}$ are extracted from the experimental results and shown in figure 6.7. An other way to estimate the nitrogen dioxide concentration could be from determining the ratio between $k_{\text{on,rev}}$ and $k_{\text{off,rev}}$. Figure 6.7 shows that upon increasing the NO$_2$ concentration, the ratio between the adsorption and desorption rate drops. The ratio $k_{\text{on,rev}}/k_{\text{off,rev}}$ drops below 1 around 20 ppb, which implies a larger desorption rate than adsorption rate. Note that this does not result in net desorption, see equation 6.5, the adsorption becomes only suppressed. We foresee difficulties in practice to determine higher concentrations NO$_2$ with this method. Because the uncertainty in determining the ratio is much larger compared to determining only $k_{\text{on,irr}}$. Furthermore, we suggest to increase the amount of measurements in the ppb as well as in the ppm regime to fully determine the behaviour of $k_{\text{on,rev}}/k_{\text{off,rev}}$ as a function of the NO$_2$ concentration. But from these preliminary results we
already see a significant influence on the adsorption and desorption ratios by changing the concentration. Therefore we believe that the Langmuir model can provide us a simple way to estimate the nitrogen dioxide concentration, and therefore make epitaxial graphene a suitable gas sensor to detect NO$_2$ down to ppb levels. However for use in air or ambient conditions, supplementary experiments are required to study the effect of other adsorbates on the surface such as oxygen or water. By extending the Langmuir model to multiple types of competing species on the surface, we could possibly model more complicated and detailed gas mixture environments. The largest challenge will be however to distinguish the contribution of each individual species in the resistance and carrier density concentration measurement.

Figure 6.7: The adsorption and desorption rates for the reversible sites $k_{on,rev}$ and $k_{off,rev}$ for different NO$_2$ concentrations, obtained from the fits of the Langmuir model. The inset shows the ratio between $k_{on,rev}$ and $k_{off,rev}$. 

![Graph showing adsorption and desorption rates for different NO2 concentrations with inset showing ratio of rates.](image)
6.4 The effect of the initial carrier density on the performance of the epitaxial graphene gas sensor

In the previous part of this chapter we have shown that the simple Langmuir adsorption model is sufficient to calibrate a single epitaxial graphene NO$_2$ gas sensor for measurements in the ppb regime. It is important to note that the extracted values of the adsorption and desorption rates are not universal, they only fit for a single gas sensor. Each gas sensor will have a distinct surface and thus a different amount of (ir)reversible sites. Also it is likely that each sensor has a different initial carrier concentration, due to inhomogeneous doping in the SiC wafers. Because, the initial doping of epitaxial graphene (n-type, see figure 6.1) strongly influences the sensitivity of the sensor, it is of great importance to understand how the initial doping affects the transport measurements and hence the adsorption and desorption rates. An interesting feature, which is related to the latter, is the different response in resistance depending on the direction in which the resistance is measured, this is along or perpendicular to the step edges of the epitaxial graphene, see figure 2.4. Figure 6.8 shows the resistance change measured parallel and perpendicular to the step edges when exposed to 100 ppb NO$_2$. The initial resistances are respectively 190 Ω and 270 Ω which can be understood since the step edges enhance the scattering of electrons to the lattice. From figure 6.8 we clearly see a difference in the measured resistance versus exposure time. The step edges are more reactive to the NO$_2$ molecules, hence adsorption to the step edges will be stronger. Also, the step edge regions could be less n-doped initially, because of the formation of bilayer graphene [4]. As a result the step edges are more sensitive to the NO$_2$ adsorbates and the change in resistance will be higher near the step edges.

Figure 6.8: The resistance of the epitaxial graphene sample measured parallel and perpendicular to the step edges of the epitaxial graphene sample when exposed to 100 ppb NO$_2$. The response of the resistance is clearly different. Note here that the initial resistance $R_0$ is lower in the parallel configuration compared to the perpendicular one. The illustration on the right shows the idea of the measurement of the resistance along and perpendicular the direction of the step edges.
The inhomogeneous doping of the surface can be even more clear for quasi free standing epitaxial graphene (QFEG). For QFEG, the silicon dangling bonds are saturated with hydrogen (see introduction chapter), and the Fermi level moves closer to the Dirac point compared to epitaxial graphene, such that the n-doping is approximately $10^{12}\text{cm}^{-2}$. As a consequence the charge neutrality point (CNP) can be crossed when a significant amount of NO$_2$ adsorbs to the surface. Intuitively we foresee the breakdown of the adsorption model since the resistance will start to drop instead of increase, when the CNP is crossed. An example is shown in figure 6.9 where the parallel and perpendicular resistance is measured for a QFEG sample exposed to 100 ppb NO$_2$. The parallel resistance firstly increases before it drops, indicating that this ‘channel’ of measurement was initially n-doped. The perpendicular resistance however, decreases immediately, which is a signature that it was already p-doped at the start of the measurement. The response of the resistance upon exposure to NO$_2$ is clearly different from the previous curves for epitaxial graphene. For $R_{\text{perpendicular}}$ we see that the resistance rises after approximately 5 minutes, which is surprising if we look at the picture that we proposed in the beginning of the chapter 6.1. The amount of holes increases, so we expect a monotonic drop of the resistance as NO$_2$ adsorbs on the surface. The unexpected resistance increase could be attributed to hole-hole interactions, when the graphene is hole doped \[76\]. Note that this effect is asymmetric, in the electron doped regime this has not been observed. Therefore, to fabricate the ideal epitaxial graphene gas sensor the sample needs to be sufficiently n-doped initially, so the CNP will not be crossed during the measurements.

