MAGNETIC PROPERTIES OF TWO
DIMENSIONAL MATERIALS: GRAPHENE,
ITS DERIVATIVES AND MOLYBDENUM
DISULFIDE

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Abstract

Graphene, an atomically thin material consisting of a hexagonal, highly packed carbon lattice, is of great interests in its magnetic properties. These interests can be categorized in several fields: graphene-based magnetic materials and their applications, large diamagnetism of graphene, and the heterostructures of graphene and other two dimensional materials. In the first aspect, magnetic moments can be in theory introduced to graphene by minimizing its size or introducing structural defects, leading to a very light magnetic material. Furthermore, weak spin-orbital interaction, and long spin relaxation length make graphene promising for spintronics. The first part of this thesis addressed our experimental investigation in defect-induced magnetism of graphene. Non-interacted spins of graphene have been observed by intentionally introducing vacancies and adatoms through ion-irradiation and fluorination, respectively. The defect concentration or the magnetic moments introduced in this thesis cannot provide enough interaction for magnetic coupling. Furthermore, the spins induced by vacancies and adatoms can be controlled through shifting the Fermi energy of graphene using molecular doping, where the adatoms were alternatively introduced by annealing in the inert environment. The paramagnetic responses in graphene induced by vacancy-type defects can only be diverted to half of its maximum, while those induced by sp³ defects can be almost completely suppressed. This difference is supposed that vacancy-type defects induced two localized states (π and σ). Only the latter states, which is also the only states induced by sp³ defects, involves in the suppression of magnetic moments at the maximum doping achieved in this thesis. The observation through high resolution transmission electron microscope (HR-TEM) provides more information to the hypothesis of the previous magnetic findings. Reconstructed single vacancy is the majority of defects discovered in proton-irradiated graphene. This result verifies the defect-induced magnetic findings in our results, as well as the electronic properties of defected graphene in the literatures. On the other hand, the diamagnetic susceptibility of neutral graphene is suggested to be larger than that of graphite, and vanish rapidly as a delta-like function when graphene is doped. In our result, surprisingly, the diamagnetic susceptibility varies little when the Fermi level is less than 0.3 eV, in contrast with the theory. When the Fermi energy is higher than 0.3 eV, susceptibility then reduces significantly as the trend of graphite. The little variation in susceptibility near the Dirac point is probably attributed to the spatial confinement of graphene nanoflakes, which are the composition of graphene laminates. In the end of this thesis, we discuss the magnetic properties in one of the other two dimensional materials, molybdenum disulfide (MoS₂). It is a potential material for graphene-based heterostructure applications. The magnetic moments in MoS₂ are shown to be induced by either edges or vacancies, which are introduced by sonication or proton-irradiation, respectively, similar to the suggestions by theories. However, no significant ferromagnetic finding has been found in all of our cases.
List of Publications


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I declare that no portion of this work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university of other institute of learning

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Chapter 1

Introduction to the Properties of Graphene and MoS$_2$

Dimensionality plays an important role in determining properties of materials. The electronic structures change dramatically when varying dimensions of materials. The observations in optics, electronics, and magnetism reflect these changes [1]. Two dimensional materials are relatively important among all dimensions, since they can be viewed as basis of other dimensional compounds. Take graphene as an example. Graphene is a two dimensional (2D) tightly packed hexagonal carbon sheet which can be wrapped into zero dimensional (0D) fullerene, rolled up to one dimensional (1D) carbon nanotubes, and stacked as three dimensional (3D) layered graphite, as in the sketches in figure 1-1.

Figure 1-1 Graphene and its different dimensional relatives. (adapted from [2])
Although graphene can be thought of as a basis of other carbon allotropes, it was considered that the thermodynamic instability of this 2D material would prevent its existence, however, the isolation of graphene in 2004 explained the instability can be conquered by having some ripples in 2D sheets [3]. Graphene can be transferred on top of any substrate or suspended on grids. This new material then opens a gate for new science: many impressive properties have already been discovered. In principle, other layered materials with only Van der Waals force as interlayer interaction can be exfoliated into 2D crystals. For example, monolayer boron nitride and layered-transition-metal dichalcogenides (TMD) can be exfoliated from 3D bulk [4-6]. These 2D materials have their individual properties and form a material library for use in various applications, such as supercapacitors. Layered TMDs are one of the 2D crystal groups with widely varying properties. NbSe₂ is metallic while MoS₂ and WS₂ are semiconducting [7]. From the views of applications, some of them can be used for sensing, catalysis, and energy storage.

1-1 Band structure of graphene

The unique band structure of graphene has been known for decades and used for explaining phenomena in other carbon systems. The discovery of graphene reveals its abundant properties, such as ambipolar electric field effect, massless Dirac charge carriers, room temperature quantum Hall effect and ballistic behaviour. These remarkable properties provide many possibilities to utilise graphene in practical applications.

This band structure of graphene can be understood simply by using the nearest-neighbour tight-binding model [8]. Spatial structure of graphene can be sketched as in figure 1-2a with two sublattices A and B in a honeycomb structure. There are two lattice vectors

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

(1.1.1)

for describing its spatial structure, where \( a \approx 1.42\text{Å} \) is the lattice constant. The honeycomb lattice contains two atoms per elementary cell. An atom of sublattice A is surrounded by three atoms from sublattice B. The reciprocal lattice is also
triangular with the reciprocal-lattice vectors

\[ \vec{b}_1 = \frac{2\pi}{3a}(1,\sqrt{3}), \quad \vec{b}_2 = \frac{2\pi}{3a}(1,-\sqrt{3}) \quad (1.1.2) \]

The Brillouin zone is presented in figure 1-2(b) along with special high-symmetry points K, K’ and M, with the k vectors

\[ \vec{K} = \frac{2\pi}{3a}(1,-\frac{1}{\sqrt{3}}), \quad \vec{K'} = \frac{2\pi}{3a}(1,\frac{1}{\sqrt{3}}), \quad \vec{M} = \frac{2\pi}{3a}(1,0) \quad (1.1.3) \]

![Diagram of a honeycomb lattice and Brillouin zone](image)

Figure 1-2 (a) A honeycomb lattice, sublattices A and B are shown in purple and blue (b) Reciprocal lattice vectors and some symmetric points (purple filled circles) in the Brillouin zone.

The nearest-neighbour tight-binding band structure of graphene has been systematically described in many textbooks [8]. In particular, following the Wallace model (1947) [9] and using the nearest-neighbour approximation, the Hamiltonian can be described by a $2 \times 2$ matrix, with nearest-neighbour hopping parameter, t.

\[
H(\vec{k}) = \begin{pmatrix}
0 & t S(\vec{k}) \\
t S^*(\vec{k}) & 0
\end{pmatrix} \quad (1.1.4)
\]

Where $k$ is the wave vector and

\[
S(\vec{k}) = \sum_{\delta} e^{i\vec{k}\vec{\delta}} = 2e^{\frac{i k}{2} a c \left(\frac{\sqrt{3}k_a}{2}\right)} + e^{-i\vec{k}} \quad (1.1.5)
\]
The energy is, therefore

\[ E(\mathbf{k}) = \pm \sqrt{3} \mathbf{k} \cdot \mathbf{f} \]  \hspace{1cm} (1.1.6)

where \( f(\mathbf{k}) = 2 \cos(\sqrt{3} k_y a) + 4 \cos(\frac{\sqrt{3}}{2} k_y a) \cos(\frac{3}{2} k_x a) \).

The valence and conduction bands are separated by band gaps except in these six touching points where \( E(\mathbf{K}) = E(\mathbf{K'}) = 0 \) as depicted in figure 1-3. The touching points are called the Dirac points or the neutrality points, located at the Fermi energy of undoped graphene. This indicates graphene is semimetal or gapless semiconductor.

Another key feature of graphene band structure is the linear dependence of energy and wave vectors near the zero energy limits, where band structure shows conical spectrum as in the top of the inset of figure 1-3. Mathematically, one can obtain a linear dependence between energy and the wave vector amplitude \( E_{\text{linear}}^{\pm} = \pm \hbar \sigma_F |\mathbf{k}| \), where \( \sigma_F \sim 10^6 \text{m/s} \) is the Fermi velocity in graphene by expanding \( E(\mathbf{k}) \) near the touching points. The similarity of this expression and the Dirac equation explains why electrons in graphene can be treated as massless relativistic particles, where the speed of light in Dirac equation is replaced by the Fermi velocity. Figure 1-4 shows \( \pi \) states form a single band based on density functional theory, with crossing points in \( K \) as illustrated in the tight-binding model. The other bands formed from \( sp^2 \) hybridized states (\( \sigma \) states) show a band gap between occupied and empty bands in figure 1-4.

Figure 1-3 band structures calculated from tight-binding model (adapted from [10])
Figure 1-4 The band structure of graphene based on density-functional theory. Solid red lines are $\sigma$ bands and dotted blue lines are $\pi$ bands. (adapted from [11])
1-2 Electronic properties of graphene

Figure 1-5 (a) shows the ambipolar field effect of graphene as the majority charge carriers can be tuned continuously from electrons to holes by electric field. The undoped graphene has the Fermi energy exactly at the neutrality point where the density of states vanishes and the resistivity is the maximum. The carrier concentration (n) in this case can be simply estimated by viewing a graphene device as a parallel plate capacitor with applied gate voltage, $V_g$.

$$n = \frac{\varepsilon_0 \varepsilon V_g}{ed} \tag{1.1.7}$$

$\varepsilon_0$, $\varepsilon$ and $d$ stand for electric permittivity of free space and relative permittivity, and the spacer thickness, respectively. It is clearly shown the neutrality point shift from $V_g=0$ to $V_g>0$. This feature indicates graphene changes from undoped to hole doping.

The discussion of the massless Dirac fermions in graphene have been systematically described in Ref.[8]. In particular, the first evidence of their existence was first reported through the half integer quantum Hall effect even at room temperature [14]. When graphene is placed in a magnetic field, the energy levels are no longer continuous. The discrete energy level is called Landau levels. Graphene shows special Landau level due to its relativistic-like nature. Zero energy states show equal distribution of electrons and holes.
1-3 Production of graphene

A great number of techniques for graphene fabrication have been developed for various purposes of applications and some of them are shown in figure 1-6. Four main ways are introduced as follows. Each one leads to graphene flakes with different sizes, shapes and qualities suitable for their particular applications.

Figure 1- 6 Methods of graphene production (adapted from [15])

1. Micromechanical cleavage
   This is the method adopted when graphene was obtained by cleavage from graphite in 2004, by Novoselov et al [16]. With this technique, graphite is peeled by sticky tape till very thin and pressed on to a substrate. The removal of tape then leaves the presence of graphene flakes on the substrate and also some graphite. Graphene can be identified simply in an optical microscope due to a thin-film interference phenomenon [17] and more accurately by Raman spectra [18]. Micromechanical cleavage is now optimized to produce high quality graphene sheet with size in the order of millimetres.

2. Chemical evaporation deposition (CVD)
   Another route to fabricate larger graphene films is epitaxial growth of carbon on
top of some particular metals, such as Ni and Cu. The first uniform graphene sheet grown on a metal substrate by CVD was reported in 2009 by Li et al., with a cm² size graphene on copper polycrystalline foil. The success is attributed to the low carbon solubility in copper and the mild catalytic activity of copper [19]. CVD graphene can be transferred to any kind of flat or curved surface in 2010 by roll-to-roll technique, with mobility up to $\mu \sim 7350 \text{cm}^2\text{V}^{-1}\text{S}^{-1}$ [20]. A high quality of CVD graphene sheet will bring it to more commercial applications.

3. Solution-based exfoliation
This method is similar to micromechanical cleavage, but in the solution phase which allows mass production. By the use of ultrasonication, graphite can be exfoliated in suitable solvents, followed by centrifugation to remove thick graphite. The resulting suspension is stable and contains sub-micrometer graphene flakes. The match of surface energy of the solvents and graphite is the key point for exfoliation [21]. The suspension can be used to make graphene laminates and achieve dried sample mass up to $\approx \text{mg}$. It therefore has great potential for industrial-scale production of graphene. This method is also what we use the most in this thesis.

4. Reduced graphene oxide
Through the Hummer’s method, oxygen groups can be intercalated in and functionalize graphite layers forming graphite oxide [22]. The crystals then can be exfoliated by sonicating in water and become graphene oxide (GO) solution. Graphene oxide is one of the graphene derivatives which will be introduced in the following section. Methods illustrated in Ref [23] can be used for graphene oxide reduction. Due to intercalation by oxygen group, there is a large proportion of single layer graphene oxide in the suspension that becomes monolayer graphene after reduction. Although this method can be used for mass production with high ratio of graphene, lower quality is achieved compared to graphene produced by other methods as there is incomplete removal of oxygen group as well as the defects left in the lattice.
1-4 Graphene derivatives

Although graphite is chemically inert, atomically thin graphene can be chemically modified. Despite its similar structure to graphene, the derivatives have distinct electronic structures and properties. The replacement of sp\(^2\) by sp\(^3\) bonds, where adatoms are attached to p\(_z\) orbitals of carbon due to chemical modification, leads to band gaps opening and the formation of insulating derivatives. Some of the derivatives are stoichiometric, and with zero-band gap graphene, these stoichiometric graphene derivatives may have extensive applications in graphene engineering.

**Graphene oxide**

Graphene oxide is the first chemical derivative of graphene. This can be produced by simply exfoliation from graphite oxide in water. Its structure is shown in figure 1-7(a). Various oxygen functional groups (such as epoxy bridges, hydroxyl and carboxyl groups) are randomly attached on graphene planes and responsible for its hydrophilic nature and analogous chemical reactivity. In this case, graphene oxide is nonstoichiometric. For use in applications, reduction of graphene oxide is of great interest for the mass production of monolayer graphene. However, the decrease in conductivity due to defects limits the electronic usage of the reduced graphene oxide. Additionally, further graphene derivatives can be formed by grafting the oxygen group to by other functional groups. For instance, the amine group of prophyrin can be attached on graphene oxide and form a further chemical compound for optoelectronic materials [24]. Except electronic and optical applications, graphene oxide laminates are also found to filter water even from liquid mixtures [25].

![Figure 1-7 Schematic structures of (a) graphene oxide (adapted from [26]) (b) graphane (adapted from [27])]
**Hydrogenated graphene**

Hydrogenated graphene, another graphene derivative, can be produced by exposing graphene to hydrogen plasma [28]. It is a relatively clean modification among graphene chemistries. Graphane is a stoichiometric hydrogenated graphene. Unlike randomly distributed groups in graphene oxide, graphane is stoichiometric double-sided hydrogenated graphene (as sketched in figure 1-7(b)) and semiconducting. The hexagonal symmetry is preserved after hydrogenation but the lattice constant shrinks to 2.42Å. The basal plane structure is no longer flat. Instead, the C-C-C bonds changes from 120° to 109.5° and the displacement of the atoms balances the energy arisen by adatoms. The hydrogenation is reversible by simply annealing at 300°C. Despite the elegant existence of graphane, not many applications utilise it due to its instability in the air.

**Fluorinated graphene**

One year after the discovery of hydrogenated graphene, a more stable stoichiometric graphene derivative has been realized [29]. Fluorographene is the first stage stoichiometric fluorinated graphene (C-F). It is fabricated by attaching the fluorine atoms decomposed in 70°C from XeF$_2$ on both sides of monolayer graphene. The structural change in fluorographene is similar to graphane, but the former is more stable. The hexagonal structure is preserved but the lattice constant extended after fluorination. The C-C angle changes due to the adatoms attachment. Fluorographene can be heated up to 400°C and stay stable. The chemical resemblance to Teflon and graphene structure means fluorographene has extensive possible applications.
1-5 Molybdenum disulphide

Bulk MoS$_2$ is a common dry lubricant and a catalyst for desulfurization. 2H-MoS$_2$ is a layered TMD material, composed of weakly interacting layers held together by Van der Waal force. A single layered sheet of MoS$_2$ is actually three atomic layers stacked by two layers of sulphur and one layer of molybdenum in the centre (in figure 8b). The single layer MoS$_2$ can be extracted by most of the ways used in graphene, such as micromechanical exfoliation [30], lithium-based intercalation[31], liquid-based exfoliation [32], and CVD methods [33-35]. The thickness of single layer MoS$_2$ is about 6.5Å [30]. Molybdenum disulphide has indirect band gap in bulk [36]. With decreasing thickness, the indirect band gap becomes wider than the bulk value of 1.29 eV up to 1.9 eV. The indirect band gap was then found to be larger than the direct band gap. The MoS$_2$ crystals undergo a crossover from an indirect to a direct gap semiconductor material in monolayer limit. The reason can be traced back to the effect of quantum confinement on electronic structure of the material. The band structures of bulk and monolayer are plotted in figure 1-9, with arrows indicating direct and indirect transition in 1-9(a) and (b), respectively. The direct band gap in monolayer MoS$_2$ provides a new possibility for photo-current devices. How the band structures of MoS$_2$ 1D nanoribbons and 0D nanofragments are relevant to magnetism will be illustrated in the next chapter. These band structures are different with respect to the bulk and two-dimensional band structures because of the edge states.

Figure 1- 8 Schematic structure MoS$_2$ (a) top view: grey and orange filled circles are represented Mo and S atoms. Area surrounded by dashed lines labels a unit cell. (b) side view: black and yellow circles are symbols of Mo and S atoms. The interlayer distance is 6.5 Å. (adapted from [30])
Figure 1-9 Band structure of monolayer (a) and bulk MoS$_2$ (b). The arrows indicate direct and indirect band gap in monolayer and bulk MoS$_2$, respectively. (Adapted from [37])
1-6 The organization of this thesis:

The aim of this thesis is to study magnetism in graphene and MoS$_2$. Although research into 2D materials, especially graphene, MoS$_2$ and WS$_2$, is quickly moving forward, there are still many questions that need to be answered. Magnetism in light elements, especially carbon systems, is of great interest in recent years. The main feature of current magnetic materials is their partially filled d or f orbitals. Despite the absence of this feature, magnetic moments in the carbon systems may exist under diverse circumstances suggested by theoretical calculations (for a review, please see [38]). Certain types of point defects, zigzag edges, and nanostructures with particular shapes are suggested to be sources of magnetic moments [8, 39]. In this thesis, we studied the magnetic properties of graphene by intentionally introducing point defects.

Ion-irradiation is one of the most commonly used techniques to introduce vacancies into graphene. However, there has been lack of evidence of the type of defects created by ion-irradiation. In theory, the properties introduced by defects in graphene depend on their geometries. Take magnetic properties as an example, defect-induced states near the Dirac point happens in graphene when the reconstructed single vacancies are created, but not when divacancies or other more symmetric defects are introduced [40, 41]. Thus, atomic-scale studies of ion-irradiated graphene are presented in this thesis for studying the effect of geometry of defects on electronic structure of graphene which tightly related to its electronic or magnetic properties.

Moreover, graphene is a promising candidate for spintronic applications due to its long spin relaxation time and weak spin-orbital coupling [42]. On possible implementation of spintronic devices is to control spin currents and their configurations by electric fields. In graphene, the electronic, optical and other properties pertained to the electronic structure are tuneable efficiently by electric fields. To this end, we studied the doping effect on magnetic properties of graphene, especially on the magnetic properties induced by point defects and the orbital diamagnetism of graphene. Eventually, the origins of magnetism in defected graphene will be discussed.

On the other hand, magnetic researches into other 2D materials, especially in TMD materials due to their variety, might provide more extensive views in magnetism. MoS$_2$ is one of the most stable and low cost TMD materials, its magnetic properties will thus be discussed.
In Chapter 2, the basic theories of magnetism and brief reviews of magnetism in graphene and MoS\textsubscript{2} will be described. Specifically, the magnetic sources of both materials in two dimensional configuration and other nano-systems will be discussed theoretically and followed by some relevant ferromagnetic findings.

Chapter 3 presents the experimental results of defect-induced magnetism. In particular, the production of pristine graphene laminates will be present, followed by the illustration of two methods using for introduction of defects, ion-irradiation for creating vacancies and fluorination for attaching fluorine adatoms. Graphene laminates are a large collection of single and multilayer graphene sheets. In our samples, large proportions of single layers exist. The magnetic properties of these two kinds of defected graphene laminates will then be investigated and discussed.

In Chapter 4, a study concerning magnetic properties of graphene influenced by doping effect will be presented. The magnetic changes due to doping effect are analogous with the phenomena of changing Fermi energy which may also be executed by controlling electric fields. In particular, characterization of chemical doping in graphene will be firstly introduced. Second, the doping effect on localized magnetic moments of defected graphene laminates will be displayed, followed by the discussions about origins of magnetic moments. Finally, the doping effect on orbital diamagnetism of graphene will be addressed.

Chapter 5 demonstrates an investigation on encapsulating ion-irradiated graphene sheets in atomic resolution. In particular, trilayer graphene is used as a sample to observe and identify the configuration of vacancies which is shown to be intrinsic even after a few minutes of TEM imaging due to the encapsulation. Defects are proven in the literature to change the electronic and magnetic properties of graphene dramatically. The studies in the current and previous chapter allow one to understand the connection between the defect-induced magnetic moments and types of defects.

