Spintronics and thermoelectrics in exfoliated and epitaxial graphene
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Chapter 2

Spin transport

Abstract

This chapter gives an introduction to the basic concepts of spin transport. The focus is on the nonlocal spin valve, which is an all-electrical, experimental scheme that is very suitable for determining spin transport properties of many materials, including graphene. The nonlocal spin valve forms the basis of the experimental work of chapters 5-8. This chapter subsequently treats spin diffusion, spin relaxation, spin injection and detection schemes and spin precession. The final section gives an overview of spin transport in graphene.

An electric current is said to be spin polarized when the total current $j$ is made up out of two contributions: $j_{\uparrow} \neq j_{\downarrow}$ (this description uses current densities $j$, rather than currents $I$). The $\uparrow$ and $\downarrow$ arrows represent the spin $+\hbar/2$ (spin up) and $-\hbar/2$ (spin down) of its constituent electrons along an arbitrary axis. The total (charge) current density is given by $j = j_{\uparrow} + j_{\downarrow}$ and the spin current density is then defined as $j_S = j_{\uparrow} - j_{\downarrow}$. If $j = 0$ but $j_S$ is not, the current is a pure spin current. This is depicted in Figure 2.1.

A spin current will exist as long as there is no interaction between a spin and its environment that causes a change in the spin direction of the carriers (spin-flip), also known as spin relaxation. Spin relaxation processes are the reason that in real materials spin currents can not exist for a very long time, nor travel over very long distances.

Analogous to how an electrostatic potential $V$ causes the flow of a charge current, a spin current is accompanied by a spin accumulation $\mu_S$. Ohm’s law states that:

$$\vec{j} = \sigma \vec{E} = -\sigma \nabla V = \sigma \nabla \mu/e,$$

(2.1)
in which $\sigma$ is the conductivity, $\vec{E}$ the electric field and $\mu$ the electrochemical potential. Because $\sigma$ is determined by the density of states at the Fermi level $\nu(E_F)$, it can in principle be spin dependent: $\sigma_{\uparrow} \neq \sigma_{\downarrow}$. This is for instance the case in a ferromagnetic metal, which has a density of states that is intrinsically spin-split. As a consequence, a charge current in a ferromagnet is always spin-polarized. In a nonmagnetic material, the density of states for both spin polarities is equal. However, it is possible to...

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*aIn this thesis, the direction along which spin up and spin down are defined is determined by the magnetization direction of the spin injector.*
Figure 2.1: Examples of a pure charge current density $j$ and a pure spin current density $j_S$. (a) The charge current transports charge carriers from left to right due to an electrostatic potential. Their is no transport of angular momentum, because the spin of the carriers is randomized. (b) On the left there is a spin accumulation due to an excess of carriers with a certain spin direction. The right depicts the spins in the equilibrium situation. Due to diffusion, the carriers will spread out through the material, effectively transporting angular momentum, but no net charge is transported.

bring the system out of its equilibrium situation, creating a small excess of one spin species. In that case, the electrochemical potential of one of the spin channels is slightly raised, while the other one is slightly lowered.

The contribution of both spin polarities to the total current density is given by:

$$\vec{j}_{\uparrow\downarrow} = \sigma_{\uparrow\downarrow} \nabla \mu_{\uparrow\downarrow}/e. \tag{2.2}$$

Here, $\mu_{\uparrow}$ and $\mu_{\downarrow}$ are the electrochemical potential for the spin up and the spin down channel. This allows for a definition of the non-equilibrium spin accumulation in non-magnetic metals as the difference between these two electrochemical potentials. Its magnitude is:

$$\mu S = \mu \uparrow - \mu \downarrow. \tag{2.3}$$

In the presence of a spin accumulation, simultaneously a net magnetization $\vec{M}$ exists, due to the excess of electrons with one spin direction (see Figure 2.2b)). Its magnitude is given by:

$$|\vec{M}| = \mu_B v(E_F)\mu_S/2, \tag{2.4}$$
with $\mu_B$ the magnetic dipole moment of one electron, called the Bohr magneton. Because the spin accumulation is associated with the magnetization $\vec{M}$ and thus interacts with magnetic fields, the spin accumulation can point along any direction and is therefore commonly described as a vector $\vec{\mu}_S$.

![Figure 2.2: Density of states $\nu(E)$ for spin up and spin down electrons in a nonmagnetic metal (a) when in equilibrium and (b) when there is a spin accumulation $\mu_S$, which means there is a difference in the chemical potentials $\mu_\uparrow$ and $\mu_\downarrow$. $E_F$ is the Fermi energy. The shaded area contributes to a net magnetization $\vec{M}$.](image)

In a diffusive spin transport channel, the spin accumulation is described by the Bloch equation:

$$\frac{d\vec{\mu}_S}{dt} = D\nabla^2\vec{\mu}_S - \frac{\vec{\mu}_S}{\tau_S} + \vec{\omega}_L \times \vec{\mu}_S.$$ (2.5)

This equation plays a central role when analyzing spin transport experiments. The right-hand side consists of three terms: the first term describes the diffusion with diffusion coefficient $D$, the second term accounts for the spin relaxation with $\tau_S$ the spin relaxation time and the final term is used in the case of spin precession due to an applied $B$-field, which happens at the Larmor frequency $\omega_L$. The three terms of the Bloch equation will be explained in the following sections.