Figure 6.9: The resistance of the quasi free standing epitaxial graphene sample measured parallel and perpendicular to the step edges of the epitaxial graphene sample when exposed to 100 ppb NO$_2$. 
7. Conclusion

Throughout this thesis we have shown that hydrogenated epitaxial graphene on SiC is potentially a very exciting material to study fundamental physics. Due to the presence of silicon dangling bonds in the SiC substrate, we believe that the hydrogen atoms preferentially adsorb on one of the two sublattices of the graphene layer. Therefore these hydrogen adsorbates break the sublattice symmetry which results in the opening of a bandgap and the emergence of so-called pseudo Landau levels in the gap, as observed in DFT calculations [12]. The theoretical results suggest that the system contains strongly localised electrons because they experience this pseudo-magnetic field. We propose that the latter could give rise to charge instabilities, which is revealed by the observation of fractal-like shapes by the atomic force microscope (AFM). The core assumption we have made here is that the observed fractal shapes in AFM do not simply reflect the positions of the hydrogen atoms, instead we believe it is related to the charge density distribution. This assumption is supported by the fact that the measured height by AFM is an order of magnitude larger than the geometrical dimension of the protrusion caused by a hydrogen adsorbate. Furthermore STM studies of hydrogenated graphene do not show fractal adsorption of the hydrogen atoms, also diffusion of atomic hydrogen on graphitic surfaces has been proven to be difficult [6][77].

We have studied the fractal-like shapes by two types of simulations, being the diffusion limited aggregation (DLA) model (describing Laplacian growth) and a Monte Carlo simulation, inspired by the work of Hughes et al. [13]. Here we have considered the fractal shapes to be an ensemble of electrons, submitted to a perpendicular magnetic field, behaving as an electron droplet. In an inhomogeneous magnetic field it has been proved by Agam et al. that the droplet shows viscous fingers, which can be explained by Laplacian growth [14]. In our case the electron droplet is established in a inhomogeneous pseudo-magnetic field. Where the inhomogeneity arises due to the non-uniform distribution of the hydrogen atoms. By comparing the fractal dimension of the experimentally observed fractals and the simulated DLA fractals we have found quantitative similarities. A phenomenological growth simulation based on DLA also shows a clear qualitative likeness. We continued with a more sophisticated Monte Carlo simulation, where the electrons are simulated by a many-body wavefunction in the quantum Hall regime. In addition we have included in this simulation explicitly the inhomogeneity of the pseudo-magnetic field. The Monte Carlo results show both quantitative and qualitative agreement with the viscous fingers obtained by DLA and what is observed in the experiments. The findings in this thesis therefore partially answer the question brought forward by Hughes [13]: Can equilibrium Monte Carlo simulations simulate non-equilibrium growth processes such as DLA? Based on the results we have obtained, we tend to say that this is possible. The important note here is that the random potential in the Monte Carlo is the crucial ingredient to simulate the fractal shapes. The randomness in the potential hence reflects the random growth process in for instance a DLA simulation. For future research we would like
to mention that non-equilibrium processes could also be captured in a kinetic Monte Carlo (KMC) simulation.

Since the above findings strongly support the idea of the presence of (inhomogeneous) pseudo-magnetic fields induced by the hydrogen adsorbates, we expect pseudo Landau levels to be observed in the electronic transport measurements. The magnetotransport experiments however, did not show any conclusive results regarding the effect of pseudo Landau levels, mainly due to the large sample size (4 mm by 4 mm). It is recommended for following experiments to fabricate Hall bars (approximately 4 µm by 20 µm) on top of a single terrace of epitaxial graphene to exclude scattering to the step edges. Moreover by decreasing the size of the sample we could eliminate bilayer graphene contributions and better define our experiment. Nevertheless we do see a clear metal-semiconductor/insulator transition when we increase the dose of hydrogen, which is agreement with results shown by Guillemette et al. Therefore we could think about hydrogenated epitaxial graphene transistor devices to be realised. In addition, the magnetotransport results indicate a p-doping effect of atomic hydrogen on epitaxial graphene. This supports our preliminary photoemission results, where a shift of the Fermi level towards the Dirac point has been observed for hydrogenated epitaxial graphene. We recommend for future research to also investigate the options of gating the hydrogenated epitaxial graphene device. Instead of sweeping the magnetic field, we could tune the Fermi level and therefore probe the presence of the pseudo Landau levels directly.