Chapter 6 addresses the experimental results for the magnetic properties of solution-based MoS\textsubscript{2} laminates. First, the ultrasonic cleavage method used for producing the samples in this chapter will be described. Second, some results from characterizations of samples will be displayed. In the end, the magnetic measurements performed on MoS\textsubscript{2} laminates will be displayed and discussed.

The final conclusion of this thesis will be presented in Chapter 7, which summarizes the main findings in this thesis and gives an outlook of further development of those findings.
Chapter 2

Introduction to Magnetism in Graphene and Molybdenum Disulfide

The basics of magnetism in materials relevant to our experimental findings will be firstly introduced in this chapter. These are followed by an overview of magnetism in graphene, in particular some computational techniques relevant to magnetic investigation, edge- and defect- induced magnetism, orbital diamagnetism and the ferromagnetic findings in the graphitic materials. Finally, a review of magnetism in MoS$_2$ will be illustrated. Most of the contents in this chapter are systematically described in many textbooks or literatures, but briefly introduced here for the consistency of the thesis.

2-1 Basics of magnetism in materials

The magnetic susceptibility ($\chi$) indicates the degree of magnetization of materials in responses to the external field. The magnetic susceptibility per unit volume is defined as

$$\chi = \frac{M}{B} \quad (CGS) \quad (2.1.1)$$

where $M$ is the magnetic moment per unit volume, $B$ is the macroscopic magnetic field intensity. In this definition, $\chi$ is called volume susceptibility and dimensionless. The susceptibility per gram ($\chi_m$) is used in this thesis. Related to volume susceptibility, $\chi_m$ can be presented as
\[ \chi_m = \frac{\chi}{\rho} \quad (2.1.2) \]

where \( \rho \) is the density of materials. \( \chi_m \) are negative for diamagnetic materials, while they are positive when the objects are paramagnetic. Figure 2-1 shows magnetic susceptibilities of diamagnetic and paramagnetic substances as functions of temperature. The mechanism of diamagnetism and Langevin paramagnetism (or called Curie’s law in quantum-mechanical view) will be introduced in the following sections. The theories of ferromagnetism are complex and irrelevant to our results. Therefore, we only introduce the phenomena that ferromagnetic materials might exhibit.

![Graph showing magnetic susceptibilities of diamagnetic and paramagnetic substances](image)

Figure 2-1  Temperature dependence of the magnetic susceptibilities of diamagnetic and paramagnetic substances (Adapted from ref. [43])

2-1-1  Theory of diamagnetism: Langevin diamagnetism

Diamagnetism is a property of a material where the charges tend to shield the interior of a body from an external magnetic field [43]. It is a quantum mechanical effect that occurs in all substances. Lenz’s law electromagnetically interprets this behaviour: when the magnetic flux through an electric circuit is changed, a current generated by the same flux but opposite direction is induced to cancel the flux.
variation sensed by the circuit. In particular, Larmor theorem is usually used for the predictions in the diamagnetism of the atoms or ions: The precession of Z electrons can be viewed as the equivalent of a current:

\[ I = (-Ze) \times \left( \frac{1}{2\pi} \cdot \frac{eB}{2m} \right) \]  \hspace{1cm} (2.1.3)

The product of I and the area of the current loop presents the corresponding magnetic moment \( \mu \):

\[ \mu = \frac{Ze^2B}{4m} \langle \rho^2 \rangle \]  \hspace{1cm} (2.1.4)

where \( \pi \langle \rho^2 \rangle \) is expressed as the area of the loop and \( \langle \rho^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle \) is the mean square distance of the electrons from nucleus. For the charges spherically symmetric distributed, \( \langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle = \frac{3}{2} \langle \rho^2 \rangle \). The diamagnetic volume susceptibility is

\[ \chi = \frac{\mu N \mu}{B} = -\frac{\mu N Ze^2}{6m} \langle \rho^2 \rangle \]  \hspace{1cm} (2.1.5)

where \( N \) is the number of atoms per volume. This is the classical Langevin result. The quantum mechanical treatment leads to a temperature independent susceptibility which is in agreement with the classical Langevin diamagnetic theory [43].

2-1-2 Theory of paramagnetism: Curie’s law

Paramagnetic materials are those having positive susceptibility in the presence of magnetic fields [43]. The paramagnetism can come from various sources. Figure 1-1 shows some distinguishable paramagnetism. In this section, the quantum mechanical treatment based on Langevin paramagnetic theory will be introduced and eventually leads to Curie’s Law.

In the quantum mechanical treatments, the energy levels of the system in a magnetic field are

\[ U = -\mu \cdot B = m_J g \mu_B B \]  \hspace{1cm} (2.1.6)

\( m_J \) is the azimuthal quantum number and has the value \( |J|, |J| - 1, ..., -|J| \). \( g \) is spectroscopic splitting factor and \( J \) is the total angular momentum. For a free electron
In general case, the total magnetic moment is the summation of population of each state multiplied by their magnetic contribution:

\[ M = N_s \sum_{m_J=-J}^{J} -g m_J \mu_B \langle n_{m_J} \rangle, \quad \langle n_{m_J} \rangle = \frac{e^{-g m_J \mu_B B/k_B T}}{\sum_{m_J=-J}^{J} e^{-g m_J \mu_B B/k_B T}} \]  \hspace{1cm} (2.1.7)

The total magnetic moments then can be expressed as

\[ M = N_s g J \mu_B B_J(x), \quad (x = g J \mu_B B / k_B T) \]  \hspace{1cm} (2.1.8)

\[ B_J(x) = \frac{2J+1}{2J} \coth \left( \frac{(2J+1)x}{2J} \right) - \frac{1}{2J} \coth \left( \frac{x}{2J} \right) \]  \hspace{1cm} (2.1.9)

Eq. (2.1.8) is known as the Curie-Brillouin function. \( N_s \) is number of spins. When \( x = g J \mu_B B / k_B T \ll 1 \), the susceptibility approaches to Curie’s law,

\[ \frac{M}{B} = \frac{N_s J(J+1)g^2 \mu_B^2}{3k_B T} = \frac{C}{T} \]  \hspace{1cm} (2.1.10)

where \( C \) is the Curie constant. In Curie’s law, the susceptibility is proportional to \( 1/T \).

A more general expression of paramagnetic behaviour in materials is known as Curie-Weiss law. It was introduced by Weiss with a perturbation correction to conclude the so-called crystal field given by the interaction between individual atomic magnetic moments. The total field can then be modified as

\[ B_{\text{total}} = B + B_e \]  \hspace{1cm} (2.1.11)

where \( B_e = \alpha M \) and so far no assumption to \( \alpha \). By substituting the field \( B \) in eq. (2.1.10) with \( B_{\text{total}} - B_e \) and \( B_{\text{total}} = MT/C \) for obeying the thermal equilibrium and Boltzmann statistics, the susceptibility can then be expressed as

\[ \chi = \frac{C}{T - T_c} \]  \hspace{1cm} (2.1.12)

where the critical temperature, \( T_c = \alpha C \), is known as the Curie temperature and a boundary between paramagnetic and ferromagnetic states of the material. For
antiferromagnetic materials, the temperature dependence of the susceptibility in paramagnetic region is the same but with \( T_c < 0 \) (or is written as \( \theta \)).

Figure 2-2 Curie-Weiss law and Curie law: temperature dependence of the magnetic susceptibility in paramagnets, ferromagnets, and antiferromagnets (adapted from [43]). The former one follows the Curie law at all temperature, while the latter two follow Curie-Weiss law in their paramagnetic region.

2-1-3 Experimental features of ferromagnetic materials

Ferromagnetism is a spontaneous magnetization arising from the tendency of magnetic moments in ferromagnets to align spontaneously, even after removing the external magnetic field. Instead of going deeply to the theories of ferromagnetism which are not relevant to our results, some features of experimental findings in ferromagnetic materials will be introduced.

A hysteresis loop is a typical feature of a ferromagnetic material in magnetic measurements. An example is shown in figure 2-3. If the initial state is demagnetized, the magnetization of the ferromagnetic material will follow route 1 to the magnetic saturation when the magnetic field is gradually increased from zero. Then when reducing the magnetic field monotonically, the magnetization will follow a different route (route 2) back. This is due to the interaction between the magnetic moments in ferromagnets. It leaves an offset magnetization when the field is reduced to zero, named the remanence \((M_r)\). The required opposite field for eliminating the magnetization to zero is called the coercivity \((H_c)\). The magnetization then follows route 3 when the magnetic field is increased from the negative saturation. From this
point, the magnetic moments align in the opposite direction. The formation of the whole loop is due to the magnetic ordering of materials. Materials with low coercivity are called soft ferromagnets while those with high coercivity are called hard ones. The former ones are used to concentrate and shape magnetic flux, as in motors, generators, transformers, and sensors. The hard ferromagnets are permanent magnets and can be used for magnetic recording, such as magnetic tapes and hard disks.

Figure 2-3 Hysteresis loop: $H_c$ is coercivity, $M_r$ is the remenance and $M_s$ is the saturation (adapted from [44]).
Superparamagnetism appears in small ferromagnetic nanoparticles since the confinement volume reduces the stability of magnetic moments against thermal fluctuation. An example is magnetite (FeO*Fe₂O₃), which is composed of two oxidization states of iron ions [45]. The field dependent superconducting quantum interference device (SQUID) magnetometer measurements of magnetite nanoparticles in figure 2-4 (b) shows the thermal effect on superparamagnetic materials. A negligible remnant magnetic moments and coercive field is shown in room temperature measurement. On the other hand, a typical hysteresis loop representing the ferromagnetic behaviour is observed in low temperature. The temperature dependent measurement shows that zero-field cooling and field cooling curves converge near 145K, indicating the superparamagnetic behaviour of the magnetite nanoparticles.

![Figure 2-4](image)

Figure 2-4 SQUID measurement on a colloidal solution of superparamagnetic magnetite nanoparticles [45] (a) in temperature dependence (b) in field dependence of room and low temperature.
2-2 Review of magnetism in graphene: formation of local magnetic moment

Magnetism of carbon materials is of particular interest as in current applications magnetic materials are usually based on partially filled \( d \) or \( f \) orbitals. Magnetic materials based on graphene will be a breakthrough due to their low cost and how easy they are to design and produce. This section provides a review of significant findings in magnetism of graphene including the scenarios shown by theoretical calculations and the experiments. In particular, the computational approaches and counting rules relevant to magnetic calculations in graphene-based systems will be firstly described. Then, the theoretical calculations of magnetism in graphene-based systems including 0D nanofragments and edges of 1D nanoribbons and defects-induced magnetism are covered. Before the defect-induced magnetism, the irradiation damage process and reconstruction of vacancies are described. In addition to these theories, the ferromagnetic findings in carbon-based systems will also be illustrated.

2-2-1 Computational approaches and counting rules

In theoretical approaches of magnetism in graphene, most commonly used methods are based on density functional theory (DFT). These calculations rely on a great number of computational codes and are illustrated in detail in several textbooks [46-48]. For understanding the origin of the magnetism in graphene, a simplified model based on Hamiltonian will be used.

The One-orbital mean-field Hubbard model is widely adopted for studying the magnetic properties in \( \text{sp}^2 \) carbon materials. This model only considers the \( \pi \) electronic structure which is constituted by the conduction electrons of \( \text{sp}^2 \) carbon systems (unhybridized-\( p_z \) orbitals in \( \text{sp}^2 \) carbon atoms). The low-energy electronic states play an important role in the properties of graphene and graphene-like systems. The Hamiltonian of the Hubbard model is composed of two parts

\[
H = H_0 + H'
\]  
(2. 1. 13)

The first part accounts for the nearest-neighbour tight-binding Hamiltonian, which can be expressed as
where the operators $c_{i,\sigma}^\dagger$ and $c_{j,\sigma}$ represent the creation and annihilation of an electron with spin $\sigma$ at sites $i$ and $j$, respectively. $t$ is the hopping parameter that has been used in Chapter 1. The notation $\langle i,j \rangle$ stands for the nearest-neighbour interaction on the lattice; ‘$h. c.$’ is the Hermitian conjugate. In this case, when graphene is neutral (half-filled), electron-hole symmetry is respected to zero energy, which means each sp$^2$ carbon atom only contribute to one unhybridized $p_z$ orbital and one $\pi$ electron and the energy states are occupied by electrons when energy smaller than zero and vice versa. In Hubbard model, the electron-electron interaction is expressed through the repulsive on-site Coulomb Hamiltonian which considers only the short-range interaction:

$$H_0 = -t \sum_{\langle i,j \rangle,\sigma} \left[ c_{i,\sigma}^\dagger c_{j,\sigma} + h. c. \right] \quad (2.1.14)$$

where $H'_i = U \sum_{\sigma} n_{i,\uparrow} n_{i,\downarrow}$

$$H'_i = U \sum_{\sigma} n_{i,\uparrow} n_{i,\downarrow} \quad (2.1.15)$$

where $n_{i,\sigma} = c_{i,\sigma}^\dagger c_{i,\sigma}$ is the spin-resolved electron density in site $i$, the parameter $U > 0$ denotes the amplitude of the on-site repulsive Coulomb interaction. In general DFT calculations for graphene, $U/t \approx 1.1 - 1.3$ are considered. The complexity of calculation can be solved by mean-field theory and the final solution of spin density, $M_i$, is given as:

$$M_i = \frac{\langle n_{i,\uparrow} \rangle - \langle n_{i,\downarrow} \rangle}{2} \quad (2.1.16)$$

at each atom $i$. Total spins of the system can be expressed as $M = \sum_i M_i$.

Since graphene is a bipartite hexagonal system there are two counting rules, the benzenoid graph theory[49] and the Lieb’s theorem[50], that can be applied to predict the magnetic properties in graphene system. The benzenoid graph theory can be used to count the zero-energy states and Lieb’s theorem allows count the net magnetic moments intuitively. The benzenoid graph theory predicts the number of zero-energy states

$$\eta = 2\alpha - N \quad (2.1.17)$$

in which $N$ is the total number of sites and $\alpha$ represents the maximum possible number of non-adjacent neighbours. Due to the Coulomb repulsion ($U > 0$), zero-energy (non-bonding) states in a half-filled $\pi$ subband particularly tend to be spin-polarized [51]. Although the benzenoid graph theory estimates the number of
zero-energy states, the correlation of these states and the spin alignment are not clear. This unclear picture is compensated by another counting rule, Lieb’s theorem. This theory determines the total spins of the ground state in the bipartite system described by the Hubbard Hamiltonian.

\[
S = \frac{|N_A - N_B|}{2}
\]  
(2.1.18)

Where \( N_A \) and \( N_B \) are the total numbers of atoms in sublattice A and B. In this theory, the bipartite system is half-filling and with repulsive electron-electron interaction. Remarkably, the two counting rules are correlated by the equation of \( \eta \geq |N_A - N_B| \). These counting rules are extensively applied to the magnetic properties of graphene nanofragments [51].

2-2-2 Defects in graphene

So far, the magnetism in defected graphitic systems has received great attention due to the possibility of defect-induced localized magnetic moments. Irradiation with high-energy ions is one of the commonly used techniques to intentionally create point vacancies in graphitic systems. The process of irradiation damage will be firstly introduced and followed by the reconstruction configuration of vacancies. After irradiation, the network near the vacancies might reconstruct or migrate to balance the ground state energy [52]. The transformation can also happen when e-beam energy is lower than knock-out energy. This has been observed in the in-situ TEM experiment immediately after vacancies have been created [53]. Some types of vacancies before and after reconstruction will then be introduced. This information is useful in Ch.5 for understanding the defects of ion irradiation which is not in-situ TEM observation. Finally, the theoretical calculations of magnetism in defected graphene will be illustrated for the background of Ch.3, 4 and 5.

Irradiation damage process

Irradiation with high-energy electron or ion beams is commonly used to produce point defects in crystallized materials. The irradiation damage process in graphite was intensively studied due to its wide occurrence in nuclear reactors [54].

During the irradiation, an energetic ion propagating in a solid target can be slowed
down by two channels, nuclear and electron stopping. The former is governed by the collision between ions and the nuclei of target atoms and only important when the incident ions are heavy and slow. In the case of proton irradiation, electron stopping is always dominated [54]. The ability to stop ions by electron stopping relies on inelastic collisions between the moving ions and electrons, which are either bound or free in the target atoms.

The atomic displacement occurs when atoms acquire enough energy to leave the lattice positions and form vacancy-interstitial pairs (or named Frenkel pairs) in the lattice. The process is called the knock-on collision and the threshold energy in order to avoid immediate vacancy-interstitial recombination is defined as $T_d$ ($T_d \approx 20eV$ for graphitic structures). When the vacancies and interstitials possess energy larger than $T_d$, they can migrate far from the collision position. Vacancies can then be combined or reconstructed. The Frenkel pairs can also be trapped and might form the interstitial clusters between graphitic planes. These interstitial clusters are proven to be free or bound in recent studies [55]. A simple sketch of the proton irradiation process is shown in figure 2-8. The number of atoms displaced by each proton is dependent on the incident energy.

The electron irradiation is always an important issue for the transmission electronic microscope samples, since electron beams can modify crystal structures by causing either atomic displacement or transformation of lattices. The defect generation is due to the energy transfer from electrons to the target atoms through ballistic collisions. The energy from high-resolution TEM (~100-300keV) can cause permanent displacement of carbon atoms in graphitic lattices. On the other hand, even lower energy electrons (~ 60-80 keV), which could not displace the atoms, but may cause damages to the target lattices, such as ionization or bonds breaking through electron-electron scattering.
Figure 2-5 Process of high energetic protons irradiation in graphite, creating vacancies and displace atoms [56]. PKA and SDG stands for primary knock-on atoms and the first couple of secondary displacement, respectively. For the samples using in Ch.3 and 4, the progressive depth is around 8-10μm with energy of the proton beam ~350kV.

**Type of defects and their reconstruction**

Reconstruction is a self-healing process for the network near vacancies. When the atomic displacement occurs, knock-on collisions leave unpaired dangling bonds in the lattice. The network near the vacancy then reconstructs in order to stabilize the system. For instance, after irradiation, a single vacancy undergoes Jahn-Teller distortion which compensates for the energy released when leaving three sp² dangling bonds in graphene lattice. In this case, two nearest dangling bonds form a covalent bond and leave one dangling bond in the network (as shown in figure 2-9(b) and 2-10(a)). The third atom is displaced 0.18Å out of plane. The benzene ring then becomes a 5-9 structure in the local network. For di-vacancy in graphene lattice, four dangling bonds reconstruct into two symmetric covalent bonds and lead to a 5-8-5 structure as displayed in figure 2-9(c). The shapes of di-vacancies before and after reconstruction are more symmetric than those from single vacancies. Along with vacancies, other types of defects may exist in graphene after irradiation, such as 5-7 defects and Stone-Wales (SW) defects displayed in figure 1-9(a). The latter type of defects is associated with the rotation of a bond[57].
Defects and their reconstructive form (a) two 5-7 (yellow) and a Stone-Wales defect (green) (b) single vacancies: before reconstruction with three dangling bonds (blue) and after reconstruction through Jahn-Teller distortion (yellow) (c) the di-vacancies: before reconstruction with four dangling bonds (blue) and after reconstruction (yellow). (adapted from [58]) (d, e, g) atomic resolution TEM images of a Stone-Wales defect, a reconstructed single vacancy, and a reconstructed divancy [59] (f) STM measurement on the single vacancy shows the intensive local density of state in its center [60].

2-2-3 Defects-induced magnetism

Structural defects remove \( p_z \) orbitals in carbon lattice, and can create net magnetic moments as understood by Lieb’s theorem. The examples of structural defects include vacancies, topological defects, and adatoms. In Chapter 3, we will focus on the magnetic investigations in two types of defected graphene: irradiation produced vacancies and adatoms created via chemical functionalization. A few calculations relevant to the defects-induced magnetism are reviewed here.

Figure 2-11(a) shows the spin-polarized density of states for hydrogen chemisorptions and vacancy-type defects. In the former case, the \( sp^3 \) hybridization and the loss of \( p_z \) orbitals induced by the hydrogen chemisorption result in some peaks in the density of states close to the Fermi energy. These peaks are so-called
quasi-localized states induced by the chemisorbed hydrogen atoms. Each defect gives rise to a magnetic moment of $1\mu_B$. In the case of vacancy-type defects in graphene lattice, the situation is more complex. Jahn-teller distortion upon relaxation (as shown in figure 2-10(a)) occurs near the single vacancy and leaves a dangling bond and loses one p$_z$ orbital [61]. Two types of states, quasi-localized states due to $\pi$ electrons and the localized states from $\sigma$ bonds are generated in graphene lattice with single vacancies. The spin density obtained by simulation and local density of state detected by STM show that the dangling $\sigma$ bond is responsible for the localized magnetic moment of $1\mu_B$, as shown in the spin-density map of figure 2-10(b). The quasi-localized states in this case are partially suppressed due to the structural reconstruction of the vacancy. The overall magnetic moments per vacancy ranges from 1.12 to 1.53 $\mu_B$ for defect concentrations from 20% to 0.5% [62].

An example of a further spin-density calculation given by quasi-localized states in a bigger supercell which contains several single vacancies is shown in figure 2-11(c) and (d). The defects are randomly distributed and shown as black triangles in figure 2-11(c). The upper and lower triangles stand for those occupied in different sublattices, respectively. The results considered only quasi-localized states can be understood by Lieb’s theorem that electron spins in the same sublattice are aligned parallel to each other, while spins in the different sublattices are arranged in anti-parallel directions.