### 2.1 Spin diffusion

For pure spin currents, the transport of the spins is diffusive in nature. The measure for how fast the spin accumulation spreads out through the material is given by the diffusion coefficient $D$. According to the Einstein relation for (negatively) charged particles:

$$D = \frac{\mu k_B T}{e} = \frac{\sigma k_B T}{ne^2}.$$ (2.6)
Here, $\mu$ is the charge carrier mobility (not the chemical potential!), $k_B$ Boltzmann’s constant, $T$ the temperature and $n$ the charge carrier density. This description holds for charged particles that behave classically. The conduction electrons of metals and doped semiconductors however, form a gas that behaves quantum-mechanically, because the particles fill up the available energy states from below. These conductors are called degenerate. For degenerate conductors (like graphene), the factor $k_B T$ can be replaced by the total energy of the conduction electrons $n \nu(E_F)$, where $\nu(E_F)$ is the density of states at the Fermi energy $\nu(E_F)$. This leads to the Einstein relation for degenerate conductors:

$$D = \frac{\sigma}{\nu(E_F) e^2}. \quad (2.7)$$

The Einstein relation for charges diffusion in degenerate conductors is equally valid for spins, under the condition that the diffusive transport processes for charge and spin are the same. In later chapters it will turn out that this condition is not necessarily true, but that the picture is in some cases a bit more complex. In these specific cases, it is useful to make a distinction between the diffusion coefficient for the charge carriers $D_C$ and the diffusion coefficient for the spins $D_S$.

Knowledge of $D$ in combination with the spin relaxation time $\tau_S$ makes it possible to calculate the average distance that spins can travel in a material before being lost due to relaxation:

$$\lambda_S = \sqrt{D \tau_S}. \quad (2.8)$$

This is the spin relaxation length $\lambda_S$, which determines the maximum length scale of practical spintronic devices.

### 2.2 Spin relaxation

The spin relaxation time $\tau_S$ is the characteristic time it takes for a spin system that is brought out of equilibrium to fall back to its initial conditions. The three original Bloch equations distinguish between a spin-lattice relaxation time $T_1$ and a spin dephasing time $T_2$. However, in many cases, and throughout this thesis, the relation $T_1 = T_2$ holds and they can be both replaced by a single $\tau_S$. In that case the three equations are equal to the vectorial description of Equation 2.5.

Spin relaxation occurs when an ensemble of spins transfer angular momentum to their environment through spin-flip events. In nonmagnetic materials, this can be caused by defects that carry spin, by the magnetic moment of the nucleus or by other itinerant spins through electron-electron interaction.

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[b]The original equations were introduced by Felix Bloch. They did not include the diffusive term, which was added later by Carr and Purcell and Torrey.
Moreover, in nonmagnetic materials spin-flip events can take place even in the absence of an extrinsic spin, through the effect of spin-orbit (SO) coupling. A particle undergoes SO coupling when it travels at relativistic speeds, and therefore experiences electric potentials in its surroundings as magnetic fields. The effect on the particle wave function can be described by a relativistic correction to the Schrödinger equation, showing up as a spin dependent term in the Hamiltonian. In solids, SO coupling arises when the spatial inversion symmetry of a crystal is broken. This can be intrinsically related to the crystal structure itself, due to boundaries, impurities or an externally applied electric field gradient.

The two most common types (especially for the case of graphene) of spin relaxation mechanisms under the influence of SO coupling are the Elliot-Yafet (EY) and the Dyakonov-Perel (DP) mechanism.

**Elliott-Yafet relaxation** A scattering event in a solid will change the $k$-vector of the scattered electron but keep its spin intact, when the scattering potential is non-magnetic (i.e. when it does not have a spin term). However, when this potential includes a SO term, the spin of the electron wave function is described by a mixture of $|\uparrow\rangle$ and $|\downarrow\rangle$. With a probability depending on the strength of this mixture, a spin-flip event can occur during the scattering event. Thus, SO coupling can cause spin relaxation during ordinary momentum scattering. This, in short, is the spin relaxation mechanism as described by Elliott and Yafet.

To experimentally investigate if the EY mechanism plays a role in the spin relaxation in a certain material, the relation between $\tau_s$ and the momentum scattering time $\tau_p$ is commonly investigated. The EY mechanism predicts $\tau_s \propto \tau_p$.

**Dyakonov-Perel relaxation** SO coupling in a solid can be described as an effective magnetic field that acts on the transport electrons. The electrons will precess around this field with a Larmor frequency that is dependent on their $k$-vector. Because there is a variation in $k$, the resulting different precession frequencies will be the cause of dephasing. This is the DP spin relaxation mechanism.

A characteristic of the DP mechanism is the fact that spin precession (spin dephasing) happens in between scattering. Moreover, after a (momentum) scattering event, the effective magnetic field term changes along with the change in $k$. Therefore, the direction and frequency of the precession will be randomized. The consequence is that the variance in the precession of all electrons in total (and thus the spin dephasing) decreases, when the number of scattering events increase. This may seem somewhat counterintuitive, but it is the principle that underlies the effect called *motional narrowing*, which occurs when the rate of fluctuations of the randomized field is higher than the Larmor frequency. Due to the motional narrowing effect, the DP mechanism can be distinguished from the EY mechanism by investigating the relation between spin and momentum scattering, which for DP spin relaxation is predicted to be $\tau_s \propto 1/\tau_p$. 