Regarding the industrial applications of epitaxial graphene, we have presented a Langmuir-type model to study NO\(_2\) adsorption on epitaxial graphene for gas sensing purposes. From these preliminary results we already see a significant influence on the adsorption and desorption ratios by varying the concentration of NO\(_2\) to which the sample is exposed to. Therefore we believe that this simple model is an accessible method to estimate the nitrogen dioxide concentration, and hence make epitaxial graphene a suitable gas sensor to detect NO\(_2\) down to ppb levels. However for use in air or ambient conditions, additional experiments are necessary to study the effect of other adsorbates on the surface such as oxygen or water.
References


REFERENCES


REFERENCES


A. Diffusion limited aggregation, MATLAB code

```
%% Diffusion Limited Aggregation in 2 Dimensions
% With a rectangular creation/annihilation radius and sticking probability
% Author:
% Calvin Kha, TU\e
% Original DLA adapted from:
% Philip Thomas, github.com/philipithomas
% Mohammad Hashim, github.com/mohashim

%% initialization variables
clearvars
clf
clc

%% Variables
% Size of the lattice (xmax, ymax)
xmax = 500;
ymax = 500;

% Number of entering particles (note that not all particles will stick!)
numparticles = 1000000;

%% Initialize the lattice
map = zeros(xmax,ymax);

% If value zero -> blank
% if value one -> Aggregated (stuck) particle

%% Set Seed in the center
map(floor(xmax/2),floor(ymax/2))=1;

%% Particle Loop (core of the DLA algorithm)
% We initialize these variables outside the loop
x=0; % int
y=0; % int
stuck=0; % boolean
particle=0; % int
escape=0; % boolean
die=0; % boolean
walk=0; % Double - be a random number
nu=1; % Sticking probability
P=1-nu;
t=1; % counter for updating injection radius
R(1)=3; % Initial radius of injection

%% Now we start randomly entering particles from a distance > 3R_g
while (( particle < numparticles) + (escape=0))!=0
```
particle=particle+1; % increase the particle count.

if t==1
    reff=3;
else
    reff=floor(R(t-1));
end

% We initialize the injection borders which is a rectangle with size 9R^2
x1=xmax/2-3*reff;
x2=xmax/2+3*reff;
y1=ymax/2-3*reff;
y2=ymax/2+3*reff;

% Two random numbers to determine the starting coordinate (x,y)
x=x1+floor(rand()*(x2-x1));
y=y1+floor(rand()*(y2-y1));

% stuck = 0; % Not stuck yet

% Now, until the particle is next to another particle, we keep moving it around in ... a random walk

% We kill the particle, or set die == true if the particle reaches the edge row.
% The edges are located on a distance 6R from the seed.

while (stuck == 0)&&(die == 0)
    % Random walk -> Move it isotropically
    walk=rand;
    left=0;
    right=0;
    up=0;
    down=0;

    if walk < .25
        y=y-1;
        up=1;
    elseif walk < .5
        % right
        x=x+1;
        right=1;
    elseif walk < .75
        % down
        y=y+1;
        down=1;
    else
        % left
        x=x-1;
        left=1;
    end

    % The particle is now walked.

    % if out of bounds - DIE->1, particle gets killed
    if ((x==xmax/2-6*reff) + (y==ymax/2-6*reff) + (x==xmax/2+6*reff) + ...
        (y==ymax/2+6*reff))>0
        die=1;
    else
        % if we do not kill it, we check for whether to stick it
        stuck=0;
    end
if (map(x+1,y) + map(x-1,y) + map(x,y-1) + map(x,y+1)) ≠ 0
% Then there is an adjacent particle, so we need to stick it with a
% probability P.
if rand(1) > P
stuck = 1;
else
    if left == 1
        x = x + 1;
    elseif right == 1
        x = x - 1;
    elseif up == 1
        y = y + 1;
    elseif down == 1
        y = y - 1;
    end
end % end adjacent check
% If there is no adjacent particle ->
% Keep random walking and move it
end % end bound check
% So now the particle is next to a current particle, so mark it on the map
if stuck == 1
map(x,y) = 1; % By setting it to 1, we now have a stuck particle there.
[row, col] = find(map > 0, xmax*ymax);
for i = 1:length(row)
    row(i) = row(i) - floor(xmax/2);
    col(i) = col(i) - floor(ymax/2);
end
rowsquare = row.^2;
colsquare = col.^2;
Rsquare = rowsquare + colsquare;
S(t) = sum(map(:)); % S and R for calculating the fractal dimension D
R(t) = sqrt(sum(Rsquare)/S(t));
t = t + 1
if t == 3001
    break;
end % end looping of particles
surf(map, 'FaceColor', 'interp', 'FaceLighting', 'gouraud', 'EdgeColor', 'none'); ...
    view(2); axis('square')
axis([150 350 150 350])
linearCoef = polyfit(log(R), log(S), 1);
B. Electron droplets simulated with DLA

In addition to the results shown in chapter 5.3, we discuss the simulation and the simulated fractals of electron droplets in a bit more detail. In figure B.1 a series of morphologies is obtained for different values of coverage and diffusion length. The simulation box consists of $100 \times 100$ grid points. For small diffusion lengths $M_{\text{max}} \approx L$ (approximately the size of the grid which is 100 steps) and low coverage (10%) no fractal shapes are established. Only tiny clusters can be observed, even at higher coverages. On the other hand, increasing the diffusion length does result in the appearance fractal shapes. The size grows for increasing diffusion lengths. For future research it would be extremely interesting to study the growth of the fractal shapes at different dosing temperatures and varying atomic hydrogen flow. The temperature of the hydrogen cracker could be varied as well as the temperature of the epitaxial graphene sample. The flow could be precisely monitored with a mass spectrometer and a flow meter. These experiments could possibly show the different morphologies as the simulated ones in figure B.1. Also in-situ measurements of the epitaxial graphene surface could be very useful. By performing real-time AFM measurements during the hydrogen treatment, the growth of the electron droplets and its fractal shapes could be imaged. An other advantage would be that the sample stays in UHV during the AFM measurements, so the amount of contaminants on the surface is minimised.

