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Shear exfoliation in liquids : a promising way to produce Graphene

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Shear exfoliation in liquids : A promising way to produce Graphene

Abstact: This internship took place as part of the Summer Student Programme organised by CERN. ISOLDE, CERN's nuclear physics facility, is the longest continuously running experiment at CERN and is celebrating its 50th anniversary in 2014. The ISOLDE collaboration obviously carries out fundamental research in nuclear physics. Solid state physics and bio physics are also an essential part of the scientific programme. My initial project was to install and test a new spectrometer for the solid state physics group. However, due to a delay in the construction of the new photoluminescence laboratory this project had to be abandoned.
Graphene is a one atom thick 2D material that presents remarkable physical properties whose applications are very promising. However, the current means of production present several limitations. They are costly in terms of energy consumption and yields are ridiculously low. Thus, to progress from the laboratory to industrial production it will be necessary to find a method to produce large quantities of defect graphene. In April 2014, a paper [13] came out in *Nature Material* demonstrating that shear exfoliation in liquids would be a scalable way to produce defect-free grahene. The aim of my project was to test this new method by trying to reproduce some of the results published in this article. It involved the setting up of the experiment, the production of samples and finally their characterisation.

Résumé: Ce stage a été réalisé dans le cadre du Summer Student Programme organisé par le CERN. ISOLDE,l'installation de physique nucléaire du CERN, est la plus vieille expérience toujours en activité au CERN puisqu'elle fête, cette année, son 50ıème anniversaire. La collaboration ISOLDE conduit, bien évidement, des recherches en physique nucléaire fondamentale mais la physique de la matière condensée ainsi que la bio-physique font parties intégrantes du programme scientifique. Mon projet initial était d'installer puis de tester un tout nouveau spectromètre pour le compte du groupe de physique du solide. Cependant, la construction du bâtiment dans lequel ce spectromètre était censé prendre place a pris du retard et nous avons dû très vite abandonner ce projet.
Le graphène est un cristal bi-dimensionel qui présente des propriétés physique surprenantes et dont les différentes applications semblent prometteuses. Cependant, les méthodes de production actuelles présentent de nombreuses limitations. Elles sont couteuses en énergie et leur rendement est vraiment très faible. Ainsi pour passer du laboratoire à la production industrielle il est nécessaire de développer de nouvelles méthodes pour produire, à grande échelle , du graphène de bonne qualité. En Avril 2014, un article [13] est paru dans *Nature Material*. Cet article démontre que l'exfoliation par cisaillement en milieu liquide présente les qualités requises. Le but de mon second projet a donc été de tester cette méthode de production afin de l'éprouver. Cela a impliqué de mettre en place une expérience de toute pièce, de produire des échantillons et enfin de les caractériser.

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Chapter 1

Introduction

1.1 The Summer Student Programme

This internship took place as part of the Summer Student Programme. This programme aims at making bachelors and masters students, around 300 students from all over the world, discover what it is like to be involved in the day-to-day work of one of the biggest laboratories in the world : CERN. Thus, I experienced at CERN my first multicultural and multidisciplinary experience.

In parallel with our physics project several activities were organised. In July the mornings were dedicated to the Summer Student Lecture Programme during which several scientists shared their knowledge concerning a wide range of topics : theoretical and experimental physics, electronics, computer science and so on. I also had the opportunity to visit some of CERN's facilities :

- CMS
- ATLAS
- Anti-proton Decelarator
- Data Center
- ISOLDE's experimental hall

Finally, quite a few workshops were proposed. I attended two workshops. One was dedicated to both the installation and a first discovery of the software *ROOT*. The second was a lot more entertaining as we realised our own cloud chamber.Then we could observe tracks created by charged particles flying through our self made detector. Thus, the summer student programme enables me to have a quite complete overview and desipated parts of the doubts I had about how it is like to work and live in such a huge and diverse environment.

1.2 CERN and the ISOLDE radioactive ion beam facility

The European Center for Nuclear Research is an international research institution whose role has been, since its foundation in 1954, to probe the fundamental structure of the Universe. Physicists and engineers are working side by side to unravel the mysteries of particle physics using the most advanced purpose-built technologies such as the Large Hadron Collider, the

biggest particle accelerator in the world. Several important discoveries were made at CERN the latest being the detection of the Higgs Boson in 2012[1]. CERN also revolutionized modern worldwide communication as the web was invented there by Tim Berners-Lee in 1989.

ISOLDE[2] is a on-line mass separator facility dedicated to the production of a wide range of radioactive isotopes. Based at CERN, ISOLDE actually is its longest continuously running experiment and it is celebrating its 50^{th} anniversary in 2014. More than 700 of isotopes can produced at ISOLDE allowing the systematic study of their nuclear and atomic properties. In addition, biophysics, astrophysics and solid state physic also benefit from the facility. ISOLDE delivers intense accelerated ions to a dozen beamlines. More than 50 different physics experiments are carried out each year[3]. This summer ISOLDE restarted after a 18 month shutdown.

1.3 Solid States Physics experiments at ISOLDE

As said before, ISOLDE is a versatile factory to produce a wide range of chemically clean, mass separated, high intensity beams of radioactive ions. Thus, since the first experiments in the late 60's, ISOLDE has become a unique facility for both solid state and bio physics research.

The production of short lived radioactive isotopes enable a growing community of material science researchers to use nuclear spectroscopic techniques such as Mössbauer, perturbed angular correlations (PAC), β-NMR or emission channeling to carry out new experiments. In addition to the nuclear techniques, diffusion studies as well as conventional non-radioactive techniques, eg photoluminescence[4] measurements, are carried out on radioactive doped samples, providing chemical signature upon correlation of the signal with the isotope half-life [2, 3]. Thus, the techniques used by the solid states physics group can be mainly divided in two types.

- Tracer Techniques : where the half-life or simply the decay particles provide the element signature information and quantification (PL, diffusion etc).
- Nuclear Techniques : where the impurity/element position on lattice sites is directly measured, or where the probe element interaction with the host matrix is investigated via the measurement of the electronic charge density and symmetry, or of the magnetic fields, in the probe's neighbourhood (PAC,β-NMR etc).