2.3 Spin transport schemes

2.3.1 The nonlocal spin valve

The device geometry used in this thesis to investigate spin transport phenomena is called the nonlocal spin valve. This device can inject and detect spins in nonmagnetic materials using ferromagnetic contact electrodes. The concept was introduced and demonstrated by Johnson and Silsbee in the late 1980’s. An all-metal nonlocal spin valve at room temperature was experimentally realized by Jedema et al. The same scheme was later used to study spin transport in carbon nanotubes and graphene. Currently, the nonlocal geometry is being widely used to study metallic and graphene spintronics.

![Figure 2.3: Schematic representation of a nonlocal spin valve.](image)

Figure 2.3: Schematic representation of a nonlocal spin valve. (a) A characteristic of this geometry is the separation of the charge current circuit (contacts 1 and 2) from the voltage circuit that detects the spin current (3 and 4). (b) By sending a current through the injector, a spin accumulation is created directly underneath the contact. The spin accumulation decays to both sides and can be detected within a distance \( L < \lambda_S \). The detector is sensitive to the spin chemical potential of one of the spin directions, depending on its magnetization. Ideally, the outer contacts are either far away or nonmagnetic.

Figure 2.3 shows a schematic representation of a nonlocal spin valve device. A major advantage of this scheme is that the generation and measurement of spin currents is done purely electrical: spin injection is realized by generating a charge current and spin detection by measuring a voltage. Another advantage is its non-locality: \( j \) and \( j_S \) are spatially separated by detecting the spins outside the current path (see Figure 2.3(a)). In the following paragraphs, the working principle of the nonlocal spin valve will be discussed. Many other experimental schemes that allow for creating and detecting spin transport have been realized in recent years. A few will be briefly discussed in section 2.3.2.
Spin injection  It is possible to inject spins, or to be more precise: to locally induce a spin accumulation, in a nonmagnetic material by sending a charge current $I$ through a ferromagnetic contact electrode into the material. A ferromagnet has a spin-split density of states at the Fermi level, where the transport takes place. Because there are more electronic states of one spin orientation available for the transport, the injected charge current is spin-polarized.\[15\] A spin injector can thus be regarded as a spin current source, with the direction of the spins depending on the magnetization direction of the contact.

The maximum spin accumulation that builds up underneath the contacts can be derived using the concept of a spin resistance $R_\lambda$, which is the resistance that the spins feel over distance $\lambda S$. The magnitude of the spin accumulation directly below the contact (at $x = 0$) is then given by:

$$\mu_0 = \frac{PIR_\lambda e}{2} = \frac{PI\lambda Se}{2\sigma A},$$

(2.9)

with $P$ the spin polarization of the current induced by the contact, given by $P = \frac{j_1 - j_\perp}{j_1 + j_\perp}$ and $A$ the contact area ($\lambda S$ and $\sigma$ are properties of the spin channel). $P$ is a property depending on the specifics of the junction. A detailed study of junction polarization can be found in Reference [19]. The factor 2 is there because spins relax both to the left and to the right, resulting in two relaxation channels in parallel.

Equation [2.9] holds only if the injecting contact is sufficiently decoupled from the transport channel. A low resistive, or transparent, contact electrode causes the spins to flow back into the contact and relax there, effectively decreasing the spin accumulation. This problem of spin relaxation induced by invasive contacts is called conductivity mismatch, which can completely diminish the spin accumulation below a detectable level. The channel can be decoupled from the injector by inserting a thin insulating layer in between them, through which the spins are injected by tunneling.\[20\] A brief analysis of the conductivity mismatch problem can be found further in this section. Elsewhere in this chapter, contacts can be considered noninvasive.

Spin detection  In principle, one can detect the spin accumulation in the channel using a ferromagnetic contact by the inverse of the injection mechanisms. Due to their higher electrochemical potential, the majority spins in the channel are available for transport into a detector circuit. By short-circuiting the spin channel, a current is generated that is proportional to the spin accumulation.\[15\]

It is also possible to detect the spin accumulation using a voltage probe, which is the method depicted in Figure [2.3]. In fact, this is the method most commonly used in the nonlocal spin valve geometry (and throughout this thesis). In this case, the Fermi level of the ferromagnet will align with the electrochemical potential of the spins with the same direction as the contact magnetization, thereby inducing a
(nonlocal) voltage proportional to the spin accumulation:

\[ V_{\text{nl}} = \frac{P\mu_S}{e} \]  

(2.10)

**Spin transport** The presence of a gradient in the spin accumulation will produce a steady-state spin current. Figure 2.3(b) shows that sending a current through the injection circuit creates a spin accumulation \( \mu_0 \) under the injector contact, given by Equation 2.9. Far away from the injection point the spins will be completely relaxed to their equilibrium situation, which means no spin accumulation at all. Thus, a gradient in \( \mu_S \) is created in the \( x \)-direction, resulting in a spin current. The spin accumulation as a function of the distance \( x \) to the injector (without the presence of any external magnetic fields) is given by:

\[ \mu_S(x) = \mu_0 e^{-x/\lambda_S}, \]  

(2.11)

The spin accumulation can be detected if the detection circuit is placed within a distance of the order of \( \lambda_S \). The signal of interest is the nonlocal resistance:

\[ R_{\text{nl}} = \frac{V_{\text{nl}}}{I} = \frac{P\mu_S(L)}{2le}, \]  