Figure 2-7 A reconstructed single vacancy (a) schematic structure, colour represent the charge density (e/Å$^3$), and (b) spin density (e/Å$^3$) of a reconstructed single vacancy in graphite. (adapted from [63])
The quasi-localized states in different sublattices interact with each other. The average magnetic moments of atoms in two sublattices against defect concentration are displayed in figure 2-11(d). The interaction strength of two vacancies increases with the decrease of their distance in all the cases. Note that the interstitials created along with the vacancies are expected to have no magnetic moments in most of the considered circumstances[40].

Figure 2-8 (a) Spin-resolved density of states (DOS) for the single vacancy and the hydrogen chemisorption defect in graphene. Red, blue and dashed curves correspond to the DOS of majority, minority spins, and perfect graphene, respectively. (b) Iso-surface representation of the spin-density distribution at the hydrogen chemisorption defect. Red and blue surfaces correspond to the majority- and minority-spin densities, respectively. (Adapted from [62]) (c) Distribution of local magnetic moments $M_i$ in a supercell with randomly distributed $p_z$ vacancies. (d) Average magnetic moments for the atoms as a function of defect concentration $x$. Lower and upper triangles stand for in sublattice A and B, separately. (Adapted from [40])
2-2-4 Findings of ferromagnetism in carbon systems

The magnetic findings have been reported in a variety of carbon forms. Crystalline p-nitrophenyl nitronyl nitroxide (p-NPNN) was reported to have magnetic ordering in 1991. In the same year, the ferromagnetism has been discovered in a charge transfer complex of C<sub>60</sub> and tetrakis(dimethylamino)ethylene (TDAE) [64, 65]. Carbon nanofoams and nanodiamonds show ferromagnetic signals at various temperatures [66, 67]. The former was cluster-assembled by laser ablation of glassy carbon target in an inert stainless-steel system [66].

![Figure 2-9 Magnetism of carbon nanofoam (a) TEM picture (b) Magnetization under different temperature measured against external field. (adapted from ref. [66])]()

A number of reports also point out that ferromagnetism exist in untreated graphite [68, 69] and attribute the findings to intrinsic point defects, such as grain boundaries. In 2003, room-temperature ferromagnetism was observed from highly oriented pyrolytic graphite (HOPG) irradiated with high-energy (2.25MeV) protons [70]. Figure 2-12 shows the hysteresis loop of a proton-irradiated sample compared to untreated HOPG at room temperature. More experiments show that the ion-bombard graphite has two dimensional characters, revealing that ferromagnetism can be controllably generated in light elements [71, 72]. Other than proton, iron and helium ions show no impact effects [70, 71]. On the other hand, the implantation of carbon ions was also reported to induce magnetic ordering in HOPG [73]. Polycrystalline fullerene thin films on Si substrates were reported to exhibit weak magnetic ordering after proton irradiation [74]. However, the sources of observed ferromagnetism in graphitic samples are still debated due to the iron contamination revealed in graphite in a recent report shows comparable ferromagnetic responses [75]. However, debated origins of ferromagnetism in irradiated carbon systems and insufficient magnetic results in
Functionalized carbon systems lead to incomplete magnetic mechanism of defected carbon systems. In 2010, the first magnetic finding in graphene system have been reported by using graphene laminate for enough magnetic signals. This finding shows the limitation of ferromagnetism of pure graphene. The graphene laminates were made by liquid exfoliation method, which described in Chapter 1. For more understanding about magnetism of graphene, we systematically investigate the defected graphene systems in this thesis with extreme care taken to avoid contaminations. This is the first time that defected-induced magnetism of graphene system has been investigated experimentally.

![Graph](image)

Figure 2-10 Magnetic moments of proton irradiated (filled circles) and untreated (empty squares) graphite as a function applied magnetic field as measured by Esquinazi et al. at $T = 300$ K. The weak hysteresis loop can be recognized. (Adaped from [70])

### 2-3 Orbital diamagnetism in graphene

Experimentally, bulk graphite [69, 70, 76, 77] and nanographite [78] exhibit extraordinary large diamagnetism. The susceptibility of graphite is about $-3 \times 10^{-5}$ emu/gOe. The large diamagnetic susceptibility shows temperature dependence (figure 2-11(a)) in single crystal of graphite and doping dependence (figure 2-11(b)) in boron-doped graphite. The absolute values of susceptibility decrease when the boron impurities added holes in graphite. The theoretical prediction shows electron-hole
symmetry (as the solid line in (b)). The temperature dependence shows the orbital diamagnetism is smaller when the temperature reaches up around 100K. The temperature dependence is predicted to be changed when doping occurs. The origin of the large diamagnetism of graphite has been studied over 60 years and associated with the orbital motion of electrons in planes.

Figure 2-11 Diamagnetism of graphite (a) Temperature dependence of orbital diamagnetism of graphite with different doping levels (as labeled). The black solid dots are the experimental data. (adapted from [77]) (b) Susceptibility varies with doping levels. The circles are the experimental data (adapted from [76]).

Monolayer graphene which has been expected to have even larger diamagnetism will be studied experimentally in Ch.4. Therefore some relevant theoretical calculations will be reviewed as follows. Due to the unusual band structures of graphene characterized by massless Dirac fermions, the orbital diamagnetism is significantly different from the conventional Landau diamagnetism. In graphene, the low energy states near the k symmetric points can be described by continuum massless Dirac Hamiltonian [79] and the diamagnetic susceptibility is calculated as

$$\chi = -\frac{g_v g_s e^2 \gamma^2}{24\pi h^2 k_B^2 T \cosh^2 \left[\mu/2k_B T\right]}$$

(2.1.19)

where $g_v = g_s = 2$ are the valley and spin degeneracy, respectively. $\gamma$ is a band parameter pertained to the nearest-neighbour coupling in a single layer, while $\mu$, $k_B$, $h$ are chemical potential, Boltzmann and Plank constant, respectively. In the clean limit and at absolute zero temperature, eq. (2.1.19) becomes a delta function:
\[ \chi = -\frac{g_v g_s e^2 \gamma^2}{6\pi \hbar^2} \delta(E_F) \]  

(2.1.20)

In this case, the diamagnetic susceptibility of graphene diverges when the Fermi energy \((E_F)\) is located at the neutrality point and vanishes inside the conduction and valence bands.

However, the effect of the spatial confinement and disorders are strong, which may affect the real observation of the diamagnetic susceptibility of monolayer graphene [80-83]. Ref. [80] studied the orbital diamagnetism in different morphology of graphene nanoflakes and size effect on them. In figure 2-13, the susceptibilities of four types of graphene nanoflakes are calculated by using tight-binding approximation and plotted as a function of the chemical potential of the systems. Instead of divergence, the susceptibility near the zero energy stays constant, which suggests that the presence of edge states plays no roles. Looking near the zero energy, the diamagnetic responses at the neutrality point of the armchair flakes tends to be greater than the zigzag ones and in the hexagonal structures is larger than trigonal ones at low temperature. The former feature is also observed in the calculations of diamagnetism in nanoribbons [81]. The susceptibility changes between diamagnetic and paramagnetic as a function of chemical potential of graphene nanoflakes, according to the subband structure formed by quantum confinement. The susceptibility approaches a thermal-broadened peak centred at the Fermi energy \(E_F = 0\) independent from the atomic configuration of flakes when the thermal vibration dominates.

The disorders in graphene also expected to influence the diamagnetic susceptibility [40, 82, 84]. Figure 2-14 shows the evolution of magnetization with different strength of long-range disorder \((W)\) at zero temperature and a fixed magnetic field. The upper panel shows the density of states as a reference to the variation in magnetization. In small \(W\), the magnetization exhibits a significant oscillation corresponding to the separation of Landau levels. Similar to the effect of thermal broadening, the amplitude and width of the zero-energy peak is reduced and broadened, and the magnetic oscillation is smeared out when the disorder strength increases. The short-range disorders affect qualitatively the same as long-range ones in figure 2-14[84].
Figure 2-12 Finite-sized and the thermal effects on the susceptibility of graphene nanostructures as a function of chemical potential (a) Hexagonal armchair (b) Trigonal armchair (c) Hexagonal zigzag (d) Trigonal zigzag nano flakes. In each graph, the upper panel presents the energy spectrum, where dashed (black) line is the non-degenerate and solid (red) stands for the two-fold degenerate levels. $S$ is the area of the nanoflakes (Adapted from ref. [80]).
In conclusion of this section, the diamagnetism of graphene is reviewed theoretically in this section. The diamagnetic susceptibility of graphene is calculated to be a delta function centred at the neutrality point and vanish rapidly when graphene is doped. This feature is pure and obvious only in the clean limit and at zero temperature. The strong effects of quantum confinement, disorders and temperature vary the delta-like peak of susceptibility. Due to the quantum confinement, finite-sized graphene nanoflakes show constant diamagnetic susceptibility when the energy near the neutrality point is varied. The susceptibility of disordered graphene also evolves into a broad and short peak centred near the zero energy when the disorder strength increases.
2-4 Review of magnetism in MoS$_2$

Graphene and defected graphene show interesting magnetic properties which may provide new perspectives of magnetic materials. For more extensive applications, the magnetism of other two dimensional materials has been intensively studied recently. In this section, the magnetism in MoS$_2$ is reviewed as the material which is easy to produce, stable and not expensive. MoS$_2$ in its bulk form is in principle diamagnetic. However, theoretical calculations suggest that ferromagnetism might be found in several forms of MoS$_2$ such as defected, zigzag-edged MoS$_2$ or the nanofragments of MoS$_2$, although the reports are scarce and there is no consensus on mechanisms [85-88]. Some results of the calculations relevant to the experiment in chapter 6 will be introduced in the first two sections, following with a review of experimental progress in MoS$_2$ and its relatives.

2-4-1 Effect of edges in MoS$_2$ nanoribbons and other nanostructures

Intact MoS$_2$ possesses non-magnetic behaviour, i.e. no spin polarization preferred. It is remarkable to achieve localized magnetic moments in non-magnetic MoS$_2$ without inducing ferromagnetic impurities. In the theoretical prediction, one of the possible sites is the edges. The effect of edges is demonstrated by a relatively simple approach, MoS$_2$ nanoribbons. Similar to graphene, MoS$_2$ can be cut in two highly symmetric crystalline directions, zigzag and armchair. Figure 2-16 shows the schematic atomic and band structures of zigzag and armchair MoS$_2$ ribbons. The zigzag nanoribbons are in metallic states independent of their thicknesses and widths, while no consistent result is concluded in the armchair one except its semiconducting behaviour after hydrogen termination [85, 87, 89]. Li et al., performed the spin-polarized first principle DFT calculations of MoS$_2$ nanoribbons [89]. The energy difference between spin-polarized and spin-unpolarized calculation shows that zigzag edges have the ferromagnetic ground state and armchair ones show non-magnetic state. The ferromagnetic behaviour is not affected by the thickness or width of the zigzag nanoribbons. Even the hydrogen termination can only suppress the ferromagnetism slightly.
In the case of nanoflakes, the shape and the sulphur coverage in the edges determine the magnetic properties. Since MoS$_2$ is not a bipartite system, Lieb’s theorem is not adopted here; instead, most of the simulations are done by DFT calculations. Zhou et al., have studied the magnetic properties of different shapes of MoS$_2$ nanodots and found only triangular nanodots have net spins [90]. Zhang et al., have calculated magnetic moments of the triangular nano-particles with various sulphur coverage of zigzag Mo and S edges. The calculation indicates that only molybdenum edge with no sulphur coverage (Mo-edge-0%S) and sulphur edge (S-edge-100%S) have magnetic moments. Figure 2-17 shows two cases of sulphur coverage in the edges of MoS$_2$ triangular nano-particles. The magnetism was pertained to the existence of edge spins on the prismatic edges of the triangle nano-clusters. The effect of sulphur coverage on magnetic properties of MoS$_2$ varies with the geometry of samples. Besides the above triangular clusters, Vojvodic et al. presented the magnetic properties of MoS$_2$ periodic stripes with different sulphur coverage under hydrodesulphurization. Among Mo and S terminated stripes, only the latter ones show magnetic behaviours while the other are non-magnetic in any circumstances [91].

![Figure 2-14](image.png)  
**Figure 2-14** Band structures and schematics of MoS$_2$ nanoribbons: (a) armchair (b) zigzag nanoribbons (Adapted from [85, 92])
2-4-2 Defect-induced magnetism in MoS$_2$

The possible origins of magnetic moments in MoS$_2$ are structural defects including adatoms, vacancies, deformation and partial destruction of the lattice structure, i.e. the edges states and its reconstruction. In the previous part, magnetism arisen from edges states has been reviewed. In this part, localized magnetic moments given by adatoms and vacancies will be reviewed, although not many studies have been performed so far.

Figure 2-18 shows the DFT calculation relevant to magnetism of diverse configurations and molecules in roles of adatoms in MoS$_2$ [86]. Six positions of individual atoms attached on the MoS$_2$ structures, namely Mo-1, Mo-2, S-1, S-2, S-3, and S-4, and their corresponding magnetic moments. The optimized adatom positions depend on the binding energies. Among the adatoms, C, Mo, S, and O are of particular interests. C was considered since it can form the stable planar, hexagonal structure and also the complex with MoS$_2$. Oxidation is always an important issue for the future applications. For Mo adatom at site S-3, there are four singly occupied d orbitals ($d_{xz}$, $d_{yz}$, $d_{xy}$, $d_{z^2}$) and $d_{xy}$ is doubly occupied. The s orbital in Mo adatoms is vacant. Therefore, each Mo adatom has local magnetic moments of $\mu = 4\mu_B$. For carbon adatoms at site Mo-1, sp$^2$-hybridized orbitals of carbon and $d_{xy}$ and $d_{x^2-y^2}$ of three surrounding Mo atoms form three bonds, but the system stays nonmagnetic. In the other case of carbon adatom at site S-3, sp$^2$-hybridized orbitals of carbon form three bonds with the three surrounding S atoms. A significant charge transfer is observed from Mo to the C adatoms due to the

Figure 2-15 Schematic structures of MoS$_2$ terminated with Mo (or S) covering by 100% S: (a) Mo-edge-100%S and (b) S-edge-100%S (adapted from [88])

![Schematic structures of MoS$_2$ terminated with Mo (or S) covering by 100% S](image-url)
interaction between the p orbital of the C adatoms and the underlying Mo d_{z^2} orbital. This results in a local magnetic moment of μ = 2μ_B on the Mo atom. S and O adatoms are nonmagnetic in all the configurations.

Figure 2-16 Adatom-induced magnetism of MoS_2 (top) Schematic atomic geometry of possible adsorption position of adatoms obtained after structure optimization. Adatoms and host Mo and S atoms are represented by red, purple, and yellow balls, respectively. (bottom) The table shows calculated values for the properties of 16 adatoms adsorbed on 1H-MoS_2. The red column is the magnetic moment induced by individual adatoms. (adapted from Ref. [86])

Vacancies are known to introduce localized magnetic moments in graphene and metal oxides. For example, the high spin states are reported in ZnO due to cation vacancies [93, 94]. Recently, effects of vacancy-type defects on electronic and magnetic properties are intensively studied in graphene-like systems. Single vacancies
in graphene crystals are proven to induce localized magnetic moments and can be understood by Lieb’s theorem. In the same sense, vacancies are considered to be possible sources for localized magnetic moments of MoS$_2$. Instead of the Lieb’s theorem, the DFT calculation is adopted. Five different types of vacancies formed in two-dimensional MoS$_2$ sheets, namely S- and Mo-single, S$_2$- and MoS- double, and MoS$_2$ triple vacancies, are considered [86]. All structures are optimized in their ground states. The DFT calculations indicate that except MoS$_2$ triple vacancies, no other types of vacancies provide magnetic moments. The origin of the magnetic states is related to the charge transfer between Mo and S around the vacancies. The Bader analysis provides detailed charge densities [86]. In the case of S and S$_2$ vacancies, the excess positive charge on the nearest Mo atoms slightly decreases and results in no magnetic moment. For Mo vacancy, the slightly reduced charge on S atom around the vacancy is partially balanced by charges provided from the other two Mo atoms. A similar situation is also applied in MoS vacancy. The charge transfer in these four kinds of vacancies is not able to lead to any magnetic states. Interestingly, six dangling bonds in MoS$_2$ lattice due to a MoS$_2$ vacancy generates the magnetic moments of $\mu = 2\mu_B$. The charge disturbance in this case is almost doubled compared to the previous four cases and causes the spin polarization. Figure 2-19 displays the charge density distribution near the MoS$_2$ vacancy.

<table>
<thead>
<tr>
<th>vacancy defect type</th>
<th>Mo</th>
<th>MoS</th>
<th>MoS$_2$</th>
<th>S</th>
<th>S$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_v$ (eV)</td>
<td>13.44</td>
<td>17.36</td>
<td>22.63</td>
<td>5.89</td>
<td>11.74</td>
</tr>
<tr>
<td>$\mu$ ($\mu_B$)</td>
<td>NM</td>
<td>NM</td>
<td>2.00</td>
<td>NM</td>
<td>NM</td>
</tr>
</tbody>
</table>

Figure 2-17 Magnetic moments of each defect types (upper table) and the isosurface of the charge-density difference ($\Delta \rho = \rho_1 - \rho_1$) of a MoS$_2$ vacancy in the $7 \times 7$ MoS$_2$ supercell (lower sketch). (Adapted from [86])
2-4-3 Experimental progress

The experimental history of magnetism in MoS$_x$ can be traced back to 1991 when the amorphous MoS$_x$ ($2 < x < 3$) has been studied by electron spin resonance (ESR) [94]. Paramagnetic centers found in ESR spectra of MoS$_x$ are attributed to the metal center, for example, Mo$^{5+}$. In 2007, nano-sheet films of MoS$_2$ have been synthesized and found to have weak ferromagnetism with the Curie temperature of 685K [88]. The magnetic ordering is attributed to edge spins on the prismatic edges of the nanosheets. Then, in 2009, discovery of large density of dangling bonds bearing unpaired electrons in MoS$_2$ fullerene-like nanoparticles, indicates the nanoparticle is more defective than the bulk material [95]. This observation explains the increased spin-lattice relaxation rate in nanoparticles in comparison with the bulk samples. SQUID measurements on the single crystal MoS$_2$ displayed the existence of ferromagnetism [96]. They discovered the ferromagnetic signals from 10K to room temperature superimposed onto the temperature-dependent diamagnetism. In the same year, an irradiation result of bulk MoS$_2$ was published. 2MeV proton-irradiated bulk MoS$_2$ with the ion fluences from $1 \times 10^{17}$ to $5 \times 10^{18}$ ions / cm$^2$ show temperature dependence of ferrimagnetic behaviour with the Curie temperature of 895K [97]. In 2013, ferromagnetism is again shown in the report of free-standing MoS$_2$ nanosheets [98]. Although many researches show that MoS$_2$ in various forms are ferromagnetic, no consistent properties can be concluded. In addition, similar to graphite during synthesis or modification of MoS$_2$, it is possible to include some magnetic impurities if not carefully avoided. Therefore, the studies of the magnetic properties of MoS$_2$ laminates mainly by SQUID magnetometer are presented in Ch. 6 with extreme care taken to avoid contaminations.
Chapter 3

Magnetism in Graphene Laminates Induced by Point Defects

Introducing magnetic moments by nonmetallic defects is always of great interest. In current applications, the magnetic materials, such as Fe or Ni, are based on partially filled $d$ or $f$ orbitals. A carbon-based magnetic material might provide a new direction for research. Especially, crystallized and thin graphene is promising to be designed for magnetic devices as defects in graphene are expected to create localized magnetic moments. In this chapter, the effect of two different types of point defects - vacancies and adatoms - on the magnetic properties of graphene laminates is presented. These defects were introduced to graphene by irradiation with highly energetic ions and chemical functionalization via fluorine atoms, respectively. Some of the experimental results in this chapter have been published in Nature Physics [75].

This chapter is organized as follows. First of all, fabrication of defected graphene laminates for magnetic measurements, including the production of pristine laminates and the methods for introducing defects, will be illustrated. Second, the magnetic properties of defected graphene laminates will be studied. The results refer to the vacancy- and adatom-induced magnetism. This is followed by some discussion and conclusion.