Note that this phenomenological model does not give insight into the time, length or energy scales of the growth mechanism. Considering the time scale, the simulation allows only one particle to move each simulation step, therefore growth processes that take place simultaneously are not included.
Figure B.1: Modified DLA simulations with the growth of multiple fractal shapes, representing the growth of electron droplets. The coverage is increased from 10% to 50% and the diffusion length is increased from $L$ to $25L$, where $L \times L$ is the size of the simulation grid.
%% Diffusion Limited Aggregation (DLA multi particle, short range interaction 1 ...
% lattice unit)
% Calvin Kha, TU/e
% Clear variables
clear
c1c
%% Variables
% Size of simulation box
xmax = 202;
ymax = 202;
% Number of particles entering the box
numparticles = 10000;
%% Initialize map
map = zeros(xmax,ymax);
% If value zero -> blank, if value one -> aggregated (?stuck?) particle
%% Particle Loop
% We'll just initialize these variables outside the loop
x=0; % int
y=0; % int
stuck=0; % boolean
particle=0; % int
walk=0; % Double - be a random number
x0=6000; % Mean diffusion length

% Core of the simulation
while (( particle < numparticles))!=0
particle=particle+1; % increase the particle count.
% Inject particle at random position on the map
occupy=0;
stamina=floor(x0+0.1*x0*randn);% Gaussian distribution of stamina ...
P=exp(-0.5*(x-x0)^2/s^2)
while (occupy==0)
pickx=rand; %get two random numbers
picky=rand;
x=floor((pickx*(xmax-3)))+2;
y=floor((picky*(ymax-3)))+2;
if map(x,y)==0
occupy=1;
end
end
stuck = 0; % not stuck yet
P = 0;
% There is a probability P that the particle does not stick even if the
% neighbour cell is occupied.
while (stuck == 0) % when stamina>0 stuck=1
% Random walk -> Move it
walk=rand;
left=0;
right=0;
up=0;
down=0;
if walk < .25
    % up
    y = y - 1;
    up = 1;
elseif walk < .5
    % right
    x = x + 1;
    right = 1;
elseif walk < .75
    % down
    y = y + 1;
    down = 1;
else
    % left
    x = x - 1;
    left = 1;
end
stamina = stamina - 1;
% The particle is now walked.
% Apply periodic boundary conditions
if (x == 1)
    x = xmax - 1;
elseif (x == xmax)
    x = 2;
elseif (y == ymax)
    y = 2;
elseif (y == 1)
    y = ymax - 1;
else
    stuck = 0;
    if stamina == 0;
        stuck = 1;
    elseif (map(x + 1, y) + map(x - 1, y) + map(x, y - 1) + map(x, y + 1)) \neq 0
        % If neighbour cell is occupied -> probability to stick
        if rand(1) > P
            stuck = 1;
        elseif left = 1
            x = x + 1;
        elseif right = 1
            x = x - 1;
        elseif up = 1
            y = y + 1;
        elseif down = 1
            y = y - 1;
        end
    end
end
% If no adjacent particle ->
% Keep random walking and move it
end %end the stuck criteria
if stuck
map(x,y)=1; % By setting it to 1, we fix the particle

if (x==2) % Applying boundary conditions for neighbour interactions
  map(xmax,y)=1;
elseif (x==xmax-1)
  map(2,y)=1;
elseif (y==2)
  map(x,ymax-1)=1;
elseif (y==ymax-1)
  map(x,2)=1;
eend % end stuck check

% Now it moves onto the next particle entering the map if there are more particles ...
to go
end% end looping of particles

surf(map(2:xmax-1,2:ymax-1), 'FaceColor', ... 
  'interp','FaceLighting','gouraud','EdgeColor', 'none'); view(2); axis('square')
C. Monte Carlo simulation of quantum Hall droplet

This appendix contains a brief summary and preliminary results of the Kinetic Monte Carlo (KMC) simulation. The Monte Carlo (MC) simulation discussed in the thesis is very similar to this simulation. The only difference is that in the KMC simulation, all the movement probabilities of all the electrons are calculated, instead of the possible moves for one randomly chosen electron. Hence the KMC could provide us the ‘time’ evolution and the formation of the droplet. A scheme illustrating the core of the KMC simulation is shown in figure C.1. Each particle on the square lattice can move in four directions (neighbour sites). For all \( N \) particles we then calculate the energy change for each of the 4 different moves and the corresponding Boltzmann exponents (in total \( 4N \)). The edge of the simulation box is as an infinite potential wall, so the electrons are not allowed to escape the simulation grid. Furthermore we do not allow two electrons sit on the same site, or on the same site as a solenoid. The probabilities are put on a ‘bar’ and we draw a random number between 0 and the sum of all probabilities, see figure C.1. Hence in each simulation step the system will look for the most probable move. The final state should be the global energy minimum of the system and therefore equivalent to the result obtained by the non-kinetic Monte Carlo simulation.