(2.12)

in other words: \( V_{\text{nl}} \), that is proportional to the spin accumulation according to Equation 2.10, normalized by the injected charge current \( I \), at distance \( L \) from the injector. Combining 2.9, 2.11 and 2.12 gives:

\[ R_{\text{nl}} = \pm \frac{p^2\lambda_S}{2\Lambda\sigma} e^{-L/\lambda_S}, \]  

(2.13)

The sign relates to the orientation of the magnetization direction of the detector relative to the injector, being positive for a parallel configuration (\( \uparrow \uparrow \)) and negative for an anti-parallel one (\( \uparrow \downarrow \)). A necessary condition for expression 2.13 is that the outer electrodes in the figure are insensitive to the built-up spin accumulation, either by increasing their distance to \( \gg \lambda_S \) or by making them nonmagnetic.

It is possible to switch the magnetization direction of the contacts one by one, by sweeping an in-plane magnetic field. This can be realized by fabricating contacts with different thicknesses and thus a different coercivity (which is the strength of the external field necessary to change their direction). The typical switching behavior between parallel and anti-parallel configuration can be seen in Figure 2.4.

One can calculate \( \lambda_S \) by measuring the spin signal as a function of distance to the injector \( x \), which should decay exponentially according to Equation 2.11. Using charge transport measurements it is possible to independently measure \( D \), making it possible to calculate \( \tau_S \) with the use of Equation 2.8.
Figure 2.4: Typical measurement of a nonlocal spin valve signal. At specific in-plane magnetic field values, a switch occurs between the parallel (↑↑) and the anti-parallel (↑↓) magnetization states of the injector and the detector. This manifests in a sudden change in the nonlocal resistance $R_{nl}$. Image adapted from Reference 21.

**Conductivity mismatch** Earlier in this section it was described how spin injection can be realized by sending an electrical current from a ferromagnetic metal into a nonmagnetic material. In practical realizations of this injection scheme, the effectiveness can be largely reduced by an effect called conductivity mismatch. Conductivity mismatch is present when there is a difference between the spin resistance of the injecting ferromagnet and the spin channel. This is for instance the case when the ferromagnet is a metal and the spin channel is a semiconductor.

A simple exercise can give an idea about the origins of conductivity mismatch. In a spin channel, spins travel on average a distance $\lambda_S$. Therefore, they feel a spin resistance:

$$R_{\lambda} = \frac{\rho \lambda_S}{A}. \quad (2.14)$$

Here, $\rho$ is the resistivity and $A$ the cross-sectional area. For two-dimensional materials this is:

$$R_{\lambda} = \frac{R_{sq} \lambda_S}{w}, \quad (2.15)$$

with $R_{sq}$ the square resistance and $w$ the channel width.

Consider now the case for a ferromagnetic contact on a two-dimensional spin channel as depicted in Figure 2.4(a). For a given spin accumulation $\mu_S$, the spin current divides between the relaxation path in the channel and in the contact, according to a current divider as in the equivalent circuit of Figure 2.4(b). The ratio between the spin currents flowing into the channel $I_S^{ch}$ and back into the ferromagnet $I_S^{FM}$, is
Figure 2.5: (a) Schematics for the conductivity mismatch of a ferromagnet and a sheet of 2D material like graphene. The dark gray and red regions represent the spin resistances for both materials. (b) Equivalent circuit for a spin current divider.

given by:

$$\frac{I_{ch}^{S}}{I_{FM}^{S}} = \frac{2R_{ch}^{FM}}{R_{ch}^{ch}} = \frac{\rho}{R_{sq}} \frac{\lambda_{FM}^{ch}}{\lambda_{S}^{FM}} \frac{2}{w_{FM}}$$  \hspace{1cm} (2.16)

In practice, this means that in order to circumvent conductivity mismatch one ideally needs a low resistive channel with $\lambda_{ch}^{S} \sim \lambda_{FM}^{S}$ or smaller. When $\lambda_{S}^{ch} > \lambda_{FM}^{S}$, as is the case with graphene and also with semiconductors like silicon, a high resistive injector is needed. One option would be to use a ferromagnetic semiconductor. These materials however have the disadvantage of a low ferromagnetic breakdown (Curie) temperature.\(^c\)

A second solution to circumvent conductivity mismatch, and the method widely used in nonlocal geometries, is the insertion of a thin insulating material as a tunnel barrier between the contacts and the channel.\(^2\) The key issue is to construct a contact with a resistance that is high enough to not influence the created spin accumulation in the channel, but not too high because a higher contact resistance decreases the signal-to-noise ratio. Usually, a thin oxide barrier of $\sim 0.8$ nm does the job. The insertion of a thin oxide layer usually results in a non-uniform contact, where most of the transport takes place through pinholes and therefore does not have tunneling $I$-$V$ characteristics. A better performance was achieved for graphene devices using more complex fabrication method.\(^2\)

Conductivity mismatch was first described in detail by Schmidt et al.\(^2\) In their work, they showed the effect by solving the diffusion equations for the equivalent resistor network of a simple device geometry. Popinciuc et al.\(^2\) also described the effect in detail in graphene spin devices, where they introduced the parameter $R = \frac{R_{C}}{R_{sq}} w$ (here, $R_{C}$ is the contact resistance) as a measure of contact induced spin relaxation. Maassen et al.\(^2\) showed how to take into account contact induced relax-\(^c\)Another way to overcome conductivity mismatch is by injecting hot electrons.\(^4\)\(^5\) In this scheme, the spins are well above the Fermi energy where their transport behavior is ballistic. This means that there is now inelastic scattering and thus the description of an Ohmic spin resistance breaks down.
ation in spin precession experiments. Guimarães et al.\textsuperscript{29} showed that the effect is stronger when the spin transport is in the oD regime, that is, when $\lambda_S$ is larger than the device dimensions.