1 This work has been performed in collaboration with R. R. Nair (from University of Manchester), who produced fluorinated graphene and measured its magnetic properties. My contribution to this study was to fabricate the consistent samples for irradiation, study the magnetic properties of irradiated graphene with M. Sepioni (from University of Manchester), and be involved in the general discussions of the results. O. Lehtinen, J. Keinonen (from University of Helsinki) and A.V. Krasheninnikov (from the University of Helsinki and Aalto University), carried out samples irradiation and the SRIM simulations.
3-1 Sample preparation

Pristine graphene laminates were produced by liquid exfoliation from graphite [21]. The process can be separated into three steps: *exfoliation*, *centrifugation*, and *drying*. In the first step, high purity HOPG (grade ZYH from NT-MDT) was sonicated in an organic solvent, N-Methyl-2-pyrrolidone (NMP) at room temperature consistently for 1-7 days which resulted in more or less extensive exfoliation. Then, the solution was centrifuged at a rate of 14,000 r. p. m. so the top could be extracted to separate it from thicker blocks of graphite and aggregations of flakes. The resulting suspension (as in figure 3-1 (a)) is filtered through a 20nm pore alumina membrane and dried on 120°C hot plate, producing graphene laminate with diameter of ~2cm (as in figure 3-1(b)) which has weight and thickness of several milligrams and micrometres. The large collection of non-interacting graphene flakes presented in these samples provides chances for magnetic studies in graphene, as the magnetic signals are sufficient to be detected by SQUID magnetometer. A SEM image shows that the flakes pack almost in parallel and are of irregular shapes but the edges tend to follow main crystallographic directions. Extreme care was taken to avoid contaminations in the whole process. In order to introduce defects in graphene laminates, ion irradiation with high energy ion beams and fluorination were adopted with the process as follows.

The process to produce fluorinated graphene laminates is similar to that used for fluorinating single layer mechanically exfoliated graphene [29]. The graphene laminates (as in figure 3-1b) were exposed in a Teflon container to atomic fluorine released by decomposition of xenon difluoride (XeF₂) at 200°C for several hours. For fluorinated graphene, the reaction formula can be written as

\[ C_n + F_n \rightarrow (CF)_n \]  

(3.1.1)

n is the percentage that carbon atoms are fluorinated. Raman spectroscopy and colour were used for monitoring the fluorinated stages of the sample. The colour changes from metallic dark grey, through brown to light yellow (as in figure 3-2) with increasing *F/C ratio*. X-ray photoelectron spectra (XPS) and energy- dispersive X-ray spectroscopy (EDS) provide quantitative information about the elemental composition and confirmed the presence of C-F bonds and relatively less C-CF, CF₂, CF₃ bonds. The *F/C* increases with longer exposure time. In the following section, results obtained on samples with different *F/C* ratios will be presented to show the dependence of the magnetic responses on adatom concentration in graphene laminates. After 80h exposure, graphene laminates become stoichiometric fluorographene, i.e. *F/C*=1. From
the elemental analysis by EDS, our samples showed no metallic contaminations.

![Figure 3-1: Pristine graphene laminates](image)

(a) graphene suspensions (b) dried graphene laminates (c) a SEM image of laminates

Figure 3-1 Pristine graphene laminates: (a) graphene suspensions (b) dried graphene laminates (c) a SEM image of laminates

![Figure 3-2: Fluorinated graphene laminates](image)

(a) Optical images of starting (b) fully fluorinated graphene laminates. The scale bar is 2 cm. The laminates consist of tens-hundreds of nanometer graphene crystallites, predominantly mono-and bilayers

Figure 3-2 Fluorinated graphene laminates: Optical images of starting (a) and fully fluorinated (b) graphene laminates. The scale bar is 2 cm. The laminates consist of tens-hundreds of nanometer graphene crystallites, predominantly mono-and bilayers

Two types of ions, carbon ions (C$^{4+}$) and protons, of high energy were used to knock out carbon atoms and create vacancies in graphene laminates. C$^{4+}$ ions were accelerated to energy of 20MeV while the vacuum maintained in a range of $10^{-6}$-$10^{-7}$ mbar. The environment was cooled by liquid nitrogen and the sample temperature was maintained below 50°C. A 500 kV ion implanter was used to produce protons in energy of 350keV-400keV. Particular energies for the corresponding thickness of graphene laminates were chosen in order to get the uniform distribution of vacancies in the sample. The appearance of the samples does not show differences before and after irradiation, but the latter are more fragile. Defect density of each sample can be
estimated by the following formula based on the corresponding fluence (flux of ions through the sample, integrated over time) and displacement per ion (dpi).

\[
\text{defect density} \left( \frac{\text{defects}}{g} \right) = \frac{\text{Fluence} (\text{cm}^{-2}) \cdot \text{dpi} \cdot A}{M(g)}
\]  

(3.1.2)

where A and M are the area and weight of the sample. According to the parameters of our samples, the defect densities in a range of \(10^{18} - 10^{20} g^{-1}\) were achieved. Comparing to fluorinated graphene laminates, the defect densities of irradiated samples are relatively low. The limitation of vacancy density is due to the disintegration of samples.

### 3-2 Magnetic responses of defected graphene laminates

The magnetic properties of graphene laminates with point defects of ion-irradiated vacancies or fluorine adatoms are presented in this section. The magnetic properties were measured by the SQUID magnetometer (Quantum Design MPMS XL7). Before presenting the results, it is worth mentioning the magnetic properties of pristine graphene laminates. Due to the tiny magnetic signal of single graphene sheet, the mechanically exfoliated graphene is not practical as a sample for the studies of its magnetic properties. Instead, the large collection in graphene laminates of mg weight provides enough signals for magnetometer to detect. Pristine graphene laminates are strongly diamagnetic at all temperatures and display very weak background paramagnetism that requires low temperature \((T < 50^\circ\text{C})\) to be noticeable, corresponding to a low density of magnetic moments, around one spin per graphene crystallite [99]. In the following two sections, the effects of adatoms and vacancies on the magnetic properties of graphene will be studied using the same magnetic measurements as carried out for pristine graphene.

Fluorinated graphene laminates with \(F/C\) ratio (defined as \(x\)) from 0.1-1 were used to study the role of adatoms to the magnetic responses of graphene by the SQUID magnetometer. The exposure to atomic fluorine gives rise to strong paramagnetism in graphene laminates (as in figure 3-4(a)). The maximum paramagnetic signal due to fluorine adatoms was an order of magnitude greater than the pristine background. The
adatom-induced magnetization as a function of the reduced field, \( M(H/T) \), were well described by the Curie-Brillouin function

\[
M = N_s g J \mu_b \left[ \frac{2J + 1}{2J} \coth \left( \frac{2J + 1}{2J} x \right) - \frac{1}{2J} \coth \left( \frac{1}{2J} x \right) \right]
\]

(3. 2. 1)

where \( x = g \mu_b H / k_B T \), as shown in figure 3-4(a). \( N_s, g, J, \mu_b \) and \( k_B \) stand for density of spins, \( g \) factor (2 for free electrons), total angular momentum number, Bohr magneton, and Boltzmann constant, respectively. To determine the magnetic status, several fits for different \( J \) values is compared in figure 3-3, showing only \( J=S=1/2 \) fits the data. The spin-half paramagnetism indicates that most of the spins are non-interacting in the fluorinated graphene. This statement is confirmed by the temperature dependence of magnetization \( M(T) \) in the same samples. The Curie-law curve

\[
\frac{M}{H} = N_s J (J + 1) g^2 \mu_b^2 / 3k_B T
\]

(3. 2. 2)

with \( J=S=1/2 \) and \( N_s \) extracted from \( M(H/T) \) curves are well fit with the observed \( M(T) \) as shown in figure 3-4(b). We carefully examined possible ferromagnetism in all of the samples due to the reports of defects-induced magnetic ordering in the other carbon systems. However, no indications were found in any fluorinated graphene laminates with accuracy of magnetometer. The inset in figure 3-4(b) shows the sample obeying purely the Curie law where the magnetisation is in inverse proportion to the temperature (\( M \propto 1/T \)) and shows no indication of ferromagnetism. Moreover, some small magnetite particles were found in HOPG and the signal provided from these impurities corresponds to the weak ferromagnetic signal detected from HOPG (more details have been described in supplementary information of ref [75]).

The observed \( N_s \) extracted from \( M(H/T) \) increases monotonically when \( x \) gradually increase from small up to \( x = 0.9 \), and then a slight drop shows afterward in stoichiometric fluorinated graphene (\( x=1 \)). The same data were re-plotted in figure 3-4c (inset) as the magnetic moments per defect (\( M/F \)) to compare with the expectation in theory. \( M/F \) fluctuated near \( 0.5 \times 10^{-3} \mu_B \) when \( x < 0.5 \) and sharply increases to a magnetic moment near \( 1 \times 10^{-3} \mu_B \) with more complicated behaviors. In other words, a magnetic moment of \( 1 \mu_B \) is generated by around 1000 fluorine adatoms. This is far smaller than the theoretical prediction of \( 1 \mu_B \) per sp\(^3\) defects [62]. The reduction of \( M/F \) ratio may be attributed to the tendency of fluorine clusters in graphene laminates because of the low migration barriers for F atoms [100-102]. The presence
of ripples [100, 102] enhances the tendency of fluorine clustering. The three-order reduction in $M/F$ ratio implies that the size of clusters is around 8nm, which agrees with the typical sizes of ripples measured in graphene [3]. The magnetic contribution may only come from the edges of clusters and the missing fluorine atom, since the magnetic moment from the interior of a cluster is expected to be zero because of the bipartite nature of the graphene lattice (no symmetry breaking between the two sublattices). Therefore, the magnetic moments contributed from each cluster to the total magnetization are expected to be a few $\mu_B$, in good agreement with our observations.

Figure 3-3 The determination of total angular momentum ($J$): symbols show a $M(H/T)$ curve and solid curves are the fits to the Brillouin function with different $J$. 
Figure 3-4 Adatom paramagnetism (a) field-dependent magnetisation curves of the samples of different F/C ratios. Symbols are the experimental data and the solid curves represent the fits to the Brillouin function of $J=S=1/2$ (b) temperature-dependent susceptibility follows Curie law (red solid curve). Inset: a clearer interpretation of the fit by Curie law (c) density of spins $N_s$ extracted from the fits to the Brillouin function. The solid curve is a guide to the eyes. Inset: The same data as the main panel replotted as the magnetic moments provided by each fluorine adatom as a function of fluorine concentration.

The generality of defect-induced paramagnetism can be explored by studying the magnetic properties of graphene laminates with vacancy-type defects. Vacancies in graphene laminates were introduced by proton (H$^+$) and carbon-ion (C$^{4+}$) irradiation. Irradiation-induced paramagnetism was observed in the irradiated samples, regardless of incident ion type. Note the paramagnetic signals from pristine graphene laminates were comparable to those induced by vacancies. Only the irradiation-induced paramagnetism is shown, in other words, the signal from pristine samples is subtracted. Figure 3-5 plots $M(H/T)$ to clarify the magnetic species contributing to $M$. Similar to the magnetization of fluorinated graphene laminate, the observed behaviour is well interpreted by $J=S=1/2$ Curie-Brillouin function, indicating the presence of
non-interacting spins. For comparison, the fitting curves for $J=1$, $3/2$, and $2$, were also shown, all of which provide very poor fits, clarifying that only $J=S=1/2$ fits the data.

More samples of different vacancy concentrations are studied and compared in figure 3-6. To analysing the effect of defect concentration on magnetism induced by individual vacancy, magnetic moments ($\mu$) per defect against defect densities were plotted. Note the magnetic moments were extracted from the fits of Brillouin function. The magnetic moments were found in between 0.1-0.4$\mu_B$ per vacancy, which is irrelevant to the defect density and reasonably consistent with the theoretical prediction for single vacancies, $1 \mu_B$/defect [62]. Accordingly, the magnetic responses of graphene laminates were independent on the type of incident ions. The fact that our observation is lower than the prediction may be due to the uncertain estimation of defect densities. First of all, SRIM simulation used for vacancy-density calculation works perfectly with graphite, but it cannot consider exactly the disordered arrangement of the graphene laminates. In addition, single vacancies are possible to reconstruct into the non-magnetic ones, such as Stone-Wales defects, chemical-terminated dangling bonds, double vacancies and so on [32, 59, 103]. Furthermore, vacancy-interstitial recombination cannot be avoided during or after the irradiation process. No evidence of defect-related ferromagnetism was found in all the cases we studied. However, the finding does not rule out ferromagnetic coupling between vacancy moments as the average distance between defects was $\sim 10nm$ which is greater than the distance required for magnetic coupling [104].
Figure 3-5 Magnetisation induced by vacancies: symbols show data for two different vacancy concentrations (lower curve $2.4 \times 10^{19} \text{ g}^{-1}$ and higher curve $7.4 \times 10^{19} \text{ g}^{-1}$) and solid fits display the description of Brillouin function. The solid curves correspond to the fits of Curie-Brillouin function with different $J$.

Figure 3-6 Vacancy paramagnetism: Magnetization and normalized magnetic moments of graphene laminates irradiated with protons (blue squares) and carbon ions (red diamonds). Main panel: average magnetic moments induced per vacancy. Inset: magnetic moment $\Delta M$ induced by vacancies as a function of the reduced magnetic field. Defect density of $7.4 \times 10^{19} / g$ is corresponding to $4.92 \times 10^{-4}$ vacancy/carbon atom.
3-3 Conclusions

In conclusion, our observations of spin-half paramagnetism in ion-irradiated and fluorinated graphene laminates support the theoretical prediction of defects-induced magnetic moments in graphene. Although several experiments report the evidences of magnetic ordering in other carbon systems [68, 69, 105], we did not find any ferromagnetic signals with the sensitivity of our magnetometer for all defected graphene laminates, not even for the highest defect density and at the liquid Helium temperature. The highest concentration of magnetic moments achieved here is ~0.1% of the maximum theoretical prediction of $1\mu_B$ per carbon atom. In the case of fluorinated graphene, the lower concentration of magnetic moments is explained by clusters of fluorine adatoms. Only a few $\mu_B$ contributed from the edges of clusters or missing fluorine atoms, even for the sample of $F/C$=1. For irradiated graphene laminates, the limitation of magnetic moments in ion-irradiated graphene laminates may be the consequences of recombination of vacancies and interstitials, over counts of defects, and reconstruction of defects and most importantly, relatively low vacancy concentration due to the integrity of laminates.
Chapter 4

Control of Magnetic Response of Graphene by Molecular Doping

Graphene has lots of unique properties, such as ambipolar electric field effect [14, 16, 106, 107], high mobility of charge carriers [14, 16, 106, 107], and relativistic dynamics [108-110]. Based on these properties, graphene is a candidate for post-silicon electronics, in which effective p-type and n-type doping of graphene are necessary. Although the ambipolar effect in graphene can make logic circuits with pristine graphene, the unintentionally induced doping in the air might affect its performance. Molecular doping provides a more realistic way to produce large scale n-type and p-type doped graphene [13, 111-114]. Doping in graphene has been therefore intensively studied by transport measurements, but not magnetically. Graphene with defects, such as adatoms and vacancies, is known to have localized spins (or more specifically paramagnetic centres) centred at defects [75]. Controlling spins through changes in electric field is always desired and regarded as a big step for graphene spintronics. Except the interest in paramagnetism, orbital diamagnetism in graphene has also gained a lot of attentions. Large diamagnetic susceptibility of graphite has been investigated over decades [76, 79]. The origin is believed to be based on the nature of graphene monolayer, which exhibits singularity susceptibility in the Dirac point [76, 79]. This leads to the fact that the orbital diamagnetic susceptibility decreases when graphite is doped [76, 79] and a similar prediction is made for graphene [80].

In this chapter, the doping effect on magnetic properties of graphene is therefore investigated by molecular adsorption. This method is promising since molecular doping is non-invasive to graphene and can be easily attached and removed by adsorption and annealing [13]. The mechanism of doping and characterization of the relevant dopants of graphene of this chapter is first introduced. In the section 4-2,
control of the paramagnetism of graphene by molecular doping is discussed. It is followed by the studies of the orbital diamagnetism of graphene and its tuning by molecular doping. In the end, a brief conclusion is given for the above experiments. Some of the results here have been published in Nature communication [115].

4-1 Molecular doping of graphene

In this section, a brief introduction to molecular doping of graphene and characterization technique relevant to our studies will be first introduced. Thereby, the characterization of HNO$_3$-induced hole-doping in graphene and graphene laminates by Raman spectroscopy and transport measurement will be presented, respectively. This will be followed by the characterization of a new dopant for graphene, namely $N,N,N',N'$-tetramethyl-p-phenylenediamine (TMPD). It is known as an electron dopant for carbon nanotubes [116], yet this is the first time that it has been used for graphene doping. In the end, the stability of dopants in the air and the thickness dependence on doping in graphene will be mentioned since they are of importance for interpretation of non- in situ SQUID measurement and the magnetic measurement of doped graphene laminates, respectively.

4-1-1 Mechanism for molecular doping of graphene

According to a large amount of literature, doping on graphene can be categorized into two methods: electrical doping achieved by changing gate voltages and chemical doping. Surface-transfer and substitution are two main methods among chemical doping in graphene. Substitution doping is achieved by replacing carbon atoms with dopants, e. g. boron or nitrogen [117, 118]. This method is invasive to the materials and causes defects. On the other hand, surface-transfer doping relies on

---

2 This work was performed with the cooperation of R. R. Nair and M. Sepioni for the magnetic measurements and experiment design; O. Lehtinen, J. Keinonen, and A.V. Krasheninnikov performed the irradiation and the estimation of defect density; A.H Castro Neto and M.I Katsnelson provided theories and I.V Grigorieva directed this project.
charges transfer between graphene and dopants which are physisorbed on the surface of graphene [119, 120]. This method is non-destructive to the materials. Surface transfer doping is adopted in this chapter to shift the Fermi energy of graphene in order to investigate its magnetic responses. Since only molecules are used for adsorbates on graphene in this chapter, the term of ‘molecular doping’ is used.

By molecular doping, graphene is hole- or electron-doped through charge exchange with the surface-physisorbed molecules. Graphene which accepts (donates) an electron from (to) adsorbates results in n-doped (p-doped) graphene. Charge-transfer direction is determined by the relative position of lowest unoccupied molecule orbital (LUMO) or highest occupied molecule orbital (HOMO) and the Dirac point of graphene as shown in figure 4-1. When the LUMO of the adsorbate is lower than the Fermi energy of pristine graphene, electrons transfer from graphene to adsorbates and form hole-doped graphene (also called p-type doped graphene). On the other hand, when the HOMO of the adsorbate is higher than the Fermi level of pristine graphene, electrons transfer from adsorbates to graphene and form electron-doped graphene (also called n-type doped graphene).

![Figure 4-1 Mechanism of molecular doping of graphene](image)

(a) hole doping: When the LUMO of dopants is lower than graphene, electrons transfer from graphene to dopants. (b) electron doping: When the HOMO of dopants is higher than graphene, electrons transfer from dopants to graphene.
Figure 4-2 Doping dependence on chemical potential and the DOS of graphene (grey shade) or conventional semiconductor (blue shade): HOMO and LUMO in (a) and (b) are located in valence and conduction band, respectively, resulting in no doping. (c) and (d) shows the doping efficiency of different dopants. Molecules using in (c) requires only small mismatch in chemical potential difference of graphene and molecules ($\Delta \mu$). (e) and (f) shows the doping in conventional semiconductor happens when $\Delta \mu > (E_{HL} + E_G)/2$. (adapted from [111])

Comparing to other semiconductors, graphene is much easier to be doped due to its electronic structure. The doping efficiency depends on several factors, including the mismatch chemical potential of graphene and dopants ($\Delta \mu$), the energy difference of HOMO and LUMO of molecules ($E_{HL}$) and the band gap of the substances. $\Delta \mu$ has to exceed $(E_{HL} + E_G)/2$ for the activated donors or acceptors in conventional semiconductors (as depicted in figure 4-2 (e)). In the case of graphene, a small mismatch chemical potential is sufficient for an activated dopants since the absence of band gap in graphene. Many adsorbates have been reported for effectively doping of graphene. Some of them are listed in table 4-1 [13, 20, 111-114, 121-124]. NO$_2$ is an example that the density of states of partially occupied molecular orbital (POMO) of NO$_2$ molecules adsorbed on graphene is significantly below the Dirac point (0.4eV). Hence, each molecule can accept one electron from graphene, inducing holes. Experimentally, graphene devices have been demonstrated as an individual molecular sensor for NO$_2$ by doping in dilute gas atmosphere [13]. On the other hand, due to the existence of many hole dopants in the air, the substances which induce weak electron
doping to graphene is relatively hard to discover. Aniline was one of the electron dopant used in our experiments which donates electrons to graphene, making it n-doped. Another example, TMPD, will be characterized in the following to understand its role of doping in graphene [116, 124].

Table 4 - 1 Molecular dopants of graphene

<table>
<thead>
<tr>
<th>Hole dopants</th>
<th>Electron dopants</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Molecules</em>: HNO$_3$(NO$_2$), H$_2$O, F4-TCNQ, TPA, …</td>
<td><em>Molecules</em>: NH$_3$, Aniline, NaNH$_2$, An-CH$_3$…</td>
</tr>
</tbody>
</table>

4-1-2 Raman spectra of pristine and doped graphene

**Pristine graphene**

Raman spectroscopy is a quick, non-destructive and versatile technique to characterize graphene. It provides a fast way to identify single layer graphene from multilayer ones and graphite [18]. Apart from this, Raman spectrum of graphene quantitatively describes the doping level [125, 126], disorder [126], and strain of graphene [127, 128].

The G and 2D bands, around 1580cm$^{-1}$ and 2700cm$^{-1}$ respectively, are corresponding to in-plane $E_{2g}$ vibrational mode and $A_{1g}$ breathing mode in sp$^2$ rings. The thickness and doping level of graphene can be identified by these two modes [18, 126]. D band, around 1450 cm$^{-1}$, is the first order of $A_{1g}$ mode activated by defects. Thus D band is a mode for defect characterization. Another presented peak in defected graphene, called D’ band, locates around 1620cm$^{-1}$ and forms a shoulder of G peak [126].