[1] P.Higgs and F.Englert received the Nobel Prize in 2013 "for the theoretical discovery of a mechanism that contributes to our understanding of the origin of mass of subatomic particles, and which recently was confirmed through the discovery of the predicted fundamental particle, by the ATLAS and CMS experiments at CERN's Large Hadron Collider."

[2] **I**sotope **S**eparator **O**n **L**ine **DE**vice

[3] More information can be found at `http://isolde.web.cern.ch/`

[4] Abridged PL in the following

Chapter 2

Extending the range of ISOLDE PL laboratory

2.1 PL spectroscopy

Photoluminescence is one of the best means of characterising semiconductors. It consists in recording the optical emission spectrum of a semiconductor excited with a laser beam.The photoluminescence technique presents several advantages. It can achieve a high spectral resolution, is very sensitive[1] and is non destructive. In addition, it is a very straight forward method. However, the main drawback is that, except in some really rare cases, photoluminescence is unable to provide a chemical identification of the impurities or defect involved in the production of the spectrum.

Here it is worth noting that the processes involved in the PL phenomenon are very diverse. When a semiconductor is excited by a laser whose energy is greater than the band gap of the material the free electrons and holes created begin to diffuse in the material. The ways that free electrons and holes or excitons[2] relax to their ground state can be summarise in 2.1.

2.2 PL experiments at ISOLDE

At ISOLDE a wide range of radiotracers are available, and this in addition to and an on site photoluminescence lab enables one to overcome the natural limitations of photoluminescence in terms of chemical identification. First, a radioactive impurity is implanted into a semiconductor. Then, a PL spectrum is recorded. The appearance or disappearance of spectral features according to a rate consistent with the half-life of the probe radioelement enables the chemical identification of the peak. This tracer type technique has a remarkable efficiency. For instance, it has allowed for the full classifiation of the dominant impurities in ZnO. Figure 2.2 on page 6 shows an example of a peak, due to the presence of an Antimony impurity, arising in a ZnO spectrum. As one can see on this figure, the peak becomes sharper and sharper as time increases from around 0.2 half-life to around 4.6 half-life.Thus, this feature enables to identify the wavenumber corresponding to an Antimony impurity in a ZnO sample 2.2.

[1] Down to parts per billion

[2] An exciton is a bound state of an electron and a hole.A bound exciton is an exciton localised to an impurity/defect. [see 6, chap.11]

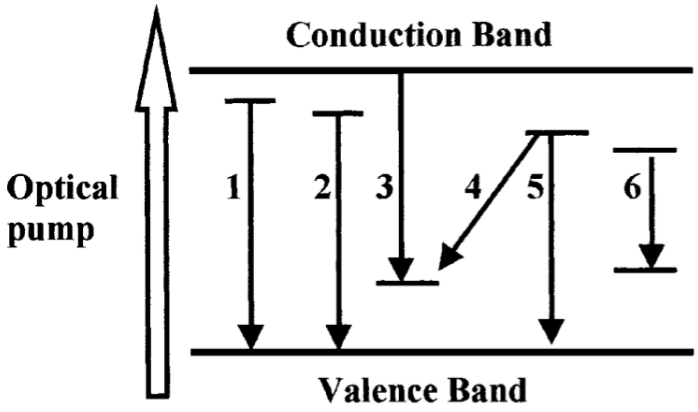

Figure 2.1: schematic showing the different possible recombination processes in a semiconduction: 1-free exciton;2-bound exciton;3-electron to acceptor;4-donor to acceptor;5-hole to donor; 6-impurity or defect internal transitions. Schematic taken from:[5]

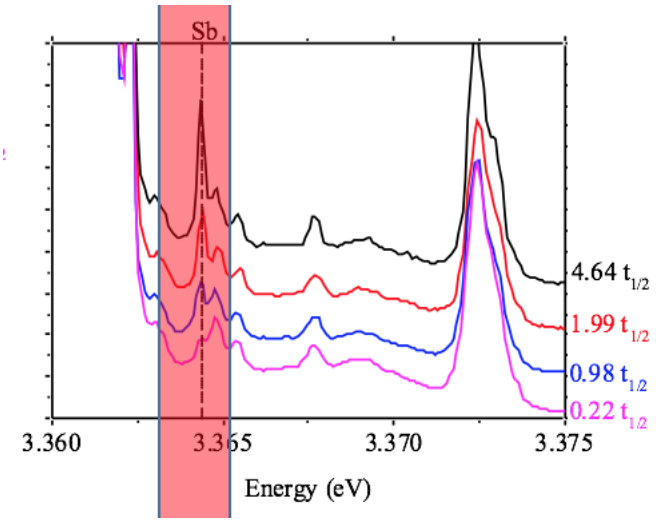

Figure 2.2: a peak due to Antimony arising in a Zn0 spectrum

Figure 2.3: The new PL lab in the end of July 2014.

2.3 The need for a new spectrometer

At ISOLDE, a custom-built PL lab has been in operation since 2004. As said before it has proved to be remarkably successful. However, the efficiency of the spectrometer is optimised for UV light but less for visible or infrared radiation. This problem will be addressed this year with the installation of a new spectrometer and monochromator. In order to centralise and consolidate ISOLDE offline experimental laboratories the construction of a new building was approved. Thus, the old PL laboratory was dismantled and the laboratory demolished. My initial physics project was to reinstall and test the improved version of the PL experimental set up in the new facility. Unfortunately, due to several factors, the project has been delayed and at present it still won't be useable until at least november 2014. As one can see on figure 2.3 page 7, even in the end of July, a half of my stay at CERN, we were completely unable to work in the lab as electricity and cooling systems had still to be installed. I arrived at CERN on the 16^{th} of June, and after two weeks the perspective that the infrastructure would not be finished before the end of my stay at CERN became a reality. My supervisor, Mr Karl Johnston, had to find a new project for me to work on. He found a paper [13] describing a non conventional way to produce few-layer graphene using a kitchen blender allong the way. This project on graphene was initially meant to occupy me a few weeks while waiting for the lab to be finished. Since the installation of the spectrometer was called off, shear-exfoliation of graphene in liquids turned out to be my main summer physics project.