2.3.2 Other spin transport schemes

Up to now, the focus of this thesis was on the nonlocal spin valve from Figure 2.3, as it is the geometry used in the experimental chapters. However, there are a number of other experimental methods to create and/or detect a spin accumulation in a non-magnetic material. In this section, three common examples of other spin transport methods will be briefly summarized. These few examples are limited to only purely electrical schemes.

**Two-terminal spin devices** The four-terminal (4T) nonlocal geometry is very well-suited for unambiguous studies of spin transport properties. One could easily think of a simpler geometry consisting only of the active parts, which are the injector, the channel and the detector. In fact, this geometry with only two electrodes is very well-known and even far more conventional than its non-local counterpart. This has several reasons. The first one is historical: it is the geometry used for the discovery of the giant magnetoresistance and many other spintronic effects such as tunnel magnetoresistance and spin transfer torque.\textsuperscript{30} A second reason is that 2T devices are used for current perpendicular to plane experiments in pillar structures, which are for instance useful for materials with short spin lifetimes.\textsuperscript{31} A third reason is that the 2T spin valve is by far the most dominant of all spintronic applications. All reading of magnetic data in hard disks is currently done by using a form of the conventional local spin valve effect.\textsuperscript{32}

In a 2T geometry, the resistance of the device can have two distinct resistance levels $R_{\uparrow\uparrow}$ and $R_{\uparrow\downarrow}$ for the two electrodes in parallel and anti-parallel orientation respectively. The magnetoresistance MR of the device is then given by:

$$MR = \frac{\Delta R}{R} = \frac{R_{\uparrow\uparrow} - R_{\uparrow\downarrow}}{R_{\uparrow\uparrow} + R_{\uparrow\downarrow}},$$

(2.17)

with $\Delta R$ the spin dependent signal.

For fundamental studies, the 2T device in lateral geometry suffers from a few drawbacks that are related to its local nature. Spin transport through the channel is always accompanied by a charge current, which can make the interpretation of the experimental data a delicate matter. In spin valve experiments a number of spurious effects can exist that contribute to the MR value, but are not caused by the presence of a spin accumulation. Examples are local Hall effects due to stray fields or interfaces,\textsuperscript{16}\textsuperscript{33} magneto Coulomb effects,\textsuperscript{34} and interference.\textsuperscript{35} Furthermore, in the regime where $R_C \sim R_{\lambda}^{\text{th}}$, the spin relaxation length cannot be determined from a measurement of the magnitude of the MR alone.\textsuperscript{36}\textsuperscript{37}
Three-terminal spin devices  In semiconductors it has been problematic to perform 4T nonlocal spin transport experiments due to the conductivity mismatch that is present for the high resistive semiconductor channel. In that light the three-terminal (3T) geometry was developed, a scheme that makes use of the same contact to create and detect the spin accumulation\cite{29,40}. Thus, the 3T geometry can be viewed as a version of the 4T non-local geometry, in the limit where contact spacing $L \rightarrow 0$. This geometry (see Figure 2.6(a)) has been successfully used to inject and detect spins into semiconductors at room temperature\cite{41,43}.

![Figure 2.6: The 3T geometry](image)

In the 3T geometry, a spin accumulation is created underneath the contact in a similar fashion as described earlier. A 3T scheme as in Figure 2.6(a) measures the contact resistance, which is in part determined by the induced spin accumulation. The contribution of the spin accumulation to the measured resistance can be separated by sweeping an out-of-plane $B$-field. The field destroys the spin accumulation due to dephasing of the spins, resulting in a Lorentzian shaped curve due to the
so-called Hanle effect\(^d\). Its width can be related to the spin relaxation time using the expression:

\[
\mu_s(B) = \frac{\mu_s(0)}{1 + (\omega_L \tau)_s^2}.
\] (2.18)

A fit with the experimental data gives a lower limit on \(\tau_s\).\(^{41}\)

The advantage of this method is the possibility to measure spin transport properties directly underneath the contact, where the spin accumulation is the largest. Also, the geometry does not necessarily involve nanoscaled devices, because the measured signal does not depend on the length \(L\) of the device, but on the product of the spin resistance and the contact area.\(^{41}\)

The downside is that a number of effects can influence the width of the Lorentzian Hanle curve.\(^{41,44}\) and that a Hanle like curve can arise from effects that are not spin-related.\(^{45}\) The picture becomes even more complex, because an effect called the inverted Hanle effect has been observed, where an in-plane \(B\)-field recovers the spin accumulation (see Figure 2.6(b)). The mechanism behind the inverted Hanle effect however, is still under debate.\(^{44,45}\)

**Spin Hall effect** The spin Hall effect (SHE) is the creation of a spin accumulation by means of a perpendicular charge current. This happens for instance in the presence of scattering on impurities that induce sufficiently large SO coupling. In the presence of such SO scattering, the carriers will have a preferred scattering direction, depending on their spin orientation. Thus, spins accumulate on either side of the material, effectively transporting angular momentum from one side to the other. This built-up spin accumulation can then be used to drive a spin current that flows perpendicular to the charge current.\(^{47}\) Another cause for the SHE is the effective magnetic field felt by the moving electrons in solids that intrinsically have SO coupling. The resulting spin-splitting of the electronic bands due to this effective field is called the Rashba effect, and it is present in solids that have a breaking in the inversion symmetry in the crystal lattice.\(^{48}\) The effectiveness of the conversion of a charge current into a transverse spin current is given by a quantity called the Spin Hall angle.