The shape of 2D peak is sensitive to the thickness of graphene as shown in figure 4-3. 2D peak of one layer graphene is a single Lorentzian peak with a FWHM typically smaller than 30cm$^{-1}$. 2D peak of bilayer graphene composed of four Lorentzian peaks is based on four parabolic bands formed by the A-B stacking of bilayer graphene [18, 129]. This consideration can be extended to multilayer graphene.
Figure 4- 3 The thickness evolution of Raman spectra of graphene: 1, 2, 3, 6 layers of graphene and graphite: The ratio of $I_{2D}/I_G$ decreases and shape of 2D peak changes. (Adapted from ref. [130])

Doping effect on graphene

When graphene is doped by either electrons or holes, some changes are listed as below [131]:

1. G peak position shifts from 1580 cm$^{-1}$ to the right and FWHM of G peak narrows down as in figure 4-4(a). Figure 4-4(b) was produced by the Raman measurements while applying gate voltage to graphene on Si/SiO$_2$ substrate to intentionally modify the electron concentration [131]. This allows determining the Fermi energy by detecting G peak position in Raman spectra of graphene, but not for the sign of doping since its almost-symmetric behaviour.

2. Ratio of $I_{2D}/I_G$ decrease

3. If doping is high enough, 2D peak position will shift in a direction which depends on dopants. Electron dopants shift 2D position to the left while hole dopants shift it to the right.
Figure 4-4 The correlation of G peak position shift and the Fermi energy: (a) Raman spectra of graphene with different doping level. The top one is neutral graphene and the lower two are different doped one. (Adapted from [129]) (b) Position of G peak in Raman spectra of graphene in a function of electron concentration (Fermi energy). (Adapted from [131])

4-1-3 Sample preparation and characterization

*Graphene doped by nitric acid (HNO$_3$)*

HNO$_3$ is used as hole dopant of graphene for shifting the Fermi level of graphene laminates in this chapter for studying the doping effect on magnetic properties [20]. In order to determine their Fermi energies, transport measurements were taken on graphene laminates, and Raman spectra were analysed for mechanically-exfoliated graphene flakes deposited on SiO$_2$/Si. Graphene flakes made by mechanical exfoliation and deposited on SiO$_2$/Si substrate were dipped in HNO$_3$ with concentration of 0-15M. These samples were then measured in Renishaw Raman spectrooscope and the spectra are shown in figure 4-5(a). The hole concentration estimated by using figure 4-4(b) is plotted as a function of molarity in figure 4-5 (b). The maximum doping level which can be achieved at 15M was $\sim$2x10$^{13}$ cm$^{-2}$.

Graphene laminates made by liquid exfoliation (please see the sample production in Ch.3) are used as samples for magnetic measurements. Therefore, it is important to understand the adsorbates effect on the carrier concentration of graphene
laminates since it may be different from the effect on exfoliated monolayers. Hall measurements were carried out in the van-der-Pauw geometry on 3 × 3 mm² samples as drawn in the inset of figure 4-6. The carrier concentrations extracted from the slopes of $R_{xy}(H)$ are in excellent agreement with those estimation from Raman spectra for exfoliated monolayer in figure 4-5 as high proportion of graphene in graphene laminates. Thus, HNO₃ is considered as a good dopant for investigating the magnetism of graphene laminates.

Figure 4-5 Hole doping of graphene induced by nitric acid: (a) Examples of Raman spectra of mechanically exfoliated monolayer graphene deposited on Si/SiO₂ substrate, after exposing to nitric acid at different concentrations; labels show molar concentrations of HNO₃. Corresponding G-peak positions are 1581, 1586, 1599 and 1603 cm⁻¹. (b) Carrier concentrations as a function of molar concentration of HNO₃.
Figure 4-6 Carrier concentrations in doped graphene laminates: Hall resistance per graphene layer in the laminate ($R_{xy}$) as a function of applied magnetic field for HNO$_3$ doped graphene. Labels show corresponding carrier concentrations in cm$^{-2}$. Inset: Hall measurements were carried out in the van-der-Pauw geometry on 3×3 mm$^2$ graphene laminate.

**Graphene doped by N, N', N'-tetramethyl-p-phenylenediamine**

*N, N', N'-tetramethyl-p-phenylenediamine* (TMPD) is a phenylenediamine and the schematic structure is shown in figure 4-7 (a). The electron transfer is through the functional groups. TMPD appears as flake-shaped solid in room temperature and is soluble in most of organic solvents. Ethanol and NMP were used as solvents for TMPD in the following experiments, Raman and transport measurements to determine the Fermi energy of graphene doped by TMPD.

To investigate the doping level of graphene induced by TMPD, the studied graphene devices were prepared by mechanical cleavage of graphite at the surface of SiO$_2$/Si substrate. The electrode contacts to graphene have been fabricated by using electron-beam lithography and then defined multi-terminal Hall bar by oxygen plasma etching. A layer of Hexamethyldisiloxane(HMDS) is applied to SiO$_2$ surface prior to the deposition of graphene, inducing holes to graphene. This method avoids applying high back-gate voltages while measuring heavily electron-doped graphene devices. The zero-magnetic-field resistivity ($\rho_{xx}$) of graphene device as a function of gate voltage ($V_{BG}$) before and after depositing TMPD are shown in figure 4-7. The
neutrality point ($V_{nBG}$) shifts from 58V to 15V by casting 0.7wt% TMPD/ethanol on graphene, indicating TMPD inducing intrinsic electron carrier concentration of $3.1 \times 10^{12} \text{cm}^{-2}$.

Figure 4-7 (a) Schematic structure of a TMPD molecule  (b) Transport measurement of before and after TMPD applying on graphene. (the Hall device was made by J.-S. Tu and measured by G. Yu ) (c) Raman spectra of before and after TMPD solution applied, 10wt% and 20wt% are compared. (d) carrier concentration of graphene as a function of TMPD/NMP concentration.

TMPD on graphene shows electron doping by back-gate measurement accurately. However, it requires incorporating graphene in a device which needs to be protected during the chemical treatment and is relatively complicated. Raman spectroscopy is an effective way to determine the doping level on graphene and G peak position shift is the most sensitive feature for monitoring doping effect of graphene. The graph in figure 4-4 is used for determination of graphene’s Fermi level by the correlation of G peak position shifts and carrier concentration in graphene of the graph.

The graphene sample for Raman measurement is also made by mechanical cleavage from graphite and deposited on Si/SiO$_2$ substrate. The sample then was dipped into a TMPD/NMP solution of known concentration. The samples were then
dried in the vacuum. Raman spectra has been taken by a Renishaw Raman Spectrometer, with a laser wavelength of 514.5 nm. Laser power was controlled below 2 mW to avoid localized heating on graphene. In figure 4-7, concentration of TMPD/NMP monotonically changes the doping on graphene as G peak shifts more when TMPD/NMP of higher concentration casting on graphene. In addition to G peak position shifts, the FWHM of G peak and ratio I_{2D}/I_G are both reduced. The carrier concentration in graphene as a function of concentration of TMPD/NMP is shown in Figure 4-7, where the maximum doping is around \( E_F \approx 0.3 \text{eV} \). Although, TMPD can dope graphene efficiently and the doping is stable in the air, we found that TMPD exhibited non-negligible paramagnetism, which is comparable with the paramagnetic signals from defected graphene. Therefore, it was not used in the studies of defect-induced magnetism.

**Stability of the molecular dopants in air**

As the samples used for magnetization measurements had to be exposed to air, we investigated the corresponding stability of NO₂, HNO₃, TMPD and Aniline. We tested the corresponding stability on monolayer graphene, micromechanical cleavage at the SiO₂/ Si substrate, by Raman spectroscopy. For testing the stability of NO₂ in the air, graphene was exposed in NO₂ atmosphere for several days, making sure that the doping reaches maximum. Raman spectra were taken immediately after exposure and then also certain duration in the air. The Raman spectra and the tendency of carrier concentration as a function of exposure time in the air are shown in figure 4-8. It was found that the doping by all the mentioned substances can last for at least two weeks. For example, the Raman spectra of the NO₂-applied graphene shows that G peak shift to around 1600cm⁻¹ and I_{2D}/I_G is lower compared with the neutral graphene, indicating heavily doping of graphene. These changes gradually recover with time as shown in panel (a). The recovery also indicates no molecules forming sp³ defects on graphene for such bonding which is not being removed by thermal disturbance at room temperature. By the decay tendency of carrier concentration in figure 4-8, doping level remains more than half of its initial values after two weeks. The atmosphere finally removed the doping in the third week (figure 4-8). Furthermore, HNO₃ and other aromatic molecules last longer than one month.
Figure 4-8 Stability of doping induced by HNO$_3$ in the air (a) Raman spectra of before (black solid curve), after (red solid curve), and three weeks after (blue dashed curve) monolayer graphene on Si/SiO$_2$. (b) The carrier concentration decreases with time exposure in the air.
Dependence of doping efficiency on thickness of graphene

To investigate a possible dependence of the doping level and stability of the number of graphene layers, Raman spectra were taken for different thickness of graphene before and after casting 7M nitric acid (HNO₃) as shown in figure 4-9. From the Raman spectra, one can estimate the carrier concentration of mono and bilayer graphene[132]. The shift in G peak of graphene is much bigger than those in bilayer graphene and graphite. The G peak in monolayer graphene shifts from 1583cm⁻¹ to 1598cm⁻¹, corresponding to carrier concentration of $1.4 \times 10^{13}$cm⁻², while the G peak shift in bilayer graphene only to 1588 cm⁻¹, is corresponding to $8 \times 10^{12}$cm². Almost no changes in the shape and position of Raman peaks of graphite due to HNO₃ treatment. The different efficiency is because the doping difficulty varies for different thicknesses of graphene, i.e. HNO₃ is not easy to intercalate in graphite [112].

![Raman spectra of graphite, bilayer graphene, and monolayer graphene](image)

Figure 4-9 The thickness dependence of doping effect on graphene: 7M HNO₃ was applied on monolayer and bilayer of graphene and graphite. For monolayer graphene, G peak was shift to 1598cm⁻¹; for bilayer graphene, G peak to 1588 cm⁻¹; and no significant shift was observed in graphite.
4-2 Control of defect magnetism in graphene by molecular doping

Graphene is expected to be a promising spintronic material [42], and paramagnetic centres were demonstrated in the previous chapter to be injected in graphene systems by point defects, such as vacancies and adatoms [75]. It is therefore of great interest to control the magnetic properties of graphene by electric field. Various properties related to the electronic structure of graphene, such as in optics and electronics, are displayed to be tuneable by electric fields [133]. To this end, the evolution of paramagnetism of graphene when varying its Fermi energy is displayed in this section. Proton irradiated and annealed graphene laminates are used for monitoring the paramagnetism introduced by vacancies and sp\(^3\) impurities. Quantum Design MPMS SQUID magnetometer is used to detect the magnetic moments of chemical doped graphene laminates. The concentration of vacancies can be controlled by irradiation with proton beams (energy: 350-400keV) and estimated by SRIM simulation as described previously in Chapter 3. On the other hand, annealed graphene laminates are produced in a 350°C, H\(_2\)/Ar environment for 3 hours. These two types of defected graphene laminates show significant spin-half Curie paramagnetism. One can obtain \(N_s^0\), the density of spins (or the density of paramagnetic centres) prior to molecular doping, by fitting the paramagnetic signals to the Curie-Brillouin function. Refer to the studies in Chapter 3, the density of paramagnetic centres is proportional to the defect concentration of ion-irradiated graphene laminates, while the density of sp\(^3\) defects were not estimated.

Molecular doping was applied to change carrier concentrations of graphene laminates. HNO\(_3\) (NO\(_2\)) was used in this experiment as p-type dopants. By using either of them, graphene can achieve the Fermi energy of \(|E_F|\sim0.5\text{eV}. On the other hand, the best electron dopant found for this experiment is Aniline, which shifts the Fermi energy of graphene to \(|E_F|\sim0.3\text{eV}. No suitable electron dopant was found for shifting the Fermi level beyond this. The evolution of magnetic moments remains more or less unchanged, while the conduction band is filled by applying Aniline until \(|E_F|\sim0.3\text{eV which is symmetric to the behaviour influenced by HNO}_3. Thus, we simply show the results of paramagnetism in which graphene is doped by HNO\(_3\).
Figure 4- 10 Sketch of HNO$_3$ molecules physisorption in graphene laminates: grey planes and coloured molecules represent graphene sheets and HNO$_3$, respectively.

Figure 4- 11 Effect of hole concentration on vacancy paramagnetism induced by vacancy: Symbols show the measured magnetization $M$ against the reduced magnetic field ($H/T$) for different carrier concentration. A linear diamagnetic background is subtracted from the raw measurement. Solid curves corresponds to fits of the Brillouin function with $J = 1/2$. Labels show the corresponding Fermi energy $|E_F|$ in the valence band.
Figure 4-12 Normalized density of spins ($S=1/2$) in two irradiated samples as a function of their Fermi energy. $N_s$ is the spin density extracted from the Brillouin function fit for the $M(H)$ dependence for each doping level. $N_s^0$ is the density of spins when graphene laminates are neutral. The dashed curve is a guide to the eyes. Annealing maximally doped sample B at $\sim$100°C for 2h recovered of density of spins as shown by the open symbol.

\[ N_s/N_s^0 = \frac{\coth \frac{2J + 1}{2J} x - \frac{1}{2J} \coth \left( \frac{1}{2J} x \right)}{\coth \frac{2J + 1}{2J} x} \]  

(4.1.1)

**Doping effect on magnetic responses of proton-irradiated graphene laminates**

Figure 4-11 shows the evolution of magnetization ($M$) as a function of magnetic fields ($H$) in one of the proton-irradiated samples while it has been doped gradually from near neutrality to 0.54eV. The linear diamagnetic backgrounds have been subtracted from each original curve. It clearly shows that the Fermi energy strongly affects the magnetic properties of graphene. All magnetization curves are well described by spin-half Curie-Brillouin function ($J=S=1/2$).

\[ M = N_s gJ \mu_B \left[ \frac{2J + 1}{2J} \coth \left( \frac{2J + 1}{2J} x \right) - \frac{1}{2J} \coth \left( \frac{1}{2J} x \right) \right] \]  

(4.1.1)
where \( x = g \mu_B H / k_B T \). \( N_s, J, g \) stand for density of spins, total angular momentum number and g factors (~2 for free electrons), respectively. \( N_s \) and \( J \) are determined by the initial slope and saturation of the curves, respectively. Density of spins, \( N_s \), of each sample can be obtained by extracting with spin-half Curie-Brillouin function from paramagnetic signals (as in Ch.3). The magnetic moments are reduced slowly until the Fermi energy reaches 0.45eV, and then more rapidly afterwards, and saturate at around half of its initial value near 0.54eV where graphene is doped maximally by HNO\(_3\) as displayed in Figure 4 - 12. \( N_s \) of the samples reduce to almost half of its initial value after the maximum doping. With mild annealing at 100°C, the magnetic moment recovers. Figure 4-12 also shows the reproducibility of the reduction trend by measuring several samples. Furthermore, spins in irradiated graphene laminates remain non-interacting (i.e. spin-half) even in high carrier concentrations.

The half-reduction of magnetic moment is universal against the defect density in graphene laminates. We tested the samples with defect density of an order of magnitude differences. The initial density of spins (\( N_s \)) is linearly dependent on the defect densities. The reduction of magnetic moment (\( \Delta N_s \)) is proportional to defect density of graphene laminates with the slope \( \approx 0.5 \) as shown in figure 4 - 13.

![Graph showing universal halving of the vacancy-induced magnetic moment by doping](image_url)

**Figure 4- 13 Universal halving of the vacancy-induced magnetic moment by doping:** Symbols show the change in the density of spins (\( \Delta N_s = N_s^0 - N_s^f \)) after doping.
maximally \((E_F \geq 0.5\text{eV})\) in samples, as a function of corresponding vacancy densities. Solid line is the best fit where \(\Delta N_s/N_s^0 = 0.47\pm0.04\).

**Doping effect on magnetic responses of sp\(^3\)-defected graphene laminates**

In order to compare with vacancy magnetism, another type of defect, adatoms, is introduced to study the doping effect on magnetism. However, it is not easy to find adatoms which do not form local clusters. The clusters in graphene derivatives tend to open band gaps and prevent us from investigating the doping effect of graphene near the Dirac point [29]. This problem was eventually solved by annealing graphene. After annealing, resonant scatterers appear in graphene. These resonant scatterers may come from the organic residues which always exist in graphene laminates [134]. After high-temperature annealing (350°C), they are bound tightly to graphene in sp\(^3\) bonds, reducing the electronic quality of graphene, and inducing a small D peak in Raman spectra. Since the concentration of defects is not as much as in graphene derivatives, the sample after annealing allows us to investigate the behaviours of graphene near the Dirac point.

![Figure 4-14 Comparison of the effect of doping on magnetism associated with vacancies (data from Fig. 4-12) and with sp\(^3\) impurities. Solid (black) curve is the theoretical dependence of normalized spin density, \(N_s/N_s^0(E_F)\), calculated by equations (4.1.2) and (4.1.3) in the main text](image)
Pristine (non-irradiated) graphene laminates are annealed at 350°C, Ar/H₂ atmosphere, carefully avoiding the metallic contamination. This induced a notable paramagnetism with magnetic moment \( N_s^0 \sim 3 \times 10^{18}/g. \) The observed \( M(H/T) \) curves were practically identical to those of irradiated laminates and, again, are accurately described by the Curie-Brillouin function with \( J=S=1/2. \) The found \( N_s^0 \) corresponds to 2-3 \( \text{sp}^3 \) bonds induced by annealing per graphene crystallite in the laminates. In contrast to irradiated graphene laminates, the treatment with HNO₃ almost completely reduces the paramagnetism in annealed graphene laminates above \( |E_F| \sim 0.54\text{eV}. \) This switch-off behavior is also fully reversible with mild annealing at 100°C, the paramagnetism is recovered to the initial values. The magnetic moment of \( \text{sp}^3 \) defects and its variation with doping effect of graphene can be expressed analytically as:

\[
N(E) = \frac{a^2 |E|}{E(1-a^2 \ln \left[ \frac{E^2}{1-E^2} \right] + E_d)} - (\pi a E)^2 \tag{4.1.2}
\]

\[
N_s(E_F) = \int_{E_s-U}^{E_s} dE N(E) \tag{4.1.3}
\]

\( N(E) \) is the density of states in graphene containing resonant scatterers, such as \( \text{sp}^3 \) adsorbates. Here, \( E_d \) is the states’ energy position and \( a \) is the hybridization parameter, both in units of the half width \( W \sim 3t \) of graphene’s energy band (\( t \) is the nearest neighbour hopping parameter). For \( \text{sp}^3 \) impurities in our case, \( E_d=0.02 \) and \( a=2/3 \) (means \( a=2t \)). Magnetic moments count the fraction of single occupied state which is determined by the Hubbard energy, \( U. \) The magnetic moments can be obtained by integrating over the occupied states as in equation (4.1.3), which is well described by the experimental data with \( U=0.5\text{eV}. \) When \( E_F \approx U, \) the curve drops sharply as detailed in the experiments. Note that the cut-off does not lead to zero magnetization, which fits with the experiment results. This finite \( N_s \) is caused by increasing the density of states of conduction electrons linearly in graphene and a renormalization of the positions of impurity states because of hybridization. Therefore, \( N(E) \) decays as \( 1/E \ln^2 |E| \) at large \( E \) leads the magnetic states become totally double occupied when \( E_F >> U \) and \( N_s \) shows long tail at high \( E_F \) as in figure 4 - 14.
In both cases (vacancy and sp$^3$ defects), susceptibility of graphene follows well the Curie law ($\chi \approx C/T$, $\chi$ is susceptibility and $C$ is Curie factor which is proportional to $N_s$). With doping maximally by HNO$_3$, the temperature dependence still follows well to the Curie law although the value of Curie’s factor decreases. This indicates that density of spins decreases and they stay as non-interacting after graphene is doped. The Curie-like temperature dependences shown in both cases (figure 4-15 and 4-16) confirm that the reduction of spin density is dependent on types of defects.

Figure 4- 15 Temperature dependence of inverse paramagnetic susceptibility for an irradiated sample well described by the Curie law (the dash lines). Measurements were done in parallel field $H= 3$ kOe. The constant diamagnetic backgrounds have been subtracted from the raw data in both cases.
Figure 4-16 Temperature dependence of inverse paramagnetic susceptibility for an annealed sample well described by the Curie law (the dash lines). Constant diamagnetic backgrounds have been removed. This sample was heat-treated at 350°C. $H = 5$ kOe.