Chapter 3

Producing graphene thanks to shear exfoliation in liquids

3.1 Generality about graphene

As said previously, graphene production was meant to be only a side project to occupy myself while waiting for the new building to be finished. It also took place as part of an existing research project on graphene carried out in the SSP Group. Then it became my major project only when there were no hope that the lab would be ready before I leave CERN. Thus, the two first weeks of my internship were mainly dedicated to the reading of several books[1] and articles[2] in order to refresh or acquire knowledge about both graphene and photoluminescence.

The first thing I studied in graphene is the structure of the reciprocal lattice. Graphene is composed of a single layer of carbon atoms disposed in a honeycomb structure. It was first isolated[3] in 2004. The primitive cell of graphene spanned by the following two vectors of the direct lattice:

$$\vec{a_1} = (\frac{3}{2}a; -\frac{\sqrt{3}}{2}a), \vec{a_2} = (\frac{3}{2}a; \frac{\sqrt{3}}{2}a) \tag{3.1}$$

Let us assume $\vec{a_1}^*$ and $\vec{a_2}^*$ to be the base vector of the reciprocal lattice. Then, the relation between the base vector of the reciprocal and those of the direct lattice is given by the relation :

$$\vec{a_i}^* \cdot \vec{a_j} = 2\pi\delta_{ij} \tag{3.2}$$

After solving this simple system of equations one can obtain the following expression of the reciprocal vectors :

$$\vec{a_1}^* = (\frac{2\pi}{3a}; -\frac{2\pi}{\sqrt{3}a}), \vec{a_2}^* = (\frac{2\pi}{3a}; \frac{2\pi}{\sqrt{3}a}) \tag{3.3}$$

One can find a schematic showing the vectors of the direct lattice and reciprocal lattices on figure 3.1 on page 9. On this figure one can see on right hand side drawing a representation of the first Brillouin zone. The Γ point represents the center of the zone, K and K' are high symmetry points whose role will be detailed in the following. Here it is worth noting that K and K' are not equivalent since they are not related by any combination of the vectors of the reciprocal lattice.

[1] [6, 19]
[2] [3, 5, 13, 14]
[3] A.Geim and K.Novoselov received the Nobel prize in 2010 for this discovery.

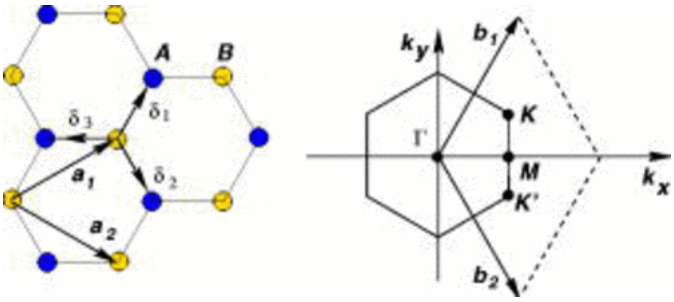

Figure 3.1: Schematic representing graphene's direct and reciprocal lattice. Credit: [1].

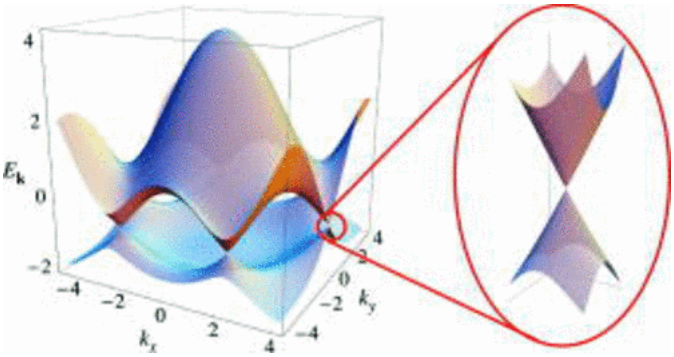

Figure 3.2: Representation of the band structure of graphene in the first brillouin zone. Credit: [1].

Graphene presents remarkable and surprising properties. It is 100 times stronger than a steel film of the same thickness would be making grahene one of the strongest known material. Electron mobility in Silicon has a typical value, at room temperature, of 1400 $\mathrm{cm^2V^{-1}s^{-1}}$. Electron mobility in graphene has been measured to be one order of magnitude higher than that of SI reaching 15000 $\mathrm{cm^2V^{-1}s^{-1}}$ [10]. This makes graphene a remarkable electric conductor. Graphene is also an excellent thermal conductor with a thermal conductivity 5 times bigger than that of graphite, the stacked version of graphene. All these properties emerge from the characteristical shape of the band structure of graphene near the K and K' points. This band structure can be easily computed using the tight binding model [see 19, chapter 2]. Near both K and K' the dispersion relation of graphene becomes linear with respect to $\|\vec{k}\|$ and can thus be expressed as

$$\varepsilon(\vec{k}) = \pm\hbar v_F \|\vec{k}\| \tag{3.4}$$

where the Fermi velocity $v_F \approx 10^6\ \mathrm{m \cdot s^{-1}}$. Electrons in graphene behave in fact as massless relativistic fermions. In equation (3.4) one can note that $\|\vec{k}\|$ is measured from the K or K'.

3.2 Towards industrial production of graphene

3.2.1 The existing methods to produce graphene

Several methods exist to produce graphene and it is not relevant to describe all of them here. This diversity only reflects the enthusiasm surrounding graphene research. Let's review the main

technique of production. Probably the cheapest way to produce this material is the micromechanical exfoliation also known as the cellotape technique. It is the historical way of producing graphen and was used to isolate this material in 2004. Graphite is an assembly of graphene layers bound together. Scotch tape exfoliation consists in pulling a few graphene layers from graphite. Repeating this process several times on the previously obtained samples enables one to reduce the thickness of graphene layers down to one. The graphene obtained is then transfered to a silicon dioxide wafer for characterisation.

