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**Doctoral School of Engineering and Applications
of Lasers and Accelerators**

**Ph.D. THESIS
Summary**

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**Graphene species
for particle acceleration experiments
with the PW class laser**

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Foreword

The development of high-power, ultrashort-pulse lasers, based on ideas introduced by Donna Strickland and Gérard Mourou in the 1980s (Nobel Prize in Physics, 2018), used a technique of chirped pulse amplification (chirped pulse amplification), which opened up new applications arising from the interaction of lasers with matter. The process leads to intensities of around 10^{21} W/cm², creating a previously unexplored field of research called "high field physics".

This new way of exploiting the laser has been put into practice as a breakthrough working technology in the ELI-NP project at IFIN-HH, by building a facility that ensures laser operation in the PW class (10-15 PW, already achieved in commissioning and calibration experiments).

The current work was carried out in the internal effort of ELI-NP to identify materials with which the newly created laser could interact to achieve large-scale applications, currently in the prediction phase. In the obligatory context formed by PW power lasers that have not been widely used, applications in form of creative ideas and trials, without a well-defined practical purpose yet, and in usual laboratory conditions used to realise materials useful to laser-material interaction, could be considered. The framework of this thesis has been confined to the conditions thus specified. We are therefore dealing with a problem of optimum, namely the practical realisation and characterisation of expressly requested materials (in particular graphene), to be subjected to an interaction with the *fs* pulse PW laser - unknown in practice for its effects -, in order to obtain an imagined spectrum of applications, which certainly excludes microelectronics (in the sense of obtaining graphene of exceptional quality), but includes revolutionary medical treatments, apart from which all other possible uses are not irrevocably set.

In the general approach, an optimisation problem means that we maximise/minimise a real function by choosing in a systematically way the input values from an allowed crowd, followed by computing that function. Accordingly, there as a must for identifying the niche of graphene-based materials that are as reproducible as possible, with low production costs for sufficient quantities - since the interaction with the laser is destructive -, allowing reasonable lead times, presenting controlled qualitative parameters (size, surface, defects) as much as necessary for the applications so far imagined.

The results of this thesis and related efforts must be continued by improving the reproducibility of the material, computational simulation of possible effects, in order to design possible applications related to the technology of the future, awaiting contributions to the extent.

Introduction

Being part of IFIN HH's ELI-NP project is an unparalleled challenge in any young person's professional life. All the more so when you are part of a team made up of leading scientific and technological personalities, professionals of renown, and you find yourself as a physics graduate facing the learning stage called PhD. In such an innovative context, the choice of topic may not be an insurmountable problem, but the consistent pursuit of its achievement becomes the real test. For even mentors cannot imagine the multiple and yet invisible possibilities of exploiting such a grandiose investment.

And then, as a recent graduate, you find yourself faced with an entire activity that is subject to optimisation, because it is necessary to simultaneously learn things that perhaps even those more experienced than you do not master perfectly, but also to be useful to group efforts that often pursue entirely futuristic goals.

The problems of optimisation, of maximum and minimum, though ancient, have succeeded by their evolution in always being contemporary with every age. As "real function" optimisation is done by a systematic choice of values from an allowed manifold, followed by the computation of that function, it is important to set the explicit context that limits the required choices.

In this situation, defined by constraints, the optimum is sought, i.e. the best solution among the feasible ones, the one that satisfies the expected goals, bounded by the circumstances, since it is widely accepted that "the goal also sets the limits". The circumstances within which the work was confined come from the following considerations:

1. The experiments are realized at ELI-NP PW - class laser, using the in-house technical and technological conditions, designed just for it.

2. The 10 PW laser and femtosecond pulse is a world technological novelty, the expected effects are in a class never seen before, so prior experiences of laser-matter interaction are not decisive but informative. Thus, the materials subject to impact with radiation must take into account the entire theoretical background previously available, which is why the work requires an excursion into the knowledge of laser-matter interaction, of the appearance and behaviour of plasmas created as result of that interaction, with all the cornucopia of formulas and theoretical explanations. The notes appended to the paper are precisely part of the effort to give a thorough knowledge, without wandering into digressions far from the subject.