Figure C.1: Illustration of the core of the Monte Carlo simulation. The probabilities \( P_{i,j} \sim \exp(-\Delta E_{i,j}) \) are calculated and put on a ‘bar’, where we assumed \( k_B T = 1 \). Here the label \( i \) represents the particle number and \( j \) one of the four directions in which the electron can move. We draw a random number that determines which electron is going to move in what direction.

The main drawback of the KMC is the calculation time, since each electron interacts every other electron the calculation time for the movement of a single electron scales with \( N^2 \). However, because we calculate all the possible moves for all the electrons, the simulation time will scale with \( N^3 \). The simulation code can be improved by using just two vectors containing the coordinates of the electrons and solenoids, instead of working with sparse matrices (see MATLAB code). The
result for the formation of an electron droplet, starting from a random distribution of electrons is shown in figure C.2. The number of electrons is here 50 and there are no solenoids in the system. As the simulation progresses the electrons start to clump. By taking a closer look at the intermediate stages we see the formation of a ‘ring’ like structure. The electrons gain effectively the largest energy by moving closer to the centre of the grid, while at the same time keeping distance between other electrons. This possibly explains the open structure in the middle of the droplet at intermediate stages. At the end of the simulation, the gap in the middle closes and a solid circular structure is formed.

Figure C.2: Simulation result of 50 electrons in a $50 \times 50$ simulation grid. Starting from a random distribution of electrons we can clearly see that the electrons start to clump as the simulation progresses.
% Dynamic Monte Carlo (CSK)
% Author: Calvin Kha, TU/e
% Clear variables
clear
clc

%% Variables
% Size of simulation box + imaginary box for applying the boundary
% conditions (check the decay length of potential)
% xmax = 50;
% ymax = 50;
% Number of particles entering the box
% numparticles = 250;
% numcoils=20;
%% Initialize map
map = zeros(xmax,ymax);
coil = zeros(xmax,ymax);
fixcoil = zeros(xmax,ymax);

%% Particle Loop
% We'll just initialize these variables outside the loop
x=0; % int
y=0; % int

for i=1:5
vec(i)=i*10-5;
end
for i=1:5
for j=1:5
fixcoil(vec(i),vec(j))=-50;
end
end

coil=fixcoil+coil;

for i=1:1:numparticles
occupy=0;
while (occupy==0)
  if (coil(x,y)==0 && fixcoil(x,y)==0) % Check if injected site is already taken
    occupy=1;
  end
  coil(x,y)=50;
end
end

coil=fixcoil+coil;

for i=1:1:numparticles
occupy=0;
while (occupy==0)
  if (coil(x,y)==0 && fixcoil(x,y)==0) % Check if injected site is already taken
    occupy=1;
  end
  coil(x,y)=50;
end
end

coils=fixcoil+coil;
if (map(x,y)==0 && coil(x,y)==0) % Check if injected site is already taken
    occupy=1;
    map(x,y)=1;
end

[row,col]=find(map>0);
[row2,col2]=find(coil~>0);

% for i=1:1:numcoils
%   phi(i)=floor(5.*randn());
%   if(mod(row2(i)+col2(i),2)==1 && phi(i)>0)
%       phi(i)=-phi(i);
%   end
%   if rand()>0
%       phi(i)=phi(i);
%   end
%   fcoil(row2(i),col2(i))=phi(i);
% end

% Calculate energy of configuration, U1, U2, U3
U1=0.25*sum((row-floor(ymax/2)).^2+(col-floor(xmax/2)).^2);
U2=0;
U3=0;
for j=1:1:length(row)
    for k=1:1:length(row)-j
        U2=U2-log(sqrt((col(j)-col(j+k))^2+(row(j)-row(j+k))^2));
    end
end
for j=1:1:length(row)
    for i=1:length(row2)
        U3=U3-coil(row2(i),col2(i))*log(sqrt((col(j)-col2(i))^2+(row(j)-row2(i))^2));
    end
end
Etot=U1+U2+U3;