Since then, several new methods have been elaborated. Another technique consists in sonication in liquids. It is the power delivered by ultrasonic waves in the liquid that produces the exfoliation mechanism. Nowadays, one of the most commonly used technique is CVD[4]. A vapor of a carbonated monomolecular gas is put together with a metal substrate such as copper. A chemical reaction with the substrate will lead to the deposition of a thin layer of graphene on the surface of substrate. All of the methods described above allow for the production of good quality graphene. The graphene nanosheets obtained, mono-layer or few-layer graphene, are defect free and unoxidized. Thus, all of these techniques are suitable for the production of graphene for research. But to progress from the laboratory to industry they present several limitations. First, all of these methods consume too much power. Sonication requires the delivery of several watts to the solution to be performed correctly. CVD needs to be performed in a very clean and precisely monitored atmosphere as it is very sensitive in terms of temperature and presure. All of these methods are also costly in terms of time. Their yield of production is very low and currently don't exceed a $0.04\ \mathrm{g \cdot h^{-1}}$ which is ridiculously low for industrial applications [see 13]. The scalability of the means of production is a necessity and none of the current methods fits this requirement.

3.2.2 The shear exfoliation mechanism

Fortunately, a possible solution came out in an article [13] in 2014. In this paper a scalable way produce a large quantity of defect-free few-layer graphene is described. Shear exfoliation in liquids is actually a very unexpensive and straight forward method. It only requires :

- Any kind of mixing device (from a chemistry lab mixer to a basic kitchen blender)
- Graphite powder (I bought it from VWR)
- A stabilising solution

Mixing the stabilising solution and the graphite powder in the right proportions in the mixer is then sufficient to obtain few-layer graphene dispersed in the solution. Using a centrifuge at the end helps in getting rid of most of the remaining graphite chunks. The graphene nanosheets produced with this method performed well in several applications.

I think it is worth focusing on the role of the stabilising solution. Such a solution is used, as its name suggested, to stabilise the exfoliated graphene sheets preventing them from reaggregation into graphite. It also eases the mixing process by weakening the bonds between the several graphene sheets constituting the graphite crystal. Different types of solvent can be used.

Organic solvents: If a solvent with a surface energy close to that of graphene is used in the mixing process the energy of mixing is very low. This results in a stabilisation of nanosheets against reaggragation.

[4]Chemical Vapor Deposition

Aqueous surfactant solution: Surfactant molecules present a hydrophobic head and a hydophilic head. When such molecules are used in aqueous solution in the mixing process the hydrophobic head will adsorb on the the graphene nanosheets whereas the hydrophilic heads will interact with water and become dissociated. The different surfactant coated graphene flakes will thus be electrostatically repelled from each other and thus will then be stabilised.

Polymer solutions: A part of the polymere chain will stick to the graphene sheets surface, the rest protruding in the solvent. Steric effect will then produce a repulsion between the flakes.

Let us consider now the role of the mixer. In article [13] and its supplementary information [14] it has been demonstrated that either a rotor-stator mixer or a blender mixer can be used to produce graphene. In a rotor-stator mixer shear exfoliation occurs because of the high shearing rate created in the gap between the rotor and the stator. It has been demonstrated in [18] that turbulence in such a system is fully developed when the Reynold's number, Re, satisfies the inequality :

$$Re = ND^2\frac{\rho}{\eta} > 10^4 \tag{3.5}$$

where N is rotor speed, D, the diameter of the rotor, ρ, the liquid density and η, the viscosity. Initially, one can think that exfoliation occurs thanks to the localised dissipative turbulence created in the solvent by the mixer. However, in a rotor-stator type of mixer, [13] shows that a fully turbulent regime is not necessary to exfoliate graphite. In a blender mixer when N reaches its maximum value, around 18000rpm, the associated Reynold's number can easily achieve 10^6 high above the threshold of 10^4. This shows that, when turbulence is not needed in rotor-stator system, it is the strong local variation of the shearing rate caused by turbulence that allows for the exfoliation of the graphene nanosheets. The process is thus not very sensitive to the conditions in which to experiment is carried out.

A simple model can be developed to describe the exfoliation mechanism. Let us consider 2 square platelets of dimension L. They are weakly bound and initially stacked on top of each other. The blades or the rotor create a velocity differential between these two platelets inducing a shear stress σ. As stress is a force per unit of surface the induced force on the platelets can be written as $F = \sigma L^2$. If we assume the solvent to be a Newtonian fluid then there exists a simple relation between the stress tensor, σ and the shearing rate,$\dot{\gamma}$: $\sigma = \eta\dot{\gamma}$. Thus we obtain the relation :

$$\dot{\gamma} = \frac{F}{\eta L^2} \tag{3.6}$$

We can now evaluate the sliding force induced. Let E_{LL}, E_{LP}, E_{PP}, be the interfacial binding energy between, respectively, liquid and liquid, liquid and platelets and finally platelets and platelets. As we see in figure 3.3 we have to consider a LxL zone occupied by the platelets but also a LxL zone not yet occupied. Let x be the distance by which the platelets are moved. Then we can write the following relation :

$$E(x) = -L[xE_{LL} + 2(2L - x)E_{LP} + xE_{PP}] \tag{3.7}$$

The minimum applied force to separate the sheets can then be expressed as follow :

$$F = -\frac{\partial E(x)}{\partial x} = L[E_{LL} - 2E_{LP} + E_{PP}] \tag{3.8}$$

We can approximate E_{LP} by writing $E_{LP} = \sqrt{E_{LL}E_{PP}}$. Replacing F in equation (3.6) and using (3.8) we obtain :

$$\dot{\gamma}_{min} = \frac{[\sqrt{E_{PP}} - \sqrt{E_{LL}}]^2}{\eta L^2} \tag{3.9}$$

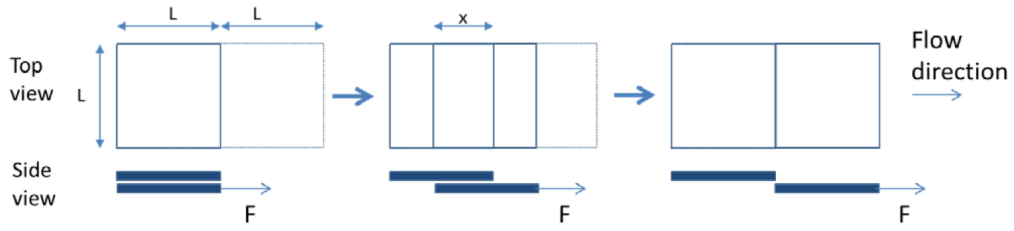

Figure 3.3: Schematic representing the exfoliation model. Taken from : [14, section 7].