3. The material to be impacted by radiation will be graphene-based. This is an apriori, imposed requirement, and in this sense the research has been conducted. But graphene is also an exceptional chemical species, with its formidable mechanical-thermal-electrical properties. On the other hand it is a material that has so far not yielded anywhere near the formidable applications claimed to develop on its unique miraculous properties. This gives rise to a more subtle question, epistemologically similar in some ways to a thorny issue of the past, which has been "successfully" taken up again today: fundamental research is not goal-oriented. Otherwise, as Costin D. Nenițescu

said, we would be dealing with an enormous mistake, because “alchemy has represented exactly those attempts that have consumed the minds and energies of many valuable people for hundreds of years, with no practical effects”. Just as alchemy is the most eloquent example of the ineffectiveness of fundamental research directed towards a practical goal, but lacking a theoretical foundation, so the mere production of sophisticated materials, without a specified goal, can be considered a failure, if it is not accompanied by a minimal theoretical attempt to clarify the many debatable questions.

4. Another major constraint comes from the fact that the imagined experiments lead to the destruction of the materials produced, therefore it is a must of having low production costs, reasonably short lead time, and production in sufficient quantities for industrial-style experiments under normal laboratory conditions.

It is precisely the lack of scalability of all processes for obtaining graphene-based materials that is the current adversary of the above desires. The golden rule of technology is that an exponential increase in size must have in equivalent a merely polynomial increase in complexity. The production of graphene, even on a small scale, contradicts the rule, which shows us that no real industrial technology for it is yet known, the attempts being, in fact, more or less searches.

5. Finally, the lack of well-defined applications is a major constraint. And applied research "in general" is a meaningless concept. The mistake can be corrected, but the nonsense cannot. In the absence of identified application, of properly defined need, development is doubtful, and can only go so far as to detach speculation from experiment. For example, the "transistor phenomenon", perhaps one of the greatest discoveries of the 20th century, understood in Bell laboratories (1947), had its first practical use coming from the requirement of a small hearing aid company (Sonotone 1010) in 1952. And it was only from that humble moment, for a requirement obviously derisory in relation to the enormous potential application, that the commercial transistor (TR-1) appeared on the market, at the peppery price equivalent today of 700\$. Without that minimal but clear requirement, everything would have remained in a perpetual search, suggesting, as usual in such situations "that there is huge potential!".

Thus presenting the initial conditions, namely the circumstances outlined above, the request is driven to the optimisation problem, due to multitude of variables, difficulty of quantifying them, lack of parameterising the function that maximised/minimised for approach the optimum, all of these urgently demanded that there be significant choices, justified by the above arguments, the related literature and the various laboratory experiments. The analyses of optimality, under the given conditions, directed the work towards the realisation of graphitic materials by graphite intercalation and subsequent chemical, liquid-phase, followed by appropriate XPS, SEM/EDS, AFM characterisations and related theoretical explanations, in order to find the repeatable procedure for obtaining the desired material, of reasonable quality, of acceptable cost and in sufficient quantities for possible PW laser experiments. On this basis, further refinements, computational simulations and the concrete impact of laser radiation on the materials produced,

could lead to identification of repeatable, quantifiable, homogeneous effects, whereby the imagination of practical applications can move from the realm of desire to that of necessity. The conditionalities listed above are all simultaneous challenges, so we devote a chapter of this thesis to each of them. Therefore:

- **Chapter 1** deals with the identification of the defining parameters of the imposed research site, ELI-NP, using for this purpose including some notable intellectual stimuli found in the "White Paper on Nuclear Physics at ELI-NP, IFIN-HH". An imaginary interview on the subject allows to bring to light some clarifying aspects in a manner less usual to the dogmatic setup of a usual PhD paper.

- **Chapter 2** deals with the physics of laser-matter radiation interaction, in line with the second challenge listed, since without an understanding of physical phenomena at the minimum scientific level, experiments with a laser of unparalleled power have no chance of a technological orientation.

- In the same vein, **Chapter 3** is devoted to carbonaceous materials, with a focus on graphene and the various processes for obtaining the materials required by the theme. The overview is absolutely necessary to solve the problem of optimality, as we consider the undertaking in this thesis to be.

- **Chapter 4** actually presents the most important results from the many experiments carried out, precisely to address that confinement with explicit requirements. The results of the experiments and related characterisations are accompanied by some theoretical considerations that seek to give more substance to possible future developments.

- Finally, the last challenge, the lack of well-defined applications, is addressed in **Chapter 5**, by conclusions and further developments, which outline a procedure to be followed, so that the materials produced can be of use to practical projects in the fields considered.