The SHE was predicted in 1971 by Dyakonov and Perel.\(^{50}\) An experimental scheme was later proposed\(^{47,51}\) and eventually experimentally verified.\(^{52,53}\) The reciprocal effect of a built-up voltage originating from a transverse spin current called the inverse spin Hall effect (ISHE), was demonstrated using a purely electrical method.\(^{49,54}\) Recently, the SHE and ISHE have become a powerful method to induce and/or detect spin currents in a range of materials. A recent review about the emergent field of the SHE and ISHE has been written by Sinova et al.\(^{55}\)

\(^d\)The more general case of the Hanle effect including diffusion will be described in detail in section \(2.4\).
2. Spin transport

Figure 2.7: Experimental scheme of electronic measurement of the Inverse Spin Hall effect. The ferromagnetic contact injects a spin current. Due to SO coupling, charge carriers from the charge current accumulate preferably either to the left or to the right, depending on their orientation. If the current is spin polarized (due to the ferromagnetic lead), this will result in a voltage difference between the two side arms. Reprinted by permission from Macmillan Publishers Ltd: Reference 49 copyright(2006).

2.4 Spin precession

The Hanle effect. It is possible to experimentally determine the spin transport properties $D$ and $\tau_S$ (and thus $\lambda_S$) by measuring the nonlocal resistance as a function of an out-of-plane $B$-field. In this case, the orientation of the spins will change on the way from injector to detector due to spin precession, as depicted in Figure 2.8(a). For diffusive transport, carriers have a distribution of transit times from injector to detector and therefore experience a dephasing of their spin orientation. This dephasing phenomenon is called the Hanle effect. The spin transport properties can then be extracted from the experimental data by a comparison with the solution of the Bloch equation (Equation 2.5), with the applied field in the $z$-direction and the injected spins in the $xy$-plane.

Under steady state conditions, the Bloch equation reads:

$$\bar{\partial} = D \nabla^2 \bar{\mu}_S - \frac{\bar{\mu}_S}{\tau_S} + \bar{\omega}_L \times \bar{\mu}_S. \tag{2.19}$$

It describes the spin accumulation in a diffusive spin channel with diffusion coefficient $D$, relaxation time $\tau_S$ and the Larmor frequency $\bar{\omega}_L = \mu_B g \bar{B}/\hbar$, where $\mu_B$ is the Bohr magneton, $g$ the Landé $g$-factor, $\hbar$ the reduced Planck’s constant and $\bar{B}$ an applied magnetic field.

The original Hanle effect is the creation or destruction of linear polarization in light scattered from an atom in the presence of a magnetic field. The similarity with the experiments described here, is that the effects are both governed by dephasing of an ensemble of electron spins.
This method for determining spin transport properties is independent of the method described in section 2.3.1. Combining both methods can be used to check certain assumptions, for instance if g = 2 and if the diffusion of charge and spin is the same, or to be more precise, if $D_C = D_S$.

**Solutions to the Bloch equation** To find an analytic expression for the measured detector signal of Equation 2.12 in the presence of an out-of-plane field $B_z$, one has to find the $y$-component of $\mu_S$, because the signal scales with the spin accumulation in the direction of the detector magnetization of the detector. Solving the Bloch equation for $\mu_S,y$ gives:

$$\mu_{S,y} = \frac{\mu_L}{f(b)} \left[ \sqrt{1 + f(b)} \cos \left( \frac{lb}{\sqrt{1 + f(b)}} \right) - \frac{b}{\sqrt{1 + f(b)}} \sin \left( \frac{lb}{\sqrt{1 + f(b)}} \right) \right] e^{-l\sqrt{1+f(b)}},$$

(2.20)

using $\mu_L = \mu_S(x = L, B = 0)$, $f(b) = \sqrt{1 + b^2}$, $b \equiv \omega_L \tau_S$ and $l \equiv L/(\sqrt{2D} \tau_S)$. This rather lengthy expression describes the $B_z$-dependence of the spin accumulation under the detector. The nonlocal resistance which is measured in the experiment can be obtained by using Equation 2.12. The result is commonly referred to as a Hanle curve, which is plotted in Figure 2.9(a). It can be used as a fitting curve for the data obtained from a spin precession experiment depicted in Figure 2.8(b).

Due to the complexity of Equation 2.20 it can be hard to see the relation between the shape of the Hanle curve on the one hand, and the spin transport properties $D$.