**Discussion: dual origins of defect-induced magnetism in graphene**

In this section, we investigate the magnetic properties near the Dirac point on ion-irradiated and annealed graphene laminates by tuning the Fermi energy via chemical doping. The neutral ion-irradiated and annealed graphene laminates (i.e. $E_F = 0$) show noticeable spin-half paramagnetism which fit the spin-half Curie-Brillouin function. The paramagnetic responses in both types of defected graphene laminates are reduced when the Fermi energy increases. The switch-off paramagnetism of annealed graphene laminates after maximum doping ($E_F \approx 0.54$ eV) indicates a candidate of spintronic materials. On the other hand, the magnetic moments are not eliminated in ion-irradiated graphene laminates due to heavy doping. Instead, the half reduction of density of spins is universal to all defect concentrations. The difference may be attributed to the presence of $\pi$ and $\sigma$ states in irradiated samples and only $\sigma$ state in annealed graphene laminates. The $\pi$ states result from the imbalance that defects create between its two sublattices, and the $\sigma$ states come from the dangling bonds [62]. Our experiments suggest that the single-occupied $\pi$ state and dangling $\sigma$ states, may co-exist in ion-irradiated graphene laminates. When $E_F > U$, the $\pi$ states become doubly occupied and the corresponding magnetic moments...
disappear, leaving unpaired dangling σ bonds for residual magnetic moments. Very heavy doping is required to achieve required energy for pairing the single dangling bonds. The half reduction of the number of paramagnetic centres indicates the hybridization of π and σ states do not play a significant role [62, 135, 136]. The doping experiments of the annealed samples are consistent with the above interpretation. In the annealed samples, sp³ defects provide no dangling σ bonds, but only localized π states. The samples with the highest doping by HNO₃ show full suppression of the magnetic moments. In other words, the paramagnetism can be fully switched off by doping to \(|E_F| \approx 0.54\text{eV}\). The reduction tendency of magnetic moments is sensitive to the shape of the density of states. This explains that the magnetic moments of \(|E_F| < 0.3\text{eV}\) are almost no changes in annealed samples and gradually decreased in ion-irradiated graphene laminates, matching with the impression that the relevant peak of density of states is much wider than in the former case [62].

4-3 Control of diamagnetic responses in graphene laminates by molecular doping

Orbital diamagnetism is strong in narrow band gap materials, such as bismuth [137] and graphite [76, 77, 79]. The diamagnetic susceptibility of graphite is around \(-3 \times 10^{-5} \text{emu/gOe}\) in out-of-plane configuration and \(-3 \times 10^{-7} \text{emu/gOe}\) in plane [77, 99]. This large anisotropy originates from the orbital diamagnetism which associated with its band structure and closely relates to the band-band transition [76, 77, 79]. In theory, the orbital diamagnetism calculation of graphite is always based on the monolayer graphene planes, which in principle gives singularity near the Dirac point. The susceptibility of monolayer graphene at zero temperature and in the clean limit can be expressed as

\[
\chi_{\text{mono}}(E_F) = -\frac{g_v g_s e^2 \nu^2}{6\pi c^2} \delta(E_F)
\]  

(4. 1. 4)

Where \(g_v = g_s = 2\) are the valley \((K, K')\) and spin degeneracy, respectively, and \(\varepsilon_F\) is the Fermi energy [77, 79, 83, 84]. M. Koshino et al. have also reported that susceptibility behaviour near the Dirac point is thickness dependent [83]. Although
many theories have been put forward to explain the large diamagnetic responses in single and multilayer graphene in the neutrality point, limited experiments have been done. In this section, we probed the diamagnetic properties of graphene laminates in the Fermi level from neutral to $E_F \approx 0.5\text{eV}$ and this is the first time that the doping effect of the diamagnetism of graphene laminates has been studied experimentally. The magnetic signals were detected by Quantum Design MPMS XL SQUID magnetometer. Each sample (made by graphene laminates) is around ‘mg’ weight and has enough signals for magnetometer to measure. The temperature-dependence and field dependence of diamagnetic anisotropy of graphene laminates have been measured from 2K-300K in a fixed magnetic field and from 0T to 5T at T=300K, respectively.

**Diamagnetic responses of pristine graphene laminates**

The diamagnetic responses of graphene laminates as a function of doping were studied at 300K and showed high anisotropy in diamagnetic responses. The diamagnetic susceptibility of out-of-plane (in-plane) of graphene laminates is defined as $\chi_{perp}$ ($\chi_{para}$) which is around $-1.2 \times 10^{-5}\text{emu/gOe}$ ($-7 \times 10^{-7}\text{emu/gOe}$) at 300K. The diamagnetic responses of these samples show linear dependence on magnetic field. Thus, their susceptibilities were determined by simply dividing magnetic field from the magnetization ($M/H$). The susceptibility of graphene laminates in direction of in-plane is higher than the core diamagnetism ($5 \times 10^{-7} \text{emu/gOe}$) [79]. This is because the misorientation of graphene flakes in the laminate which allows some orbital diamagnetic contribution in the parallel direction. In this section, we only consider the value:

$$\chi_{perp} \bar{\chi} = \chi_{para} \bar{\chi} \chi$$  \hspace{1cm} (4.1.5)

$\chi_{perp}$ ($\chi_{para}$) is the susceptibility in 300K and measured when the magnetic field is perpendicular (parallel) to the sample plane and $\chi_{orb}$ is supposed to be contributed only by the large orbital diamagnetism of graphene laminates [79].

Figure 4-17 shows $\chi_{orb}$ of several graphene laminates in 300K. The pristine graphene laminates were produced by liquid exfoliation in NMP which was described in Chapter 3. The average value of $\chi_{orb}$ is around $-1.1 \times 10^{-5}\text{emu/gOe}$. Another observation in the orbital diamagnetism of graphene laminates is its temperature dependence. The
diamagnetic susceptibility increases when lowering the temperature as shown in figure 4-18. \( \chi_{orb} \) is inversely proportional to the temperature from 2K to 40K, with slope \( C = \frac{\Delta \chi_{orb} + \text{const}}{T} \), and more complex dependences in higher temperature. The complex dependence is probably due to the thermal expansion of density of states near the Dirac point.

Figure 4- 17 Diamagnetic susceptibility of graphene laminates at 300K: The red dashed line is their average value, \(-1.1 \times 10^{-5}\) emu/g Oe.
Control of diamagnetic responses of graphene by molecular doping

In this section, controllable diamagnetic responses of graphene laminates will be demonstrated by simply applying chemical doping for shifting their Fermi level. In terms of hole (electron) doping, electrons in graphene laminates are delivered to (from) dopants and shifted the Fermi level to valence band (conduction band). In the following studies, HNO$_3$ and NO$_2$ are used as hole dopants of graphene, and aniline and TMPD as electron dopants. By using HNO$_3$, graphene can achieve $|E_F| \approx 0.54$eV, but for electron doping, it is hard to find a suitable dopant to achieve the Fermi level up to $E_F \approx 0.54$eV. Instead, aniline and TMPD allow us to study the diamagnetism of graphene laminates till $|E_F| \approx 0.3$eV. Similar to the previous section, only the results of applying HNO$_3$ will be shown due to the symmetry of the evolution.

The diamagnetic susceptibility of graphene laminates was measured by Quantum Design MPMS SQUID magnetometer at 300K. Several concentrations of HNO$_3$ were applied to graphene laminates to shift their Fermi energy. $\chi_{orb}$ changed
from $1.2 \times 10^{-5} \text{emu/gOe}$ to $5 \times 10^{-6} \text{emu/gOe}$ after the sample was dipped into 70wt% HNO$_3$ (15M). This change can be recovered by mild annealing which detaches HNO$_3$ molecules from graphene laminates. The whole doping process can then be reproduced using the recovered graphene laminates. In figure 4-19, the susceptibility shows very slow decay when $|E_F| < 0.3$eV and a significant decrease afterwards. The diamagnetic susceptibility is not vanished at 0.5eV and at a value of $\approx -5 \times 10^{-6} \text{emu/gOe}$. However, higher Fermi energies could not be achieved in our experiments for the further information.

The doping effect is also reflected in the temperature dependence of the orbital diamagnetic responses in graphene laminates. The responses are plotted in figure 4-20 as a function of temperature in doping level from 0.04eV to 0.53eV. The temperature dependence in pristine graphene laminates has a feature of decreased orbital diamagnetic susceptibility at high temperature. This feature becomes less noticeable when the electron population of valence band is reduced. The magnetic responses are constant to the inverse of temperature without a remarkable tail. The tails in pristine samples are due to the temperature broadening of the density of states near the Dirac point at high temperature. However, this broadening will not be relevant when the Fermi level moves away from the Dirac point. When $|E_F| < 0.3$eV, the observed decay is very similar to the tendency calculated in ref. [76] where the variation of diamagnetic responses in different doping levels is predicted in the temperature regions which have been used in the experiments. However, the diamagnetic susceptibility is nearly constant near the Dirac point which seems disagreed with the predicted delta peak. The reason will be discussed in the next subsection.
Figure 4-19 Diamagnetic susceptibility of graphene laminates in a function of the Fermi energy at $T = 300\text{K}$. The error bar shows the uncertainty estimation of the Fermi energy (horizontal) and the magnetic measurements (vertical).
**Discussion**

Some of the comments on the observation mentioned above are discussed here. The values of $\chi_{\text{orb}}(E_F)$ of graphene laminates varies a little near the Dirac point and then drops rapidly after certain Fermi energy, in contrast with the prediction of a delta peak centred at the neutrality point. The rapid decay tail fits with the expectations. However, the saturated susceptibility in 0.5eV does not vanish. The contradiction of this observation and the theories may attribute to the finite-size effect of graphene nanoflakes. The spatial confinement seems to restrict the diamagnetic responses near the neutrality point. Instead of a sharp delta peak centred at zero energy, the shapes of graphene nanoflakes’ susceptibility depends on the ambient ($k_B T / \epsilon_0, \epsilon_0 \propto 1/\sqrt{S}$) and its morphology [80]. The finite size features contain flat top of the susceptibility against the Fermi energy and the magnetic oscillation. The finite size effect can be eliminated by temperature, leading to a broad Lorenzian peak. In our case, the ambient and the size of flakes allowed our systems to stay in the region where the effect

![Graph showing temperature dependence of the susceptibility of graphene laminates](image)

Figure 4- 20 Temperature dependence of the susceptibility of graphene laminates in $E_F = 0.04 - 0.53 \text{ eV}$ (from top to bottom)
remains. We did not see the magnetic oscillation since it requires very high quality and monocrystallized structures. Note that our system was supposed to be a mixture of all the morphologies of graphene nanoflakes. The reason that susceptibility near $E_F \approx 0.5\text{eV}$ does not approach to zero might attribute to the finite size effect and the temperature broadening. The spatial confinement not only flattens the top of the susceptibility, but widens the shape comparing to the expected delta peak. $E_F \approx 0.5\text{eV}$ was not achieving the saturation region. Moreover, the doping levels depend also on the thickness of graphene sheets. It is much easier to dope the single layer graphene sheet than the others. We change the Fermi energy by molecular doping, using e. g. HNO$_3$. With HNO$_3$, it has been known that the doping efficiency is the best in monolayer graphene. 15M HNO$_3$ allows us to shift the Fermi energy to 0.53 eV in graphene, while it stays less than 0.4eV in bilayer graphene. For bilayer graphene, the doping efficiency is much less than that in monolayer graphene [132]. Although large proportion of graphene in graphene laminates have been shown by Raman spectra and transport measurements, we could not avoid the little inhomogeneous doping through the laminates, which is possibly a limit for the saturation toward zero.

4-4 Conclusions

In this chapter, paramagnetic and orbital diamagnetic responses of graphene laminates were demonstrated to be controlled by molecular doping. In pristine graphene laminates of nearly zero Fermi energy, the diamagnetic signals were observed in any temperature and noticeable paramagnetic signals when $T< 50K$. When the valence band is gradually filled by holes, both diamagnetic and paramagnetic responses are reduced. However, different mechanisms are suggested behind them.

Density of spins of graphene laminates with vacancy-type defects was reduced to half of the initial value when the Fermi energy $\sim 0.5\text{eV}$, while density of spins of graphene attached with adatoms almost fully suppressed by the same shift of the Fermi energy. This suggests the existence of dual-origin magnetic moments in defected graphene. The paramagnetic signals created by vacancies in graphene laminates are attributed to the coexistence of dangling bonds ($\sigma$ state) and imbalance of $p_z$ orbitals ($\pi$ state). In this case, only the latter one is responsible for the changes in density of spins of graphene laminates and only half of the signals have been reduced. In the case
of adatoms, functionalization only creates the imbalance of $\pi$ state in graphene lattices and results in fully suppression when $E_F > U$.

On the other hand, the reduction of diamagnetic responses in graphene laminates that was induced by holes, was attributed to that the band-band transition only happens near the Dirac point. However, the reduction when $E_F < 0.3$eV is not as rapid as a delta peak which has been expected in the theoretical calculations. Instead, no significant decreases of the diamagnetic susceptibility were observed near the Dirac point, and this was attributed to the finite-size effect of graphene nanoflakes. Furthermore, the reduction was performed as significant and similar to the tendency of graphite when $E_F > 0.3$eV.
Chapter 5
Non-invasive Transmission Electron Microscopy of Vacancy Defects in Graphene Produced by Ion Irradiation

Studying the morphologies of atomic-scale defects in graphene helps to engineer it for various applications. Some new conceptual devices have been suggested to be carried out by modifying graphene by intentionally introducing of defects. For instance, the magnetic moments associated with single vacancies [75, 115] or voids [135] in graphene make it a candidate material for spintronic devices. Furthermore, grain boundaries may be used to engineer transport properties in graphene. For example, line defects can act as metallic one-dimensional wires or as filters for charge carriers which occupy in different valleys, thereby possibly developing unconventional electronic applications, called valleytronics [138-140]. In principle, the configuration of defects, such as the presence of dangling bonds, saturation of dangling bonds and reconstruction of vacancies strongly affects the band structure of graphene. Irradiation is one of the most widely used techniques to introduce vacancies into graphene, but the exact atomic structure of irradiation-induced vacancies and their corresponding effect on electronic structure of graphene remains unknown and controversial. For instance, recent observations of magnetic properties of irradiated graphene can only be understood if reconstructed single vacancies can be identified in such samples [75, 115]. However, instead of supporting this assumption, previous microscopic observations of vacancy-type defects in irradiated graphene shows that single vacancies, which are believed to be more unstable, often coalesce and transform into divacancies or more complex defects [141, 142], or the dangling bonds become saturated e.g. with hydrogen preventing the Jahn-Teller reconstruction [103, 136].
Detailed study of the geometry of point defects can only rely on the high resolution transmission electron microscope (HR-TEM). Due to aberration corrections by the hardware and minimizing the spread of the atoms’ contrast in the image, a single atom can be detected even at relatively low accelerating voltage $\leq 80\text{keV}$, which much less than the high voltage required for the conventional HR-TEM [143-148]. However, the requirement for atomic resolution of high doses of electron beam for atomic resolution may cause sputtering of individual carbon atoms or defect transformation [149-151]. Therefore, the observed defects are either created or modified by electron beams. In particular, single vacancies are relatively unstable which may transform to divacancies by knocking out a nearby carbon atom during electron bombardment [53, 59, 141]. The observations also show that the hydrocarbon contaminations tend to cover the graphene samples with high defect densities, thus reducing the possibility of imaging defects. Taken all the above factors together, so far it has been impossible to reliably characterize atomic-scale defects in graphene.

In this chapter, we demonstrate that the above limit is overcome by encapsulating defected graphene with two other graphene sheets. Aberration-corrected transmission electron microscopy (AC-TEM) is used to provide reliable identification of vacancy-type defects created by proton irradiation. The outer graphene layers act as a window to protect the studied defects from: ambient disturbances, edge saturation and against radiation damage from the electron beam due to the high electrical and thermal conductivity, chemical stability, transparency and crystallinity of graphene [152-155]. The last feature is important for post-processing Fourier filtering to get rid of the signals from the outer shields. The encapsulation by graphene sheets has been used successfully as a transparent cell for monitoring liquid phenomena, such as colloidal Pt particle growth [152] as well as the study of radiation sensitive monolayer of MoS$_2$ encapsulated between two layers of graphene [154, 155]. In the previous work, it is relatively easy to separate the target signal from graphene background due to the large difference in their atomic numbers. Our work is the first time that graphene sheets are used for viewing defected graphene which have similar contrast as the outer shields and make the image analysis become difficult. In this work, we also show the middle defected graphene can be seen and analyzed by applying reliable simulations. Most of the contents here have been submitted.$^3$

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$^3$ This project has been performed in collaboration with O. Lehtinen who observed and analyzed the samples via HR-TEM and performed the ion irradiation. My contribution in this work is to fabricate encapsulating TEM samples with the assistant of R. Jalil and I was also involved in the discussion and design of the experiments.
5-1 Sample preparation

Encapsulating graphene oxide on TEM grid:

Single layer of graphene (~100μm) and bilayer of graphene oxide were isolated mechanically from natural graphite and graphite oxide (made by Hummer’s method), respectively, and deposited on SiO₂/Si (from IDB Technologies Ltd: 290 nm SiO₂, n-type doped, one side polished) for characterizing its thickness [17]. The thickness of each layered materials was identified by the colour in an optical microscope. Encapsulating G-GO-G sandwich was made by wet-transferring graphene oxide and graphene in sequence on another graphene which was deposited on SiO₂/Si (figure 5-1(a)). The wet transfer process is using a layer of e-beam-resist PMMA (polymethylmethacrylate) (MicroChem, 950,000 MW, 3 wt. % in anisole) was spin coated onto the substrate. The PMMA layer with the attached layered material was isolated from the substrate by partially etching the underlying SiO₂ surface with an aqueous solution of KOH (0.5M). After several rinses with deionised water, the PMMA-graphene membrane transferred to the target. Finally, the PMMA layer was gently dissolved in acetone. G-GO-G sandwich on SiO₂/Si was transferred on TEM grid by also wet transfer (schematically shown in figure 5-1). In the last step of wet transfer, the TEM grid dipped in acetone was dried in a critical point dryer (CPD).
Figure 5-1 Wet transfer procedure of graphene oxide encapsulated by two graphene sheets: (a) encapsulating G-GO-G sandwich on SiO$_2$/Si (b) spin-coating PMMA on top of the sandwich (c) partially etching SiO$_2$ for detaching PMMA-sandwich, which is then attached to TEM grid and dissolving PMMA by acetone afterwards (d) dried sandwich sample on TEM grid.

**Graphene on TEM grid:**

Graphene or multilayer graphene on TEM grid using as pristine sample for proton irradiation was made as follows. Mechanically exfoliated graphene (~100μm) was isolated from natural graphite and deposited onto Si/SiO$_2$. The monolayer and trilayer are identified by the colours under optical microscope as in figure 5-2. Wet transfer is applied for moving the desired graphene from SiO$_2$/Si substrate to the TEM grid. As seen in panel (b) of figure 5-2, the monolayer graphene deposited on TEM grid is transparent and cannot easily be seen even in the optical microscope.
**Graphene covered with MoS$_2$ nanocrystallites on TEM grid:**

To fabricate graphene covered with a small amount of dispersed MoS$_2$ crystallites, graphene were mechanically isolated from graphite onto SiO$_2$/Si substrate (Figure 5-2(a)). To prepare thin (few-layer) MoS$_2$, liquid exfoliation is used to obtain 0.1g/L dispersion of MoS$_2$ in N-methyl pyrrolidone (NMP) [32]. 50 mg of MoS$_2$ powder (Sigma Aldrich) was sonicated in 10 ml of NMP for 20h. The obtained suspension was centrifuged to remove large multilayer crystallites and then carefully dropcast over the graphene flakes on SiO$_2$/Si. The substrate was then heated at 50 °C for 10 minutes and then cleaned using standard solvent treatment (acetone and isopropyl alcohol (IPA)) – see Figure 5-3(b). Finally, graphene covered with the remaining MoS$_2$ crystallites were wet-transferred onto a TEM grid (Figure 5-3(c)).
Figure 5- 3 Graphene covered by MoS$_2$ nanocrystallites (a) Optical image of graphene flakes on SiO$_2$/Si substrate with a monolayer region marked 1L and a large trilayer region marked 3L. (b) MoS$_2$ nanocrystallites deposited on top of graphene; blue and yellow colours indicate thin and thick layers of MoS$_2$ flakes, respectively. (c) optical image of MoS$_2$-graphene flakes after transfer onto the TEM grid. All of the scale bars correspond to 50μm.

*Resonicated graphene clusters on TEM grid:*

Clusters of graphene prepared by liquid exfoliation are the closest sample of those used for the previous project. The graphene laminates (see method in chapter 3) were resonicated in NMP for 1 hour. Afterward, the suspension centrifuged of 10,000 r.p.m. for removing the large and thick clusters. The top suspension was then dropcasted on TEM grid and dried on hot plate for 100°C.

*Irradiation process:*

The ion irradiation is performed by 350 keV proton beams using a 500 kV ion implanter system (the same method as mentioned in the previous two chapters for ion irradiation). For a direct comparison with the experiment of vacancy-induced magnetism, the energy, fluence and other irradiation parameters were chosen to be similar [75, 115]. Total ion fluence is around 2·10$^{16}$ ions/cm$^2$. Except the encapsulated graphene oxide, all of the above samples are irradiated under this condition.
5-2 Point-vacancy studies of encapsulated ion irradiated graphene by TEM

The HR-TEM micrographs were recorded using hardware and an aberration-corrected FEI TITAN 80-300 operated at 80 kV. All TEM images except figure 5-4 and 5-11 were averaged over 3-10 frames (where atomic structure of the defect does not change during imaging) to improve the signal-noise ratio. The models for the image simulation were relaxed by the density-functional tight-binding formalism [156, 157]. The image simulations were conducted for 80 keV electrons, with spherical aberration coefficient of 0.02 mm and a focal spread of 6 nm. The typical pre-TEM annealing of the samples was omitted in these experiments in order to avoid migration, coagulation or recombination of point defects in the samples. The cleaning method used in this chapter will be illustrated in the last paragraph of results in this section.