Here, E_{PP} and E_{LL} are in fact the surface energy of graphene and of the liquid. Taking the numerical values given in [14, section 7] we can compute the minimum shear rate needed to exfoliate the graphene sheets : $\dot{\gamma}_{min} \approx 10^4$ s^{-1}. This can be easily expressed in terms of power density delivered by the mixer. Thus, any type of mixer can be used as long as the power volume ratio,P/V, is greater than :

$$P/V \sim 100 \text{ W/L} \tag{3.10}$$

3.3 The preparation of the samples

During this internship I tried to reproduce the results obtained in [13]. Thus, one of my first tasks was to get an overview of how the method works and what is required to carry out the experiment. As decribed before the shear exfoliation mechanism is rather insensitive to the condition in which the experiment is carried out. Even a crude device, such as a kitchen blender, is sufficient as long as condition (3.10) is verified. I bought, in an electrical goods store, a kitchen blender that can deliver 700 W in 1.3 L. According to [14], simple dishwashing detergent would be sufficient to act as a surfactant. Finally, graphite powder was ordered from the company VWR. In order to weigh the graphite powder a high precision balance was used. Once the solution was obtained, the remaining graphite chunks were removed by centrifugating a small amount of solution in a centrifuge at 3000 rpm. This initially, took quite a while toget the lab ready.For instance, it took a week for the graphite powder to finally arrive instead of 2 days as expected. Then, as everything constituting the old PL lab had been packed and stored in cardboard boxes, we had a hard time finding what I needed, that is the balance, the centrifuge, and miscellanous lab tools such as beakers, plastic tubes or mircro pipettes. It took almost a week and a half to find all the pieces. I would like to thank Adeleh Gerami for her help and her advice in preparing samples.

Once the lab was ready, it was time to start preparing samples. Taking [13] as a reference, as always, the mixing parameter were chosen as follows :

- Graphite concentration C_i : $20 \leq C_i \leq 100$ g/L
- Mixing time t : $10 \leq t \leq 30$ min
- Ratio surfactant to graphite : $\frac{C_i}{C_{FL}} \sim 8$
- Centrifugation time : 3000 rpm during 2h30.

All these parameters had to be adjusted to the specification of our blender. Indeed, it happened that during the mixing process, as the dishwashing detergent produced a large amount of foam, the solution overtoped of the blender. We found out that using only 200 mL of water would

Figure 3.4: A picture showing the blender used in this work.

prevent this unconvient phenomenon. After the protocole was fully finalised, it was decided to stick to a C_i of 70 g/L and a mixing time of 30 min to prepare samples for characterisation. These figures were chosen randomly. Nonetheless according to [13] the longer the mixing and the higher C_i higher is the graphene concentration in the end of the process. Then, in the following weeks, this solution was used to produce several test samples. µL of the solution was drop casted onto different substrates : Si wafer, glass slides, filter paper, aluminium foil. Once the deposition is done the samples obtained had to be dried. Again, here several methods were used to try to optimise the chance of imaging the graphene flakes. I simply dried some of the samples in the air. Some other were dried in an oven. Finally, I tried vaccum filtration on microporous filter paper. Figure 3.4 shows the experimental set up and some sample solution in pastic tubes.

Chapter 4

The characterisation of the samples

In 3.3 I explained how I produced the samples. Let's now examine the different methods I used to characterise my samples. It is important to note that, even though a material science engineering team can be found at CERN, the lack of suitable characterisation devices was an important limitation to my work. Other methods of characterisation, such as Tunelling Effect Microscopy or X-Ray Diffraction, could have been tested however due to the limited time available or their unavailability at CERN only 3 methods were carried out.

4.1 Scanning Electron Microscopy

Thanks to Mr Joao Pedro Ramos, member of ISOLDE target group, I could image some samples using an SEM device. I would like to thank him for the time he allowed in order that we could image my samples. To produce an image, a Scanning Electron Microscope uses a beam of electron which is incident on a sample. The interaction between the electrons and the samples produces various signals, mostly secondary electrons, that are detected by the SEM. These signals in addition with the position of the electron beam enables software to compute an image. The SEM used was a Carl Zeiss SMT SIGMA with a maximum resolution of 1.5 nm at 20kV. To prepare the first session, I found information on how to image and interpret an SEM image of a graphene sheet in [11, 20, 21]. Unfortunately, due to its characteristic monoatomic thickness graphene is very difficult to image with an SEM. Indeed, a very low voltage of 1 kV is required otherwise the electron simply pass through the sample and nothing can be seen. Using a low voltage induces secondary problems such as a loss in resolution, from 1.5 nm at 20 kV to around 20 nm at 1 kV. Besides, the difficulty encountered to focus the electron beam at a low voltage results in a bad quality of the picture. In any case, graphene is difficult to image and the nature of the substrate plays a crucial role in the contrast, and thus the visibility, of the flakes. The best substrate, or at least the most commonly used, to image graphene samples is $Si0_2$. The aim of this internship was trying to do with the minimum and with what was available in SSP group stock. Thus, the first substrate I tried was simple aluminium foil. It worth noting that using a conductive substrate for an SEM is of crucial importance as the interaction between the electrons and insulator could create charged spaces which is in any case good.