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1This solution was first given in Reference 18 but can be traced back even further to the works of Lewis and Carver 57 on spin transmission resonance. For a comprehensive approach for finding the nonlocal resistance using the diffusion picture see Reference 58.
and $\tau_S$ on the other. The overall shape of the Hanle curve is uniquely defined by the ratio $\lambda/L$. The Hanle curve has a clearly observable zero-crossing when the detector is placed more than one relaxation length away from the injector ($L > \lambda_S$). Because $\lambda_S = \sqrt{\tau_S D}$, a change in either $\tau_S$ or $D$ will have an effect on the shape as well.

Roughly said, $\tau_S$ is related to the width of the Hanle curve (Figure 2.9(b)). The effect of $D$ is a bit more subtle. A sufficient increase in $D$ results in a longer $\lambda_S$ and therefore the zero-crossings become less apparent (Figure 2.9(c)). In the limit of $L \ll \lambda_S$, the transport can be regarded as oD and the spin accumulation underneath the injector and the detector is approximately the same (Figure 2.9(d)). The field dependent behavior of such a device is very similar to the 3T geometry described in section 2.3.2 and, if $D$ is sufficiently small, the Hanle curve can be approximated with a Lorentzian.

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8The same argument can be made for an increased $\tau_D$, but then the effect on the width of the curve is dominant.
Spin precession as a measurement tool  The Hanle precession experiment can be used to derive spin transport properties of a material. The measured relaxation time $\tau_S$ can give information about the important relaxation mechanisms in the material, as described in section 2.2. Additionally, Hanle precession is a suitable method to investigate all intrinsic properties of a material, or modifications to it, that have an effect on the Larmor precession frequency. These include $B$-fields due to magnetic moments and modifications to the $g$-factor due to many body effects like electron-electron interaction.

One of the possibilities is to measure paramagnetic moments that are directly coupled to the spin channel. In this case, spins experience a torque by exchange interactions with the magnetic moments that act as a randomly fluctuating magnetic field. This field effectively enhances the $g$-factor, thereby narrowing the Hanle curve. Ferromagnetic order in these moments will show up in a similar fashion, but in addition causes a hysteresis loop due to the reminiscent magnetization. Magnetic moment in graphene for instance can originate from vacancies or adatoms that change the nonmagnetic carbon $sp^2$ bonds into an $sp^3$ bond which has a spin 59,60.

Another example is the effect of nuclear fields due to hyperfine interaction. In equilibrium, these nuclear spins are randomized, but they can align along an applied field or be polarized by dynamic nuclear polarization (which is achieved by interaction with polarized electrons). The nuclear field effects the Larmor frequency and thereby the shape of the Hanle curve, for instance resulting in asymmetries when it is under an oblique angle with the applied field 40,61.

In this thesis, Hanle measurements are used to probe a more exotic phenomenon, namely the effect of localized states on spin transport, which can be observed in epitaxial graphene on silicon carbide (see chapter 6–9).

2.5 Spin transport in graphene

This section gives an overview of the experimental works on graphene spintronics, a field that started in 2007 with the work of Tombros and colleagues 17. Recently, there have been a couple of reviews on the topic, which can be found in the references 62–64.

Exfoliated graphene  In 2007, room temperature spin valve and Hanle precession measurements on exfoliated graphene on a doped Si + 300 nm SiO$_2$ substrate revealed a $\tau_S$ of 200 ps, a $D$ of 200 cm$^2$s$^{-1}$ and a $\lambda_S$ of 2 $\mu$m 17. Subsequently, properties for bilayer 65,66 and multilayer graphene 67 were found (see table 2.1).

While these property were remarkable, theoretical studies predicted even higher values for $\tau_S$ and thus $\lambda_S$. These theoretical predictions took into account a number of factors limiting the spin relaxation time, including SO coupling caused by ripples and scattering centers 68,72 charged impurities and optical surface phonons of the substrate 73 and spin relaxation due to interaction with local magnetic moments 68,72,73.
Furthermore, the SiO$_2$ substrate with its high roughness and intrinsic charge impurities leads to a low charge carrier mobility $\mu$. The presence of polymer remains from the nanofabrication process has a similar effect. Following Equation 2.6, low mobility devices have a small $D$, in turn limiting $\lambda_S$.

![Figure 2.10: Three different ways of improving the spin transport properties of graphene spin valves. (a) An example of an improved tunnel contact using a TiO$_2$ seeded MgO barrier. Reprinted with permission from Reference [23] Copyright (2010) by the American Physical Society. (b) Spin transport device of graphene that is freely suspended above the substrate. (Reprinted with permission from Reference [74] Copyright (2012), American Chemical Society) (c) Spin transport device of graphene with a flake of thin h-BN as the substrate material. Reprinted with permission from Reference [75] Copyright (2012) by the American Physical Society.](image)

Several experimental works have investigated the dominant causes of spin relaxation in graphene. One of the strategies was to increase the efficiency of the spin injection and detection electrodes. Common spin transport devices make use of ferromagnetic electrodes with a thin, mostly nonuniform, AlO$_2$ barrier with pinholes. The device performance was improved by changing to more uniform TiO$_2$ barrier and even to contacts in the tunneling regime using TiO$_2$ seeded MgO barriers, shown in Fig. 2.10(a). Recently, hexagonal boron nitride (h-BN) of only a few atomic layers thick seems to be a promising material for making tunnel barriers because of its suitable tunneling characteristics.