% Apply metropolis algorithm, core
for n=1:100000
    [row,col]=find(map>0);
    num=floor(rand()*(length(col)-1))+1;
    x=col(num);
    y=row(num);
    mapnew=map;
    mapnew(y,x)=0;
    walk=rand;
    if ((x==1) + (y==1) + (x==xmax) + (y==ymax))==0
        if walk<.25
            x=x+1;
        else
            x=x-1;
        end
    elseif walk<.5
        % right
        x=x+1;
    elseif walk<.75
        % down
        y=y+1;
    end
    if random walk
        mapnew(y,x)=1;
        mapnew(y,x)=0;
    end
end
else
% left
x=x-1;
end
else
  if (x==1 && y==ymax)
    if walk<.5
      y=y-1;
    else
      x=x+1;
    end
  elseif (x==1 && y==1)
    if walk<.5
      y=y+1;
    else
      x=x+1;
    end
  elseif (x==xmax && y==ymax)
    if walk<.5
      y=y-1;
    else
      x=x-1;
    end
  elseif (x==xmax && y==1)
    if walk<.5
      y=y+1;
    else
      x=x-1;
    end
  elseif x==1
    if walk<.33
      y=y-1;
    elseif walk<.66
      x=x+1;
    else
      y=y+1;
    end
  elseif y==1
    if walk<.33
      x=x-1;
    elseif walk<.66
      x=x+1;
    else
      y=y+1;
    end
  elseif y==ymax
    if walk<.33
      x=x-1;
    elseif walk<.66
      x=x+1;
    else
      y=y-1;
    end
  elseif x==xmax
    if walk<.33
      x=x-1;
    elseif walk<.66
      y=y+1;
    else
      y=y+1;
  else
else
y=y-1;
end
end

if (map(y,x)==0 && coil(y,x)==0)
mapnew(y,x)=1;
[row, col] = find(mapnew>0);
[row2, col2] = find(coil>0);
U1=0.25*sum((row-floor(ymax/2)).^2+(col-floor(xmax/2)).^2);
U2=0;
U3=0;
for j=1:1:length(row)
    for k=1:1:length(row)-j
        U2=U2-log(sqrt((col(j)-col(j+k)).^2+(row(j)-row(j+k)).^2));
    end
end
for j=1:1:length(row)
    for i=1:length(row2)
        U3=U3-coil(row2(i),col2(i))*log(sqrt((col(j)-col2(i)).^2+(row(j)-row2(i)).^2));
    end
end
dE=(U1+U2+U3)-Etot;
if dE<0
    Etot=U1+U2+U3;
    map=mapnew;
else
    a=rand();
    if a<0.23
        Etot=U1+U2+U3;
        map=mapnew;
    end
end

% surf(map, 'FaceColor', 'interp'); view(2); axis('square')
% drawnow
% pause(0.001);
E(n)=Etot;
if mod(n,1000)==0
    n
end

map(row(length(row)),col(length(col)))=0;
h = fspecial('average', 2);
subplot(1,3,1)
surf(filter2(h, map), 'FaceColor', 'interp', 'EdgeColor', 'None'); view(2); ...
axis('square')
subplot(1,3,2)
surf(coil, 'FaceColor', 'interp', 'EdgeColor', 'None'); view(2); axis('square')
subplot(1,3,3)
plot(E); axis('square')
D. The observation of viscous fingers in hydrogenated epitaxial graphene
The observation of viscous fingers in hydrogenated epitaxial graphene: exposing pseudo-magnetic fields∗

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To date, the unfolding of electron droplets in strong inhomogeneous magnetic fields into remarkable viscous fingers has been only described in a thought experiment. In this article we present, for the first time, a direct experimental observation of viscous fingers in hydrogenated epitaxial graphene by the atomic force microscope. We propose that the manifestation of these ‘finger’ shapes is an exciting way to reveal the presence of strong and non-uniform pseudo-magnetic fields, which is predicted by DFT calculations for hydrogenated epitaxial graphene. Furthermore we complement our findings with Monte Carlo simulations of electron droplets in an inhomogeneous magnetic field, which surprisingly show similar fractal dimensions as the experimentally observed fractal shapes.

The formation of fractal shapes occurs in a enormous variety of physical phenomena down to the nanometer scale. A theoretically predicted example are the so-called viscous fingers of electron droplets in the quantum Hall regime, which arise when a two-dimensional electron gas (2DEG) is submitted to a strong (≥ 20 T) and inhomogeneous magnetic field. An experimental observation of these viscous fingers is challenging since 2DEGs are usually embedded in semiconducting layers. As a consequence, imaging the fractal shapes with surface probe techniques is extremely difficult. Furthermore, experimentally realising an electron droplet requires low temperatures (≤ 4 K) in addition to the high magnetic field.

An interesting system that circumvents the aforementioned experimental difficulties is hydrogenated epitaxial graphene (HEG). First of all, the surface of graphene (a 2DEG) can be easily imaged by surface probes such as the atomic force microscope (AFM) at room temperature. Secondly, recent theoretical findings based on DFT calculations show that hydrogenated epitaxial graphene embodies pseudomagnetic fields exceeding 300 T. This intrinsic magnetic field could plausibly establish an electron droplet in the quantum Hall regime, even when no real magnetic field is applied. In the DFT calculation, a periodic arrangement of hydrogen atoms is assumed in a low coverage regime. Increasing the coverage of hydrogen atoms will lead to a non-uniform distribution of hydrogen atoms. This could result into inhomogeneities in the pseudo-magnetic field. Hence all the ingredients are present to expect fractal shapes to be observed in hydrogenated epitaxial graphene.