A picture of one of the first and best resolved SEM image can be found figure 4.1. The scale of the picture is too large to see any graphene flakes. Howerver, one can assume the black circular shaped structure to be a nucleus of graphite. Moreover, one can see the edge of the drop.The only thing qualitatively consistent with what I found in [11, 20, 21] was this fractal like flower that one can see near the edge of the drop. A closer zoom on this structure is shown

in figure 4.2. These flowers seem to be constituted of several flakes. The scale of these flakes is consistent with the size of the graphene flakes imaged in [14]. A sample, on a Si substrate dried in an oven, was also tested but nothing was seen this time. However, investigating the fractals appeared worth following up.

Suspecting these flowers to be consituted by an assembly of graphene flakes, I discussed my results with Adeleh Gerami, my supervirsor's PhD student. We contacted one of her friends, Sedighe Salimian, who works on graphene in the University of Siegen in Germany. I asked her if these fractals could be surfactant residues. In her opinion they are not. She also gave me interesting advice to improve my experimental protocole and she diverted me towards an article dealing with fractal growth of graphene produced using the CVD method. In parallel, I had already started a bibliographical research concerning fractal growth of graphene and seen the paper she recommended [see 4]. But CVD is quite diffrent to shear exfoliation, so the explanation had to be found in other articles. In the end, I found 2 articles [12, 16] reporting the growth of qualitatively similar fractal structures when a monomolecular layer of water is trapped between a substrate and a graphene sheet. This effect has been proved to be reversible and strongly dependent on the ambient humidity rate. The lower the humidity rate the more developed the fractals are. Indeed, lowering the humidity rate creates depletions in the water adlayer as molecules are then able to flow on the edge of the graphene sheets, graphene is known to be impermeable to gaz. The graphene layer on top of the water molecules is so thin that is can follow these depletions resulting in the contrast pattern seen with the SEM. This explanation would be consistent with the fact that :

- We are working in aqueous solution.
- The samples have to be stored under vaccum for at least half a day resulting in a low humidity rate and potentially fully develloped fractals.
- The SEM is carried out under vaccum.
- This phenomenon was seen for both mono and few-layer graphene nanosheets.

The best way to test this hypothesis would be try to image the samples under different humidity conditions. Unfortunately, the way the SEM was used does not allowed that. Another possible way, to support this hypothesis, would be to measure the apparent height of these fractals hoping that it can be relied to the size of water molecules. Joao had no idea how to do that and the person in charge of SEM was unfortunately not available.

Using the references, presented in [16], I found that fractal patterns are typical of 2D diffusion-limited aggregation processes. Our solution can be seen as a colloid, a substance in which microscopically dispersed insoluble particles are suspended throughout another substance. When particles in a colloid reaggregate they act as random walkers resulting in a fractal crystalisation presenting a fractal dimension of 1.7 [see 15]. Thus, fractal patterns could arise from either reversible dewetting or direct graphene flakes reaggregation. An attempt to calculate the fractal dimension of the flowers was made using the software *Fractalyse*[1]. However, this software only works with black and white images. The conversio from grayscale images to black and white images decreased the resolution so much that nothing relevant could be done with them. The fractal flowers were also seen in an another aluminium deposited sample,dried under vacuum and not in an oven. They were seen on Si subtrate samples dried under vacuum. At this point of the analysis, both hypotheses are still valid. However, the second being simpler one could possibly rely upon this one.

[1]More details on http://www.fractalyse.org/

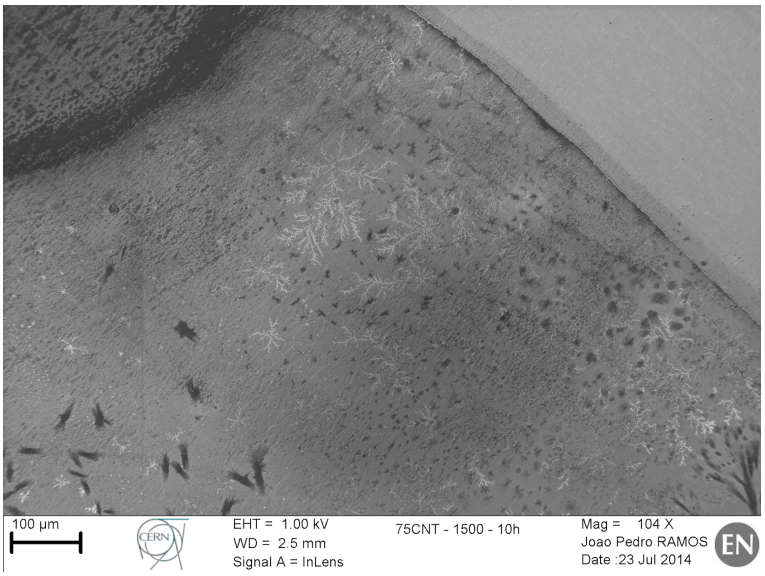

Figure 4.1: SEM image of a sample, deposited on an aluminium substrate and dried in an oven, presenting an overview of the droplet.

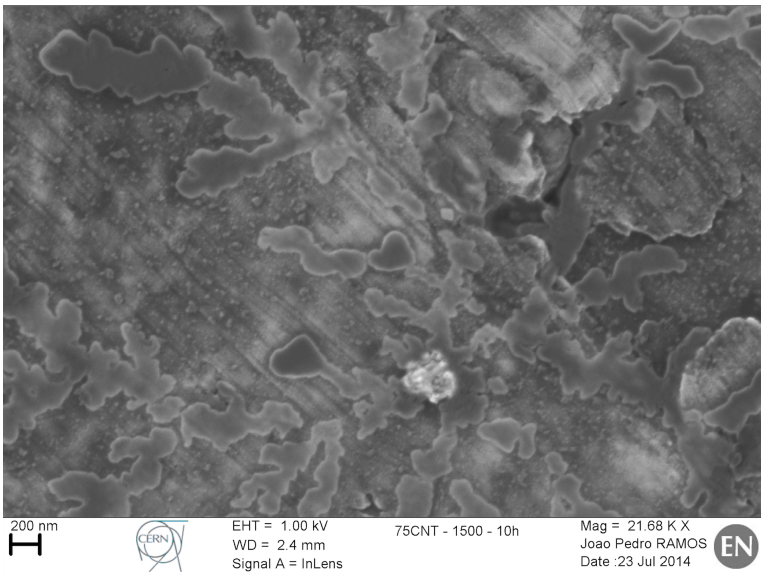

Figure 4.2: Zoom on the center of one of the flower like structure.