In the beginning, the atomic-scale observations of the irradiation effect on graphene would preferably be conducted directly on the ion-irradiated clusters which have been used for the previous magnetic studies. The samples were fabricated by irradiating resonicated graphene clusters (see methods in Sample preparation) with proton beams. The picture for an overview of a cluster is shown in figure 5-4(a). The investigations were mainly operated near the edges of the clusters where the thinnest area of the cluster is. Figure 5-4(b) shows that the graphene lattices were clean and lack of defects before conducting irradiation, while point defects were present in the sample after irradiation in figure 5-4(c). However, identification of types of defects is relatively hard due to the limitations of the microscope where larger flat area of the sample is required for a more efficient study. We thus change our samples to mechanically exfoliated graphene which can provide ~100µm homogeneous and flat flakes.

A bilayer graphene oxide made by mechanically isolation from graphite oxide is encapsulated by two graphene sheets (G-GO-G), shown schematically in figure 5-5 to provide a promising method for imaging intrinsic defects of graphene by encapsulating them in a graphene cell. The corresponding images of HR-TEM are shown in figure 5-6. The image of the entire sandwich sample is shown in panel (a). The typical moiré pattern indicates misoriented overlapped graphene layers and three sets of diffraction patterns correspond to three individual layers of graphene. In order to extract the individual layers, digital post-processing Fourier filtering was adopted. Panel(b)-(d) show the images of removing two regular graphene lattices by filtering the corresponding sets of diffraction
patterns. Several point defects as well as atomically resolved graphene lattice are displayed. Remarkably, neither the location, nor the presence of defects changed during imaging, indicating the absence of atomic displacement, transformation and migration of defects under electron irradiation. However, it is unlikely to identify the exact situated layer of defects in the multi-stacking of such design since the presence of defects in all three images.

Figure 5-4 Clusters of graphene flakes made from resonicated graphene laminates (a) overview image of the cluster (b) before and (c) after irradiation. Panel (a) and (c) are the images in the same cluster while panel (b) is not.

In order to have more systematic studies, graphene trilayers are used to monitor the defects by proton irradiation for two reasons: First, encapsulation of samples might avoid the damage or transformation of defects in the middle of trilayer created from ion irradiation, second, the perfect ABA stacking allows us to analyze the defects located in middle layer as assisted by reliable simulations. In the case of trilayer graphene, post-processing Fourier filtering is not practical; instead, the systematic simulations displayed in figure 5-7 provide reliable identification of types and locations of defects in the TEM images. The slightly different contrasts suggest the locations of defects and the shapes of simulated bright area indicate the type of defect in a certain focal distance. Only faint variation in contrast could be observed at defect sites in the standard focus condition, since the lattice signal from the other layers obscures the defects. However, the signal from the periodic graphene structure was suppressed when defocus was adopted, and the less regular defect sites became clearer. 13-16nm defocus was therefore used in our observations due to the optimum contrasts. The experimental identification of point defects
in trilayer graphene where defects have been created in the middle layer will be mainly discussed in the following paragraphs. ABA stacking trilayer graphene provides an effective model to investigate not only encapsulation effect, but importantly the intrinsic defects created by proton irradiation.

![Figure 5-5 Schematic structures of the defected graphene in between two perfect graphene sheets. Colored areas of the middle layer represent defects.](image)

Figure 5-8 and 5-9 show some examples of defects found in trilayer graphene. The average separation over all acquired images was around 8.4nm. This value matches well with the expected defect density for 350 keV proton irradiation and a fluence of $2 \times 10^{16}$ ions-cm$^{-2}$ as used in our experiments. The latter was estimated by SRIM software (with displacement threshold 28eV) and yielded 8.1nm separation between defects in graphene layer.

Figure 5-8 displays an example of a reconstructed single vacancy under several focus conditions. An initial monovacancy (also called non-reconstructed single vacancy) has three dangling bonds with three-fold symmetry. When it is reconstructed through so called Jahn-Teller distortion, two nearest bonds form and only one dangling bond left, leading to a asymmetric geometry as in the top schematic picture of Figure 5-8(b). Three experimental images show the same area of the sample recorded at different focusing condition, going from the Scherzer focus in panel (a) to approximately -15 and -16nm defocus in panels (b) and (c), respectively. The strong asymmetric characteristic for a reconstructed single vacancy is more obvious at -15nm defocus. Much less pronounced asymmetry at a defocus 1nm away from the optimal condition [panel(c)]. The images taken at both defocus conditions match the simulation of the reconstructed single vacancy in the middle of trilayer graphene very well, thus allowing unambiguously identification of the defect. In contrast, the three-fold symmetric non-reconstructed single vacancy does not match with the asymmetric observation (cf. figure 5-7).
More defects were found in other areas of the same trilayer graphene sheet and displayed in figure 5-9 which have similar defocus as in figure 5-7. The defects in panel (a)-(c) were identified as single vacancies as well as the downside defect in panel (d). The defect in upright corner in panel (d) was recognized as a 5555-6-777 defect.

The reconstructed double vacancies have been observed in many HR-TEM studies and are expected to be more stable than the single vacancies. Since both types of vacancies have a qualitatively similar asymmetric feature shown in figure 5-7, a more detailed comparison is performed in figure 5-10. Panels (e) and (f) show the difference between single and double vacancies via simulations. The latter is more elongated, has longer dark wings and shows a brighter round spot in the centre. In addition, a pixel-by-pixel difference is calculated when the experimental image in panel (a) is aligned with simulated images of reconstructed single and double reconstructed vacancies. The standard deviation of the former is 52% lower than the latter. Accordingly, we identify the defects in all our samples based on the above features. The majority of defects were identified as reconstructed single vacancies, with only a few divacancies. This is in contrast with the previous findings on unprotected monolayer graphene where most of the observed defects are double vacancies or more complex structures [53, 60, 142, 158]. We believe that the contrast comes from the protection by outer graphene layers which prevented the transformation of the single vacancies into other types of defects under electron irradiation.

It is important to mention that defects in trilayer graphene stay for a period (enough for taking images) without transformation. However, in agreement with other HR-TEM studies, no defects in monolayer and bilayer graphene prepared and irradiated together with trilayer graphene have been found stable in the same imaging time. We can therefore conclude instead of using monolayer graphene, trilayer graphene provides, for the first time, an opportunity to observe the truly intrinsic defects.

In the end, we would like to discuss an important issue in atomic-resolution imaging: contaminations. The size of the clean area is important for the atomic-scale observation. In our case, despite the extreme care in sample preparation, only a few <5nm clean spots can be found in entire ~100μm size sample before any cleaning treatment. This is worse than the normal pristine graphene TEM samples due to the sub-optimal vacuum condition during irradiation and the sample tend to be covered by contamination after irradiation. Prior to the HR-TEM imaging, a typical in-situ annealing in the high vacuum of electron microscope is often applied for cleaning the surface of samples. However, it is
not adoptable in the case of intrinsic point defect imaging as defect transformation induced by annealing, producing misleading results regarding the type of intrinsic defects created by proton irradiation. Therefore, an alternative method to enlarge the clean area without causing changes in defects was needed. We found that the contamination can be drastically reduced by depositing a small amount of nanoscale crystallites of MoS$_2$ onto the graphene samples before proton irradiation. The low-magnification images in figure 5-11 indicate that the clean area was enlarged from $<2$nm (left panel) to uninterrupted $>20$nm (right panel) due to the presence of MoS$_2$ nanocrystallites. We emphasize that the drop casting of MoS$_2$ nanocrystallites was the only difference between two panels. The mechanism behind cleaning effect of MoS$_2$ is still unknown, but it is likely due to the catalytic activity of MoS$_2$ with respect to hydrogen evolution [159, 160] which helps cracking the hydrocarbons on the graphene surface. This simple technique provides a valuable alternative to the typical removal of contamination from graphene by annealing and can be particularly useful in the studies of intrinsic defects geometry where annealing is not feasible.

5-3 Conclusions

In conclusion, the non-invasive observation in HR-TEM has shown by using trilayer graphene and reliable simulation. Comparing to monolayer graphene, trilayer graphene seems to be more promising in observing intrinsic point defects produced by non-in situ proton irradiation. Instead of perfect focusing conditions, defects become visible with optimal defocus since it effectively ‘filters out’ the regular honeycomb lattice revealing the imperfections. By adopting these simple techniques, the majority of defects found in proton-irradiated graphene are identified as reconstructed single vacancies rather than double vacancies or more complex defects. This scenario explains the magnetic and transport properties found in such defected graphene, and also clarifies the uncertainty of the effect of ion irradiation on the band structure of graphene.
Figure 5-6 Atomic resolution images of graphene oxide sandwiched between two layers of graphene: (a) before filtration: Three sets of diffraction patterns in FFT shown in the inset and the obvious moiré pattern indicates misoriented three-layered stacking (b)-(d) two regular honeycomb layers corresponding to two of three sets of diffraction patterns (labelled as black spots) have been digitally removed by Fourier filtering. The scale bar corresponds to 1nm.
Figure 5-7 Systematic simulations of defects in triple layer graphene with different defocus distances. The optimum contrasts show in 13-16 defocus region. The top four rows show simulated contrast for the cases that defects situate either on top or bottom protective layer. All other images correspond to defects in the middle layer. The red and green highlight defects are reconstructed single and double vacancies as discussed in the main text.
Figure 5-8 Reconstructed single vacancy in the middle layer of proton-irradiated graphene at three different focus condition: (a) standard focus (Scherzer focus) (b) approximately 15nm and (c) 16nm underfocus. The bottom-left insets show simulated images of the same defect in the two sublattices of graphene. The top inset in panel (b) shows schematic atomic structure of a reconstructed single vacancy (not to scale). The scale bar corresponds to 1nm.

Figure 5-9 Further examples of reconstructed single vacancies: (a)-(c) single vacancies (d) single vacancy in the left-down and a divacancy in the upper-right corner. The scale bar corresponds to 1nm.
Figure 5-10 Reconstructed single vacancy v.s. reconstructed divacancy: (a) and (b) show the raw images with -15nm underfocus of single and double vacancies, respectively. (c) and (d) correspond to the above two pictures after adopting the low-pass filter. (e) and (f) show the corresponding simulated images obtained using an underfocus of -14.8 nm.

Figure 5-11 Cleaning effect of MoS$_2$. Overview HR-TEM images of irradiated triple layer graphene with (a) and without (b) MoS$_2$ crystallites deposited on top of graphene before irradiation. Only small clean patches are visible in the left panel, whereas the clean areas enlarge to ~20nm (a few overlapping MoS$_2$ flakes are visible on the left image). The only difference in preparation process is the dropcast of MoS$_2$ suspension.
Chapter 6

Magnetism of MoS$_2$ Laminates: Effect of Sonication and Irradiation

Since graphene was isolated experimentally, it has never ceased to surprise scientists. The paramagnetism of graphene is shown to be induced by point defects, especially vacancies and adatoms, and controlled by the field effect [75]. In addition to zero-band-gap graphene sheets, other finite-gap layered materials might open a range of extensive applications of two dimensional (2D) magnetic materials. As one of the most stable layered transition metal dichalcogenides (TMD), the electrical, mechanical and optical properties of MoS$_2$ have been investigated intensively [5, 30, 161, 162]. However, most of the magnetic studies are limited to the theoretical calculations. According to these calculations of MoS$_2$ nanoribbons, zigzag edges are metallic and exhibit magnetic moments in all widths of nanoribbons [85, 87], while armchair edges do not have consistent results but most believe armchair nanoribbons have semiconducting and nonmagnetic properties with hydrogen-terminated edges [85, 87]. Moreover, certain types of defects are considered to have magnetic moments [85, 86, 90, 163]. For example, a MoS$_2$ triple vacancy is suggested to have a magnetic moment of $2 \mu_B$, while other types of vacancies composed by Mo or S have zero net spins [86]. Indeed, the ferromagnetic signals were found in proton-irradiated bulk single crystal MoS$_2$. However, limited experiments and controversial results of ferromagnetic findings in different forms of MoS$_2$ leave the magnetism of MoS$_2$ as an open issue. In this chapter, we investigated the dependence of magnetic properties of NMP-exfoliated MoS$_2$ laminates on the effects of sonication and proton-irradiation.

The organization of this chapter is as follows. First, the production of MoS$_2$ laminates by NMP-based exfoliation will be introduced. Second, characterization of the samples which gives an idea about their elements, bonds, morphology will be presented. The techniques include scanning electron microscope (SEM),
energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. Third, the magnetic responses of MoS$_2$ laminates as the main issue of this chapter are discussed.

6-1 Sample preparation

Similar to the magnetic studies of graphene in the previous chapter, solution-based exfoliation is used to fabricate monolayer MoS$_2$ in order to have samples of milligram for obtaining the signals above the minimum detection of SQUID magnetometer. First, bulk MoS$_2$ powder from Sigma Aldrich (see SEM picture as in figure 6-1a) is mixed with N-Methyl-2-pyrrolidone (NMP) and then the mixture is ultrasonicated for several hours, which resulted in extensive exfoliation. The suspension is then centrifuged to remove thicker flakes. In the end, the resulting dark-green suspension (Figure 6-1d) filtered and dried as suspended MoS$_2$ laminates (Figure 6-1c). Low temperature drying is needed due to the decomposition of MoS$_2$ at high temperature. The SEM image is shown in figure 6-1b. The flakes are in irregular shape but with crystalline edges. They have an average size of roughly tens of nanometres and stack almost parallel to each other. The atomic resolution of MoS$_2$ flakes shows the existence of single layer MoS$_2$ with both zigzag and armchair edges (as the atomic resolution image in figure 6-1e). The details of characterization on MoS$_2$ laminates will be presented in the following section.
6-2 Characterization of MoS$_2$ laminates

Scanning electron microscope (SEM)

Scanning electron microscope allows us to study morphology of flakes. MoS$_2$ suspensions have been sonicated from 50 minutes to 24 hours and changes to the flakes have been monitored by SEM. The sonication process starts from bulk MoS$_2$ powder which size is around 3μm. After 50 minutes of sonication (figure 6-2a), MoS$_2$ flakes have sizes on average of 140nm. The variation of size and thickness in this stage remains large. Sizes of flakes gradually become smaller for longer length of sonication time. After 24 hours sonication (figure 6-2c), flakes have sizes in average of 50nm. The decay curve in figure 6-2d is extended to sonication time of 72 hours.
Figure 6-2 SEM images of MoS$_2$ flakes on Si substrate which have been sonicated for different duration (a) 50 minutes (b) 12 hours (c) 24 hours (d) size decrease with sonication time: black solid dots are the experimental data and the open circles are the data extended from fits to solid dots.

**Energy-Dispersive X-ray Spectroscopy (EDS)**

MoS$_2$ laminates and their original powder were analyzed their elements by EDS. The EDS data shows that carbon, sulfur and molybdenum atoms exist in both laminates and powder, while oxygen only exists in the laminates. The high portion of oxygen (0.1 at%) found in the sample might come from oxygen trapped between MoS$_2$ flakes although the measurements were done in high vacuum. XPS data supports this hypothesis. S/Mo ratios of bulk and laminates are ~ 1.6 less than the expectation value, might due to the missing sulfur atom in both bulk and laminates. No Iron (Fe) has been found in the limit of EDS resolution (< 0.1 at%).
Figure 6-3 EDS spectra of (a) MoS$_2$ laminate (b) MoS$_2$ powder. Iron is especially labelled although no detectable signals have been found in both samples.

**X-ray photoelectron spectroscopy (XPS)**

XPS allows us to study the bonds of elements in the samples. Two samples which have been ultrasonicated 24 hours and 72 hours, along with their origin powder are examined in XPS. Peaks of binding energies, 232eV, 229eV, 162eV, and 163eV, are peaks related to Mo$^{4+}$$_{3d5/2}$, Mo$^{4+}$$_{3d3/2}$, S$_{2p3/2}$, and S$_{2p1/2}$ (figure 4), respectively. These peaks correspond to the bonding within MoS$_2$. Comparing to the bulk MoS$_2$ powder, a small peak near 236eV is present in the MoS$_2$ laminates, sonicated for different times and absent in bulk may come from Mo$^{6+}$$_{3d5/2}$. According to the intensity of the peak
with energy of 236eV, Mo$^{6+}_{3d5/2}$ is around 2% of total Mo bonds. This amount does not change while varying ultrasonic time indicating that MoO$_3$ is induced during heating of the production[164, 165] rather than the ultrasonic process. The shoulder in MoS$_2$ powder comes from 1T-MoS$_2$.

Figure 6- 4 XPS data of MoS$_2$ laminate: 72h sonication (black solid curve), 24h sonication (red dashed curve). These two curves offset for $20 \times 10^3$ CPS. XPS of MoS$_2$ powder (blue solid curve).

**Raman spectroscopy**

Raman spectroscopy is a quick way to characterize thickness of mechanically exfoliated MoS$_2$. Two main peaks, $E_{2g}^1$ and $A_{1g}$, represents in-plane and out-of-plane vibration in MoS$_2$ crystals, respectively, situated around $383cm^{-1}$ ($E_{2g}^1$) and $408cm^{-1}(A_{1g})$ [13]. The distance between these two peaks depends on the thickness in mechanically exfoliated MoS$_2$. Characterization of MoS$_2$ laminates made by NMP-exfoliation were performed in 514.5nm Renishaw Raman spectroscopy. The comparison of MoS$_2$ bulk powder and laminates in Raman spectra is shown in figure 6-5. MoS$_2$ laminates remain crystallized after chemical exfoliation, but no distance changes between Raman peaks in the comparison with the bulk. We attribute the difference in Raman of liquid-based and mechanical-exfoliated methods to the sizes of flakes. The MoS$_2$ laminates obtained from solution-based method are around 50nm which is much smaller than the laser beam size ($\sim 2\mu m$) while normally the flake size
is around 50µm for mechanically exfoliated MoS\textsubscript{2} sheets. Therefore, it is hard to obtain the position-shift signal in liquid-exfoliated MoS\textsubscript{2} stacks.

![Figure 6-5 Raman spectra of MoS\textsubscript{2} powder (black solid curve) and MoS\textsubscript{2} laminate (red dashed curve)](image)

**6-3 Magnetic responses of MoS\textsubscript{2} laminates:**

**Effect of sonication and irradiation**

The magnetic properties of MoS\textsubscript{2} pristine laminates is first presented and discussed. “Pristine” here means that no more treatment after made as MoS\textsubscript{2} laminates. The magnetic measurements of MoS\textsubscript{2} pristine laminates are performed by Quantum Design MPMS SQUID magnetometer. Since MoS\textsubscript{2} has low anisotropy (our results fit with the literature, where $\chi_{\parallel}/\chi_{\perp} \approx 1.1-1.5$ at high temperature [96]), only in-plane magnetic responses of MoS\textsubscript{2} laminates is shown here.

Bulk pristine MoS\textsubscript{2} has very weak paramagnetism which is comparable to the background signals. Its diamagnetic susceptibility is around $-3 \times 10^{-7}$ emu/gOe. Figure 6-6 shows $M$-$H$ correlation of 37-hour-sonicated MoS\textsubscript{2} laminates in 2, 10, 100, and 300K. In 300K and 100K, Magnetization depended only linear diamagnetically on the external field. The diamagnetic susceptibility in 300K does not vary from the bulk one. However, the susceptibility in 100K is smaller than that in 300K suggests the
temperature-dependent paramagnetism. Significant paramagnetic responses are clear at low temperature. In our experimental limits and at any temperature, no ferromagnetic signals have been detected (as shown in figure 6-9), in contrast to other recent studies [88, 96-98]. To have better idea about the paramagnetism in MoS$_2$ laminate, the signals after subtracting diamagnetic background has been shown in figure 6-7. The curves at different temperature collapse are universal in a function of $(H/T)$ and the collapse curves can be well interpreted by Curie-Brillouin function with $J = 1$.

$$M = N_s gJ \mu_B \left[ \frac{2J + 1}{2J} \coth \left( \frac{J + 1}{2J} \right) - \frac{1}{J} \coth \left( \frac{1}{J} \right) \right]$$ (6.1.1)

From this fit, one can also obtain the density of spins ($N_S$) of the sample. The $N_S$ of this sample is $4.8 \times 10^{18}$/g and the magnetic moment is $9.6 \times 10^{18} \mu_B$/g.

Figure 6- 6 $M - H$ curves of MoS$_2$ laminates measured at the temperature of 2K (black dotted curve), 10K (red square curve), 100K (blue triangle curve), 300K (cyan square hollowed curve).
Figure 6- 7  Universal paramagnetic curves of MoS$_2$ laminates at temperature of 2K (red symbol) and 10K (blue symbol) as a function of the reduced magnetic field ($H/T$), comparing with graphene laminates (dotted dashed curve) and MoS$_2$ bulk powder (black dashed curve).