Since it has been shown by a semi-classical analysis that the growth of viscous fingers follows the Laplacian growth (LG) equations and is strongly connected to diffusion limited aggregates (DLA), we analyse the experimentally observed fractal shapes by determining its fractal dimension. We use this to verify whether the fractal shapes could be indeed viscous fingers. In addition we use an equilibrium Monte Carlo method to simulate the fractal shapes. By comparing the experimentally observed viscous fingers and the simulations we also answer the intriguing question proposed by Hughes et al.: “Can we use equilibrium Monte Carlo simulations to efficiently simulate non-equilibrium growth processes such as DLA; in other words what can the quantum Hall effect tell us about DLA?”.

Model.- To simulate the shape of the electron
droplet by the Monte Carlo method we consider the many-body wavefunction given by [4]:
\[
\psi(z_1, ..., z_N) = \prod_{i<j} |z_i - z_j| e^{-\frac{1}{4\ell_b^2} \sum_{j=1}^{N_e} |z_j|^2},
\]
where the positions of the electrons are defined in the complex plane and represented by the complex variable \(z_i (i=1,2,...,N)\), the magnetic length \(\ell_b = \sqrt{\hbar/eB_0}\) and the total number of electrons \(N_e\). This wavefunction is identical to the Laughlin wavefunction in the case of filling factor \(\nu = 1\), and effectively represents an ensemble of electrons exposed to a strong magnetic field. To obtain the energy of the system we make use of the fact that \(\langle \psi^2 \rangle \sim \exp(-\beta U)\) and \(\psi(z_1, ..., z_N) = \exp[\sum_{i<j} \ln |z_i - z_j| + \frac{1}{4\ell_b^2} \sum_{j=1}^{N_e} |z_j|^2]\), where we have defined \(\beta = 1/2\). Due to the extremely large pseudo-magnetic field and the exchange splitting in hydrogenated epitaxial graphene, the lowest Landau level is half filled, corresponding to \(\nu = 1\). Also, the large effective field results into a small magnetic length, for which we know that at high electron densities the electron liquid phase is preferred over a Wigner crystal phase.

Now to include the inhomogeneity in the magnetic field we add magnetic fluxes at random positions. Because a magnetic flux quantum can be interpreted as an orbiting electron (tiny solenoid), we describe the source of the randomly positioned magnetic fluxes as a distribution of localised impurity charges. Therefore the Ansatz for the energy of the system reads:

\[
E = -\sum_{i<j} \ln |z_i - z_j| + \frac{1}{4\ell_b^2} \sum_{j=1}^{N_e} |z_j|^2 \hspace{1cm} (2)
\]

\[+ \sum_{a=1}^{N_s} \sum_{j=1}^{N_e} \Phi \ln|z_j - z_a| ,\]

with \(N_s\) being the number of impurities charges or solenoids in the system, \(\Phi = 0, \pm 1, \pm 2...\) being the amount of flux quanta per solenoid and \(z_a\) the corresponding positions. The first term in equation 2 describes the effective Coulomb interaction between two electrons, while the second term describes the energy gain due to magnetic screening. The third term describes the interaction of the electrons with the magnetic fluxes, impurity charges.

**FIG. 1:** a) The distribution of 500 electrons on a square lattice in an inhomogeneous magnetic field due to the presence of 500 randomly distributed solenoids. The yellow tones correspond to higher electron densities while the blue tones reflect lower densities. b) The map illustrates the positions of the 500 solenoids. The yellow and blue dots correspond to the solenoids with strength \(\Phi = 10\) and \(\Phi = -10\) respectively.

**Simulations.** For our simulations we define a square lattice with a size of 100 by 100 grid points. In this simulation box we distribute at random \(N_e\) electrons and \(N_s\) charge impurities at the start of the simulation. The positions of the charge impurities do no change during the simulation, only the electrons are allowed to move. For the Monte Carlo simulation we make use of the Metropolis algorithm. In each simulation step we allow one electron to move one lattice unit in a random direction, by calculating the change in energy \(\Delta E\), we accept or reject this step. If \(\Delta E < 0\) we accept the movement, while in the case \(\Delta E \geq 0\) we invoke an acceptance rate of 0.5.

An example of the electron distribution of an electron droplet in an inhomogeneous field of flux quanta is shown in figure 1. Here we have used \(N_e = 500\) particles and \(N_s = 500\) randomly distributed solenoids with \(\Phi = \pm 10\), furthermore we have assumed that \(\ell_b = 1\). For
half of the solenoids we choose $\Phi = -10$ while the other half is $\Phi = 10$ , representing the attractive and repulsive electron-flux interactions respectively. From figure 1 we can see the electron droplet forming ‘finger’ shapes. In a homogeneous magnetic field the electrons prefer to clump and form a circular droplet, however the inhomogeneous distribution of the solenoids breaks the droplet apart, resulting in a fractal shape. The equilibrium of the Monte Carlo simulation is reached in approximately 40000 simulation steps. To estimate the fractal dimension $D_f$ of the obtained shapes from the Monte Carlo simulation we make use of the scaling relation:

$$S \sim R^{D_f}, \quad (3)$$

where $S$ is the volume of the fractal and $R$ is the radial distance from the origin. We extract the fractal dimension $D_f$ from calculating the area $S$ of the fractal within a circle of radius $R$. The result for two independent electron droplets are shown in figure 2. Each fractal contains 500 electrons, however the underlying distribution of flux quanta is different. From an average over 6 different droplets consisting of 500 electrons, we obtain $D_f = 1.68 \pm 0.04$. This result is in agreement with the typical fractal dimension for DLA fractals ($\sim 1.7$). Our findings suggest that indeed equilibrium Monte Carlo simulations can effectively simulate non-equilibrium DLA fractals. The important note here is that the random potential in the Monte Carlo is the crucial element to simulate the fractal shapes. The randomness in the potential hence reflects the random growth process in the DLA simulation. This outcome can be intuitively understood since DLA fractals are generated by two key ingredients. Firstly the attractive interaction between particles, which leads to the formation of a DLA cluster. Secondly, the growth of the droplet mainly occurs at the tip/perimeter of the cluster. The attractive interaction is effectively governed by the magnetic screening, this is second term in equation 2. The growth at the perimeter is led by the presence of a Coulomb type interaction which prevents the droplet to collapse into circular droplet, this is covered by the first and third term in equation 2.

![FIG. 2: The fractal dimension $D_f$ extracted from a linear fit of $\ln(S)$ versus $\ln(R)$. The inset images in the upper left and lower right corner show the shape of the corresponding fractal ($N_e = 500$). The fingering of the two electron droplets are different since the distribution of flux quanta is randomised.](image_url)

**Experiments.**- With an atomic force microscope (AFM) we investigated peculiar shapes appearing on the surface of hydrogenated epitaxial graphene on silicon carbide as shown in figure 3. To exclude the possibility that we observe aggregation of hydrogen atoms, or fractal growth of a hydrogen crystal, we would like to mention that the AFM does not simply reflect the positions of the hydrogen atoms. Instead we believe it is related to the charge density distribution, this assumption is supported by the fact that the measured height by AFM is an order of magnitude larger than the geometrical dimension of the protrusion caused by a hydrogen adsorbate. Furthermore STM studies of hydrogenated graphene do not show fractal adsorption of the hydrogen atoms, also diffusion of atomic hydrogen on graphitic surfaces has been proven to be difficult.

The fractal dimension is determined by an analysis of the fractal its perimeter $\Omega$ versus its surface area $S$. For a perfect circle we know that $\Omega \sim S^{1/2}$ while for a straight line we expect $\Omega \sim S^1$. Therefore the fractal dimension...
that we obtain experimentally, $D_{f,\Omega}$, can be extracted from the scaling $\Omega \sim S^{\frac{1}{2}D_{f,\Omega}}$, where $1 \leq D_{f,\Omega} \leq 2$. Starting from epitaxial graphene with a hydrogenation time of 3 minutes at the cracking temperature of approximately 1000 K (3 a) we increase the treatment time to 30 minutes at a temperature of 900 K and 1000 K (3 b and c respectively). The ensemble of analysed fractals for each sample is shown in the second row (the green coloured perimeter highlights the fractal shapes). The fractals at the edge are not taken into account in the analysis. Also, small electron droplets ($\leq 1000 \text{ nm}^2$) are not included in the averaging process. The third row shows the $\log(\Omega)$ versus $\log(S)$ plot, where we use the slope to calculate the fractal dimension $D_{f,\Omega}$.

We find for the shortly hydrogenated sample, shown in figure 3a), a fractal dimension $D_{f,\Omega} = 1.68 \pm 0.03$. This value overlaps with the previously obtained fractal dimension of our simulated droplets by the Monte Carlo simulation. This is a clear indication that the observed fractal shapes are viscous fingers of an electron droplet. When the size of the viscous fingers becomes larger, interactions with surrounding droplets start to influence the fractal dimension, hence the obtained fractal dimensions for figure 3 b) and c) deviate from the shortly hydrogenated sample and the simulation result. For figure 3 b) and c) we find a fractal dimension of $D_{f,\Omega} = 1.58 \pm 0.02$ and $D_{f,\Omega} = 1.62 \pm 0.03$ respectively. The lower $D_{f,\Omega}$ can be attributed to the fact that the electron droplet cannot grow radially since the growth is obstructed by a neighbour droplet. As a consequence the perimeter of the fractal is reduced, leading to a lower fractal dimension.

In summary, we have shown the first experimental observation of viscous fingers of an electron droplet in hydrogenated epitaxial graphene. The emergence of viscous fingers is a strong indication of the presence of inhomogeneous pseudo-magnetic fields. The latter supports the theoretical findings that predict strong pseudo-magnetic fields to be present in hydrogenated graphene systems. Moreover our results suggest that hydrogenated epitaxial graphene is a quantum Hall system at room temperature without any externally applied magnetic field. This opens a new world of possibilities to study (fractional) quantum Hall effects and exotic strongly correlated electron systems.

FIG. 3: AFM topography images of three hydrogenated epitaxial graphene samples. The samples are fabricated for different hydrogen treatment duration and cracking temperature. The first row shows the AFM topography ($700 \text{ nm} \times 700 \text{ nm}$), the second row the fractal shapes that are used for the fractal analysis and the third row the diagrams which are used to determine $D_{f,\Omega}$.