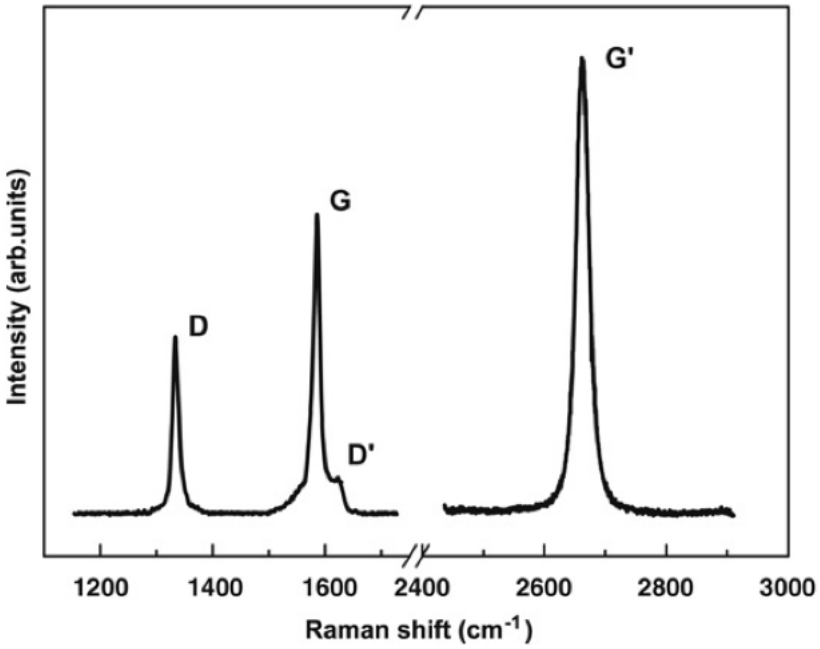

Figure 4.3: A typical Raman spectrum of the edge of a mono-layer graphene (laser energy 2.41 eV). Taken from : [8]

4.2 Raman spectroscopy

We saw the limitation of scanning electron microscopy in the previous section. The best way to characterise graphene samples is the Raman spectrocopy technique.The latter is based on the inelastic interaction between a monochromatic light and the vibrations modes, phonons, of a material. This interaction results in a small shift, up or down, in the laser frequency. Thus, after removing the main contribution of the excitation laser one can obtain series of peaks typical of the material probed. A typical raman spectrum can be found in figure 4.3 on page 17. The most prominent features in the spectrum are the so-called G-band and G'-band. The D and D'-band arise from a disorder in the sample or if we probe the edge of a graphene flake. The processes from which the peaks arise being non linear, the position of peaks are dependant on the laser excitation energy. A very comprehensive paper concerning raman spectrocopy of graphene,and graphene based material, can be found in [8]. The reading of this article required some knowledge in group theory [see 7, 17] In the latter, one can find more details about the origin of the different peaks. In this paper, the effect of the number of graphene layers in the shape of the spectrum is also detailed. Indeed, the more graphene layers the samples have the broader the G'-band is. Thus we can summarize why Raman spectroscopy is the ultimate and inevitable method used to characterise graphene samples.

- It provides a chemical identification : it can make a difference between graphene from graphene oxide for example.
- The study of the D-band gives information about the possible structural defects.
- The study of the G'-band can give information about the thickness of the flakes.
- The raman D/G intensity ratio is proportional to the inverse of the flakes length.

Unfortunately, a Raman spectrometer is not available at CERN. Thanks to Adeleh Gerami and her contacts in the University of Geneva I contacted the Pr Hans-Rudolf Hagemann from the physical chemistry department. He agreed to let me use their raman spectrometer. He was not available in August, so he told me to contact one of his post doctoral student Dr. Jakob Bierwagen. After a short preparatory meeting with me and my supervisor we realised that their spectrometer could not reach the wavenumber regime needed to see the G'-band which is of great importance in the analysis. The good point was that their laser excitation energy is the same as that used in [13]. When I went to the University of Geneva we tried to acquire a spectrum thinking that the lower part of the spectrum would,at least, give clearer information than the SEM images. It took Dr Bierwagen and me a whole morning to set the spectrometer without success. In the end, we could not even reproduce the spectrum of a well known reference sample. We tried to image my sample and of course nothing interesting was seen. The Raman spectrometer being a custom built set up we decided to wait for Pr Hageman return in the last week of August. However, it turned out that neither Pr. Hageman nor Dr. Bierwagen were actually available this week. Dr. Bierwagen sent me an e-mail saying that other Raman set ups might be available in other departments but it was already too late to organise myself with them as my stay at CERN ended on the 29^{th} of August. Unfortunately, this attempt brought us no interesting information on our samples.

4.3 Optical characterisation

After the failure encountered with the Raman spectroscopy, I finally decided to buy glass slides, in a local glass manufacture, to try direct optical microscopy. Indeed though it is one atom thick graphene absorbs 2.3 % of white light [see 9]. My supervisor told me that Dr. Jens Roder, from ISOLDE SSP group, has a hobby in UV microscopy and has his own personal set up at his home. As a last chance attempt to characterise my samples, I asked him if he could try to see anything. He agreed and I dried 100 µL droplets of graphene solution on glass slides. I also prepared glass slides on which I only dropcasted a solution containing water and surfactant in the right proportion. Some fractal flowers where seen under UV light. However none of them were seen in the samples containing only water and surfactant. This is an important result : the fractal flowers took their origin in the graphene flakes or the microscopically small graphite chunks still present in the solution after the centrifugation. Figure 4.4 shows an example of a well-developed flower seen by the reflection of UV light. The experiment was carried out at ambient conditions in a house in a mountain region. No humidity rate measurement was made during the experiment. However, the geographical location and this year's particularly wet summer in the Geneva area is not in favor of the reversible dewetting mechanism.