Another strategy was to study higher quality graphene by removing the substrate or, instead of SiO$_2$, using the more suitable h-BN (Fig. 2.10(b)-(c)). Such devices usually consist out of a high quality inner region between injector and detector, and an outer region (not suspended or encapsulated) which has the electronic and spintronic properties of regular graphene on SiO$_2$. Due to the diffusive nature of the spins, the influence of the outer regions is significant. Thus, the extracted values for $\tau_S$ can be assumed as an underestimation of the true value.

To gain more insight in the relaxation mechanisms in graphene, the effect of adatoms and defects to the spin transport properties was addressed in a number of works. These studies included the effect of gold clusters acting as charge impurity scatters and partially hydrogenated graphene, creating magnetic moments. Also, the effect of relaxation due to nuclear spins was excluded, by investigating
graphene with 100% of its atoms consisting of the spin carrying isotope $^{13}\text{C}$.

<table>
<thead>
<tr>
<th>Graphene type</th>
<th>$\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$D_S$ (cm$^2$ s$^{-1}$)</th>
<th>$\tau_S$ (ps)</th>
<th>$\lambda_S$ (µm)</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exfoliated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>single layer</td>
<td>2 000</td>
<td>130 – 210</td>
<td>100 – 170</td>
<td>1.5 – 2</td>
<td></td>
<td>[7]</td>
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<tr>
<td></td>
<td>2 000</td>
<td>140 – 180</td>
<td>450 – 500</td>
<td>2.5 – 3</td>
<td>MgO tunneling contacts</td>
<td>[23]</td>
</tr>
<tr>
<td></td>
<td>100 000</td>
<td>1 000</td>
<td>&gt;150</td>
<td>4.7</td>
<td>suspended</td>
<td>[74]</td>
</tr>
<tr>
<td></td>
<td>40 000</td>
<td>520</td>
<td>390</td>
<td>4.6</td>
<td>on h-BN</td>
<td>[75]</td>
</tr>
<tr>
<td></td>
<td>15 000</td>
<td>800</td>
<td>1 900</td>
<td>12.1</td>
<td>h-BN incapsulated</td>
<td>[80]</td>
</tr>
<tr>
<td>bilayer</td>
<td>400 – 1 300</td>
<td>130</td>
<td>447</td>
<td>2.4</td>
<td></td>
<td>[66]</td>
</tr>
<tr>
<td>few layer</td>
<td>–</td>
<td>~100</td>
<td>100 – 500</td>
<td>3</td>
<td>transferred to SiO$_2$, single and bilayer</td>
<td>[82]</td>
</tr>
<tr>
<td>Epitaxial</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>growth by CVD</td>
<td>1 400/2 100</td>
<td>70/63</td>
<td>180/285</td>
<td>1.1/1.35</td>
<td>transferred to SiO$_2$, single and bilayer</td>
<td>[82]</td>
</tr>
<tr>
<td>growth by sublimation</td>
<td>1 900</td>
<td>2.4</td>
<td>1,340</td>
<td>0.6</td>
<td>values modified by localized states (see chapter 5)</td>
<td>[61]</td>
</tr>
<tr>
<td></td>
<td>17 000</td>
<td>-</td>
<td>-</td>
<td>&gt;100</td>
<td>multilayer on C face of SiC, 2T local geometry, at 4K</td>
<td>[34]</td>
</tr>
</tbody>
</table>

Table 2.1: Room temperature spin transport properties of various graphene systems.

**Epitaxial graphene** Graphene that is mechanically cleaved with the Scotch tape method is still regarded as the material with the highest electronic quality. A downside is that the production time per flake area of such a device is very poor. There have also been studies on larger area graphene. Though the dimensions of the spin transport device still have to be in the order of $\lambda_S$, large area graphene makes it possible to create an array of devices on a single chip, which is important for investigating graphene as a possible material for spintronic applications. One of the methods is graphene grown by CVD (chemical vapor deposition) on a copper substrate, which is then subsequently transferred to SiO$_2$. Avsar et al. [82] found this material to behave quite similar to exfoliated graphene.

Another method to produce large area graphene is by sublimation of silicon carbide (SiC). In this case, the SiC also acts as the insulating substrate. Because this graphene type is one of the main topics of this thesis, the growth process and material characterization of epitaxial graphene on SiC is more thoroughly described in chapter 4. Spin transport in such devices is the topic of chapters 5-9.
There are some other works that also study spin transport in epitaxial graphene on SiC. In the work of Birkner et al.\textsuperscript{83} the 4T nonlocal measurements were compared with the 3T geometry as described in section \ref{sec:2.3.2}, showing a good agreement between the two methods. Annealing resulted in contaminations by magnetic particles, leading to a discrepancy between $D_C$ and $D_S$, the diffusion constant measured by charge transport and spin transport respectively. The effect was only observed at lowered temperatures.

Dlubak et al.\textsuperscript{37} used the 2T local technique to arrive at an impressive $\lambda_S$ of up to 285 $\mu$m. The authors attribute the long $\lambda_S$ to the high mobility and the absence of any curvature of the graphene (grown on the C-face of SiC). In a related work it is claimed that spin transport properties of 4T devices underestimate the spin transport properties due to relaxation through the additional, low resistive contacts.\textsuperscript{84} These claims of graphene with substantially improved spin transport properties when compared to other studies show that graphene spintronics is still an active research field.

References


2. Spin transport