Effect of sonication

Further to the existence of paramagnetic centres in pristine MoS$_2$ laminates, duration of ultrasonication is found as a parameter of controlling paramagnetic responses of MoS$_2$. MoS$_2$ laminates which have been sonicated for the length of time varied from 18h to 168h were measured in Quantum Design MPMS SQUID magnetometer. Qualitatively, all the observations possess significant Curie paramagnetism and the density of spins extracted from the field dependent magnetization $M(H/T)$ are shown in figure 6-10 against sonication time. The density of spins increases from 3.8 to $6 \times 10^{18}$ /g monotonically as the length of sonication time extended. The same data is replotted against the size of flake in the inset of figure 6-10 and shows linear dependence. The $N_S$ obtained from the temperature dependent measurement in the same samples supports the above observations. Figure 6-11 shows the temperature dependence of MoS$_2$ laminates of two different sonication times. The temperature dependence proportional to $1/T$ follows Curie’s law.
\[ \chi = \frac{C}{T} \]  

(6.1.2)  

\( C \) is a constant and proportional to \( N_s \). The slope represents the Curie constant and can be used to estimate \( N_s \).

\[ C = \frac{N_s J (J + 1) g^2 \mu_B^2}{3k_B} \]  

(6.1.3)  

\( N_s \) is the density of spins, \( J \) is total angular momentum number, \( g \) is g-factor, \( k_B \) is Boltzmann constant, and \( \mu_B \) is Bohr magneton. The slope of \( \chi_{72h} \) (the susceptibility of MoS\(_2\) laminates made by 72 hours sonication) is larger than \( \chi_{24h} \) as a function of \( 1/T \). This results from the variation of density of spins, \( N_s = 4.5 \times 10^{18} / g \) for MoS\(_2\) laminates of 24 hours sonication and, \( N_s = 5.7 \times 10^{18} / g \) of 72h. These estimations are close to what is calculated from the field-dependent measurement.

The increased number of paramagnetic centres might be attributed to the existence of longer length of edges. In theory, one of the possible sources of magnetic moments in MoS\(_2\) is edges. The zigzag edges and missing sulfur atoms at edges may contribute localized magnetic moments to MoS\(_2\) sheets [85, 87, 91]. The linear dependence of density of spins on the size of flakes shown in inset of figure 6-10 indicates edge effect. For 50nm flake, the magnetic moment is around 0.09\( \mu_B \) per unit cell. This value slightly decreases with the reduction of flake size. For 30nm flake, the average magnetic moment is around 0.075\( \mu_B \) per unit cell. In principle, zigzag edges and missing sulfur edges contribute to 2\( \mu_B \) per edge atom. However, only part of the edges lead to magnetic moment and also the passivated termination might cause the reduction of magnetic moment [85, 88]. In the calculation of zigzag MoS\(_2\) nanoribbon, the reduction in magnetic moment due to hydrogen termination can be down to \( \mu = 0.47 \mu_B \) per unit cell, depending on the configuration of termination [85]. The reason of slight reduction of magnetic moments as size of flake decreased is still unknown and required more theoretical investigation. Another possible source is vacancies and adatoms which are possible to be introduced during sonication. The magnetic properties of MoS\(_2\) with several types of vacancies and adatoms have been calculated in theories [85, 86]. In all species of adatoms calculated in ref.[86], only Mo and C atoms are considered as possible adatoms in MoS\(_2\) laminates for creating magnetic moments. Among all types of vacancies, only MoS\(_2\)-triple vacancies are expected to contribute the magnetic moments (2\( \mu_B \) per defect).

In conclusion of this section: The magnetic properties of MoS\(_2\) laminates which
have been made by ultrasonication MoS\(_2\) powder in NMP solvent were measured their magnetic properties. In the limit of our magnetometer, MoS\(_2\) laminates shows no ferromagnetic findings, but significant Curie paramagnetism with total angular momentum number \(J = 1\). The density of spins increases linearly with the size of flakes. This might indicate the edges as the sources of localized magnetic moments. Indeed, missing-sulfur atoms at the edges have been found by TEM observation. However, we could not exclude the magnetic moments coming from vacancies or adatoms introduced during sonication although not significant difference observed in the vacancies of MoS\(_2\) flakes which have been sonicated for different length of time.

![Diagram](image)

**Figure 6-8** Universal paramagnetic curves fit by total angular momentum \(J=1/2\) (green dashed dotted curve), 1 (red solid curve), 3/2 (dashed blue curve).
Figure 6- 9 Hysteresis measurement at $T=2K$: the diamagnetic background is subtracted.

Figure 6- 10 Density of spins ($N_s$) of MoS$_2$ laminates which have been sonicated for the duration varied from 18 to 168 hours. Inset: the density of spins against inverse of lateral size of flake.
Figure 6-11 Temperature dependence of susceptibility in MoS$_2$ of 72h and 24h sonication. The diamagnetic constant is subtracted.

**Effect of proton irradiation**

Irradiation is a way to control vacancies in materials for changing their electronic and magnetic properties. Vacancy-induced magnetic moments are of interest in materials without partially filled d or f orbitals. So far, lots of theories predict that defects result in magnetic moments in MoS$_2$. Experimentally, Mathew et al. showed the results of ferromagnetism in proton-irradiated bulk MoS$_2$. However, the ferromagnetic findings in MoS$_2$ are controversial. To this end, the studies of magnetic properties of proton-irradiated MoS$_2$ laminates are presented in this section.

MoS$_2$ pristine laminates containing monolayer flakes have been produced by NMP-exfoliated methods for fixed sonication time as described previously and the existence of magnetic moments has been shown. Using 350keV proton beam to create defects and SRIM simulation to estimate the defect density, MoS$_2$ laminates with defect densities varying from $4.7 \times 10^{17}$/g to $4.8 \times 10^{18}$/g (considering only Mo vacancies exist) were made. In terms of estimated defects per flake, it varies from 1-2 defects to 15 defects per 50nm flake according to the defect densities. The magnetic signals are detected by Quantum Design MPMS SQUID magnetometer. Paramagnetic responses due to irradiation have been discovered as shown in figure 6-12. No
ferromagnetic signals have been discovered in the limit of magnetometer in any of the defected MoS\(_2\) samples. The paramagnetic responses are increased with higher defect density. \(N_s\) of sample in three doses, \(D_1\), \(D_2\), and \(D_3\) are extracted from the fit of \(J = 1\) Curie-Brilluoin function in the values of \(1.2 \times 10^{18}/g\), \(7.8 \times 10^{17}/g\), and \(4.9 \times 10^{17}/g\), respectively. Comparing to the density of spins induced by effect of sonication, proton irradiation seems to have much less of an effect. This can be explained by the comparison of total number of unit cells of the edges and the density of vacancies created by irradiation. The estimated density of unit cells along the edges of 50nm-flake MoS\(_2\) is around \(1 \times 10^{19}/g\), which is ten times more than the defect density introduced by irradiation. The same data are replotted in figure 6-13 as \(N_s\) per defect against defect concentration. The magnetic moments are between 0.4 to 1.82\(\mu_B\)/Mo vacancy.

This paramagnetic finding due to irradiation may come from the localized magnetic moments of MoS\(_2\) vacancies as predicted in theory [85, 86]. In theory, only MoS\(_2\) triple vacancies produce localized magnetic moments [85, 86], and calculated magnetic moments of 2\(\mu_B\) per vacancy fit with our result. In the sample of higher defect density, the vacancies are possible to reconstruct into non-magnetic ones and result in less total magnetic moments. However, more theoretical studies and microscopic observation are required to understand the real mechanism of magnetic responses in MoS\(_2\) due to irradiation.
Figure 6- 12  Magnetic moments induced by proton irradiation: $D_1$, $D_2$ and $D_3$ represents the samples with $4.8 \times 10^{18}/g$, $1.136 \times 10^{18}/g$ and $4.742 \times 10^{17}/g$, respectively. The red solid curves are the fits by Curie Brillouin function ($J=1$).

Figure 6- 13  Magnetic moments of each defects ($\Delta M$) induced by irradiation. The magnetic moments per defect vary from 0.4 to 1.82 $\mu_B$. 

6-4 Conclusions

In conclusion, the paramagnetic centres in MoS$_2$ laminates can be introduced by both sonication and irradiation. In both kinds of samples, no ferromagnetic signals have been found in the limit of detection. The sonication time for liquid exfoliated MoS$_2$ changes the average flake size significantly as well as the density of paramagnetic centres. The correlation of flake sizes and the magnetic properties of corresponding MoS$_2$ laminates may indicate the magnetic contribution from zigzag or missing-sulfur edges as predicted in theoretical calculations. On the other hand, proton irradiation also introduces localized magnetic moments. The total magnetic moments monotonically increased with the defect density introduced by proton irradiation. However, the magnetic moments per defect reduce while defect density increases. The magnetic moment per defect of the sample with low defect density is close to the theoretical prediction ($2\mu_B$). The absence of ferromagnetic coupling might attribute to the distances of magnetic centres. For a 50nm flake, the density of magnetic centers due to proton irradiation is around 1-2 per flake which may not be intensive enough for magnetic coupling. The reduction of density of paramagnetic centres for samples of higher defect density may indicate reconstruction of the vacancies to non-magnetic ones which lead to no ferromagnetic signals. It also shows the limitation of ferromagnetic finding in MoS$_2$ due to proton irradiation.
Chapter 7

Conclusions and Future Plans

Main experimental results

In summary, this thesis addressed the investigations of the magnetic properties of graphene and MoS\textsubscript{2}. The first part of our work is associated with defect-induced magnetism and the diamagnetism of graphene. The defects have been introduced by ion irradiation, fluorination, and annealing in the inert environment in this thesis. The former introduces vacancies and the latter two methods are using to attach sp\textsuperscript{3} defects to graphene. The other part is associated with the magnetic properties of MoS\textsubscript{2}, one of the potential two-dimensional materials which can be possibly applied for graphene heterostructural devices. A Quantum Design MPMS SQUID magnetometer was used to measure the sensitive magnetic responses. Although the magnetometer is currently one of the most sensitive pieces of equipment available, milligrams of graphene laminates were required to produce detectable magnetic signals. Graphene and MoS\textsubscript{2} laminates have been made by liquid-phase isolation of HOPG crystal and bulk MoS\textsubscript{2} powder in NMP. The atomic-resolution micrographs were performed by hardware aberration-corrected FEI TITAN 80-300 operated at 80 kV, to study the geometry of defects in ion-irradiated graphene.

In particular, chapter 3 displayed the experimental data associated with magnetic responses induced by point defects in graphene, supporting directly many theoretical studies. Fluorine adatoms which form sp\textsuperscript{3} bonds with carbon atoms were introduced by exposing graphene to fluorine atomic gas decomposed by XeF\textsubscript{2}. On the other hand, vacancy-type defects in graphene are created by ion-irradiation. Both types of defects were found to induce remarkable spin-half paramagnetism, but no magnetic ordering could be detected even for the largest defect density at T=1.8K. This agrees with the theoretical prediction. The magnetic moment achieved in our case is 0.1\% of the maximum hypothetic moment of $\sim$1$\mu$\textsubscript{B} per carbon atom. The fluorine clusters on
carbon sheets lead to the inefficiency of inducing magnetic moments by fluorine adatoms. Instead of the contributions from all the fluorine adatoms, magnetic moments only come from edges or vacancies of clusters. On the other hand, structural integrity of ion-irradiated graphene laminates limited the vacancy concentration. Although the achieved magnetic moment is much larger than those of the ferromagnetic findings reported in the other carbon systems, the distance between two localized spins (~8nm), obtained from the atomic-scale observations in chapter 5, is too large for magnetic ordering.

In chapter 4, the magnetic moments injected by introducing sp$^3$ and vacancy-type defects in graphene laminates were demonstrated to be controlled by molecular doping. Although no ferromagnetic coupling has been found in either the graphene laminates before or after doping, we were interested in controlling the paramagnetic centres in two types of defected graphene laminates. The paramagnetic centres induced by sp$^3$ defects are completely suppressed when $E_F$~0.5eV, while only half of the initial magnetic moments are eliminated when the Fermi energy of graphene with vacancy-type defects shifting to the same level. This observation matches the scenario of dual origins of paramagnetic centres in defected carbon lattices. Two localized states, $\pi$ and $\sigma$, are associated with imbalance of two sublattices and the dangling bonds, respectively. In principle, the former is expected to be existed in both types of defects while the latter only risen by vacancy-type defects. The distinguishable suppression of the magnetic moments in two types of defected graphene on the effect of doping reflect the $\pi$ states is closed to the Fermi energy, while the energy for pairing the spins in the $\sigma$ states is much higher than those achieved by chemical doping. Furthermore, the almost complete suppression of spins in sp$^3$ defected graphene is suggested to be useful in spintronics development. On the other hand, large orbital diamagnetism of neutral graphene and its rapid reduction when graphene is doped are expected. However, the sharp changes of diamagnetic susceptibility were not observed in the molecular-doped graphene. Instead, when the Fermi energy is less than 0.3eV, almost no variation shows in diamagnetic susceptibility of graphene. When the Fermi energy is higher than 0.3eV, a reduction in the susceptibility comparable to graphite displayed. This is attributed to the spatial confinement due to graphene laminates are composed by the nanometer-sized flake.

In chapter 5, the defected graphene encapsulated by graphene cells were demonstrated to be feasible to observe the intrinsic point defects avoiding their damage or
transformation by electron beams. In particular, proton-irradiated trilayer graphene and systematic simulations were shown to provide a reliable identification of the location and types of defects through high resolution transmission electron microscope. This method can view intrinsic defects when it has similar contrast as the outer cell. In addition, the required clean process of in-situ annealing prior to high resolution imaging is altered by drop casting nanocrystallites of MoS$_2$ due to the possible transformations of defects by annealing. Reconstructed single vacancies are in majority of the defects observed in all of our samples. This observation explains the magnetic and electronic properties discovered in the ion-irradiated graphene. The contradiction of this result to the previous observations, where more divacancies and other more complicated defects have been discovered, is explained as encapsulation protecting the defect from e-beam sensitive transformation.

In the chapter 6, MoS$_2$ laminate has been investigated about its magnetic properties on the effect of edges and vacancies through the modification by sonication and ion-irradiation, respectively. In all our cases, no significant ferromagnetic ordering has been found. The total length of edges of nanoflakes in MoS$_2$ laminate produced by sonication shows significant effect on the paramagnetic signals of MoS$_2$ laminates. The increase of total edge length is proportional to the addition of paramagnetic centres. This agrees with the theoretical expectation that zigzag and missing sulphur edges can induce the magnetic moments in MoS$_2$. Moreover, the effect of ion irradiation on the magnetic properties of MoS$_2$ was also studied. Paramagnetic signals induced by ion-irradiation are detected. Low density defects create the magnetic moments of 1.82μ$_B$ per defect which agrees with 2μ$_B$ per defect in the theoretical expectation. The total magnetic moments increase when the defect density increases, but the magnetic moments per defect were decreased. The reason of the latter phenomenon is still unknown, requiring further microscopic studies.

**Future work and perspectives**

In the end, we would like to mention some further techniques possible to be developed based on the above projects. Spintronics, also known as magnetoelectronics, is a new technique using spins alongside with electric charges to control solid-state devices. The injection of spins by structural defects, spins possibly controlling by the electric field and the engineering of vacancy graphene by ion irradiation, maybe open a gate for the graphene spintronics devices. In addition, a device based on graphene
nanoribbons or defect-engineered graphene is probably a solution for current problems in spin valve devices. One of the problems is the interface scattering between magnetic and nonmagnetic materials, which usually stack on each other. A device entirely made by graphene-based materials can solve this issue and also the magnetoresistance of zigzag-edged graphene nanoribbons is predicted to have values higher than the previous reported value. This encourages the realization of graphene spintronics devices achieving better performance than the current devices.

Moreover, the sources of sonication-induced paramagnetic centres in MoS$_2$ are still unknown. By analysing the percentage of single layer MoS$_2$ in each states of sonication, one may be able to tell the origins of paramagnetic centres. An efficient analysing technique, which can be also used for making samples for magnetic measurements, is waiting to be developed. On the other hand, it is known from this thesis that the magnetism can be induced by irradiation which introduces holes or vacancies in MoS$_2$. However, the vacancy types are not identified. To know more about the mechanism of irradiation-induced magnetism in MoS$_2$, it is important to discover the structures of vacancies created by ion-irradiation.

The atomic imaging of e-beam sensitive materials, such as live cells, is always of great interests. High voltage and intensity of electron beam and the high vacuum in TEM chambers are not promising for the biological cells imaging or liquid environmental experiments. Encapsulation of these materials by graphene shields may be a solution. Graphene as a shield cell has been proven in this thesis as well as several papers to protect inner materials from high energy electron beams. In addition, a perfect graphene is hydrophobic and impermeable which allows the liquid or special gas environmental experiments. Real-time and multiplexed imaging of biomolecules (e.g. glucose, DNA) or cells (e.g. cancer cells, stem cells, bacteria or viruses) can be realized by this method, providing more information about the mechanisms of cells and molecules.
Appendix A

SQUID Magnetometer

Quantum Design MPMS XL SQUID magnetometer is used to obtain most of the magnetic measurement in this thesis. The method and some principles for measuring the magnetic properties of graphene and MoS$_2$ laminates are illustrated in this appendix. The magnetic field performs in a range of ±7 Tesla and temperature can be operated between 1.8K - 400K. The absolute resolution in reciprocating sample option (RSO) and DC mode is $2 \times 10^{-8}$ emu at 25kOe [167]. This allows us to investigate the small magnetic signals from graphene and MoS$_2$ laminates of milligram in weight. The components of MPMS sample chamber are sketched in Figure A - 1. A sample which size is around 4×4 mm$^2$ is inserted by the sample rod into the sample chamber. Temperature inside the sample chamber is isolated from the liquid Helium environment by several layers insulation, such as inner and outer jacket walls. Thus, the temperature of the chamber can be controlled. The magnetic fields are provided by the superconducting magnets. Once the sample is inserted, the voltages are detected by the gradient sensing coils (as illustrated in Figure A - 2 (a)-(c)), and then the detecting voltages are converted to magnetic moments by the fits of linear or iterative regression as in Figure A - 2 (d). Linear regression is used when sample position fixed in the centre. Otherwise, iterative regression is adopted for the unintentional moving samples. The two regressions are based on an assumption that samples are magnetic dipoles, which limits the sample in millimetre size.
Figure A-1 Schematic pictures of MPMS sample chamber: The picture in right-hand side is the zoom-in image of the square region in the left picture (Adapted from [168])
Figure A - 2 (a)-(c) voltage gain when sample moving in the gradient sensing coil (d) linear and iterative regression [168]

Figure A - 3 displays the samples mounted in the parallel and perpendicular direction respected to the magnetic field, which allow the magnetometer to detect the magnetic responses from in plane and out of plane of the samples. In parallel direction, samples are mounted on a thin transparency fixed inside a transparent straw. Cement and eicosane (C_{20}H_{42}) are used to fix samples on the transparency. These two materials are useful in our case since their responses to the magnetic field do not cover the signal from the samples and stable in the cryogenic system. On the other hand, for the sample mounted perpendicular to the external field, a circular transparency is placed for the support of sample in the middle of a straw and then a section of kapton tape wrapped around the straw to fix the transparency. Samples are fixed on the centre of the transparency by eiconsane and cement. Symmetry of the samples is important since the sample is viewed as magnetic dipoles for magnetic moment calculation.
Figure A-3 Sample (dark brown square) mounted in the direction where c-axis is perpendicular and parallel to the magnetic field: the brownish cylinder (right) is a round of kapton tape.

In order to get the signal of the sample from the entire message obtained by using SQUID magnetometer, subtraction of backgrounds is needed. The entire message includes not only samples, but backgrounds. Two kinds of background exist in the whole measurement. First one is the homogeneous background (in 8cm length in z-direction), which can be reduced by the gradient sensor of magnetometer automatically. This kind of background can be neglected in the analysis. One of the examples is the long transparency used in figure A–3 for mounting the samples in parallel. The other type of background is those which cannot subtract automatically by SQUID magnetometer, i.e. inhomogeneous in the range of sensing coil. Those backgrounds are needed to be subtracted by hand. In our experiments, cement, eicosane, and the perpendicular holder are the backgrounds needed to be considered. In parallel measurement, cement and eicosane used for fixing samples on transparency are the main inhomogeneous background considered in the measurement. In figure A–4, the magnetization of cement and eicosane are measured and rescale to 1g. We
recorded the weight of them in all of the samples and then the corresponding contributions of cement and eicosane can be subtracted. In the same sense, perpendicular background contains a circular transparency, a section of kapton tape and cement is measured. The signal from the perpendicular holder is much larger signal than the contribution from cement and eicosane, so that the accuracy of the same small signals in perpendicular measurement is less than in parallel.

Figure A-4 (a) Magnetisation (emu/g) of Eicosane (b) Magnetisation (emu/g) of Cement. Equations are the fits of magnetization in different temperature.
Figure A-5 The magnetisation of perpendicular holder (contain Kapton tape, circular transparency and a drop of cement as usual amount). Equations are the fits of each temperature curves.
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