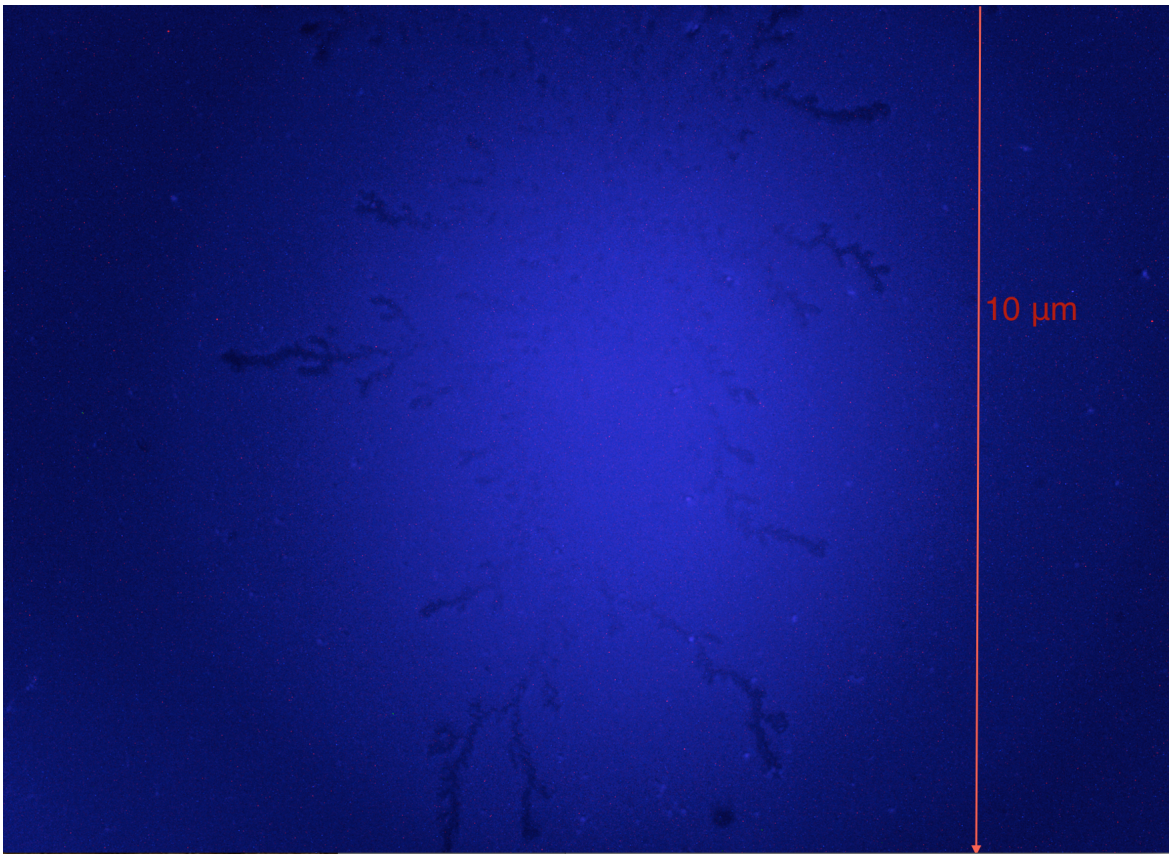

Figure 4.4: Fractal flower imaged under uv light : wavelength 405 nm, scale 23470000 pix/m

Chapter 5

Conclusion

To conclude, understanding the details and performing the shear exfoliation of graphite in liquids was not the hardest part of this internship. It tooked time to finally be fully operational as the blender and the graphite powder had to be obtain from external companies. Locating things in the storage room also took some time. The trickiest part was actually the characterisation of the samples. Indeed, due to the lack of suitable characterisation devices I couldn't come to an absolute answer. The SEM characterisation highlighted a curious and spectacular fractal shaped structure. The optical microscopy enables us to be certainly sure that those flowers come from the graphite like compounds dispersed in the solution : microscopical graphite chunks or few-layer graphene. Raman spectroscopy would be the ultimate way to entirely characterise our samples allowing to identify the chemical nature, the size, the thickness and even the presence of defects. Unfortunately, the attempt at Raman spectroscopy was a complete failure. The first step of my project is indeed not fully achieved. And I regret it. The next step would have been trying to carry radioistope experiment on the graphene flakes and see how it goes.

From personal point of view, I must say that despite all the disappointments encountered I don't regret my stay at CERN. I will enrole in the NPAC master programme in September because I aim at doing research in nuclear physics. Thus, I was really looking forward to see how the disproportionate size of CERN would make me feel. The summer student programme was an amazing opportunity to discover how it is like to work and, more importantly, to live at CERN. I didn't feel overwhelmed at all. It is true that there are lot of people working at CERN but I didn't feel there presence at all. On the contrary, most of the time I ended up working and talking with a restricted amount of people. It was also interesting to experience the social life that one can have at CERN. The large variety of clubs available is very pleasant and provides an interesting way to relax after work. I was really glad to work at ISOLDE which is CERN's nuclear physics facility. People there seem really nice person to work with. However, given all the technical problems that ISOLDE encountered during this summer and the delay that they induced I would probably think twice if I had to spent part of of my phd here. This of course has to be put in perspective as the facilty was only restarting after a long shutdown. During this internship I really experienced disappointment and discouragement with everything that happened concerning the PL lab and the failure of the characterisation attempts. This was an unpleasant yet important experience as it really showed me the reality of experimental physics. As far as physics is concerned, I learned a lot about graphene and the different methods used in solid state physics to characterise a sample. However, I regret that my intial project had to be cancelled as it would have brought much more useful knowledge for my future carrier in experimental nuclear physics, if nothing goes wrong. Initially I was really hoping to do experimental nuclear physics and not solid state physics but the summer student selection mechanism decided otherwise. I had the time to learn how to use

LaTeXwhich was really helpful in the writing of this report.

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