In order to keep the text flowing and to focus as accurately as possible on the topic, a rich **Notes section** has been prepared, in which calculations that may sometimes seem excessive have been detailed, out of desire to make available all the steps of a reasoning, which is rare in works and which we hope will be understood as a proof of authenticity. A **Glossary of terms** completes the work, so as not to leave uncovered the use of notions particular to the subject, which may not be familiar to readers.

Chapter 1

This chapter deals with the identification of the defining parameters of the imposed research site, ELI-NP, using for this purpose including some notable intellectual stimuli found in the "White Paper on Nuclear Physics at ELI-NP, IFIN-HH". An imaginary interview on the subject allows to bring to light some clarifying aspects in a manner less usual to the dogmatic setup of a usual PhD paper.

A significant guiding reference for our topic is the official statement recently made by U.S. Department of Energy's Office of High Energy Physics, which states that, "while much research is being conducted in the area of medium-high power lasers for industrial or military applications, the unique, one-of-a-kind requirements imposed by scientific drivers for lasers that are needed are leading toward a resource management program targeting areas of ultrafast laser research and development."

The realisation of high-power lasers is being rigorously pursued in Europe, which has developed a multinational project called Extreme Light Infrastructure (ELI), currently consisting of ELI-ALPS (Attosecond Light Pulse Source, in Hungary), focused on ultra-short pulses (attoseconds) to explore dynamic interactions in chemistry, materials science and biology, ELI-NP (Nuclear Physics, in Romania), focused on the generation of ultra-bright γ -ray sources, to explore the interaction of electromagnetic radiation with atomic nuclei, ELI-BL (Beamlines, in the Czech Republic), organised for the generation of high harmonic, high repetition rate laser systems of 1-10 TW to obtain very high quality electron beams to drive free electron lasers (FELs), as well as for high energy X-ray and γ -ray sources using PW-class lasers to generate ion beams for medical applications. Furthermore, new phenomena are being explored, by understanding the structure of vacuum, using power densities above 10^{23} W/cm². This news source highlights the expectation that "lasers are becoming essential for modern high-performance accelerators," and further, "on this assumption rests the hope that future generations of accelerators will use lasers as a power source, allowing science to reach new horizons in the orders of magnitude of phenomena, towards the attosecond, angstrom and teravolt regions."

Lasers already have a long history of use as "accelerators' parts", advanced light sources (pump-probe beam generation experiments), as particle sources by photoemission or photoionisation, and in femtosecond level manoeuvres and beam diagnostics. However, accelerator applications have needs that are crucial and completely different, and telecommunications lasers, defence and security applications are also generally out of step with new ideas in the field.

Future accelerator applications therefore need to accomplish several characteristics as:

- high peak power (much energy in very short pulse);
- high average power (many pulses/second);
- high electrical efficiency ("wall-plug")

"High peak power enables ultra-high field research, increasing fundamental understanding of light-matter interactions, opening new directions for particle acceleration. High average power is essential to achieve high average brightness and high luminosity light sources in particle-beam

collisions. And high wall-plug efficiency is essential for cost-effective operation of lasers and the facilities that support them". In all cases, beam quality, adjustability, stability and reliability are of paramount importance. Primary development tasks for accelerator laser technology were also identified as:

1. finding a set of key applications of laser technology related to accelerator operation and important for the scientific opportunities it could create;
2. assessing the laser needed enabling the applications;
3. identify technical gaps between current capabilities plus performance necessary to laser technology applications.

Identifying key applications needs the laser technologies development that can be divided into two categories. One is the development of systems with important repetition rates and huge average power needed for chemistry, physics, biology and medicine, others being the development of high intensity laser sources, for new physical phenomena discovery, giving access to physical regimes exploration, not accessible by other means. Today, using high-energy and very short-pulse lasers is becoming routine, capable of achieving focused intensities, leading to relativistic regimes having the electron in the laser field vibrational velocity reaching the speed of light. Such lasers are driving new fields of science such as:

- "- electrons, protons and ions acceleration by laser excited electric fields;
- generating coherent light in the extreme UV, X-ray and γ -ray fields;
- exploring vacuum structure through radiation reaction forces and high-intensity particle-photon interactions;
- nuclear reactions producing."

One of the most encouraging applications is linked to the 'medical accelerator' (proton/ion beams) that can improve the existing treatment of cancerous tumours by radiation. Compared to X-rays and γ -rays, ion energy is stocked at narrower depth, towards their penetration end. And as a consequence the damage to surrounding tissues can be minimised. Usually, proton/ion treatment is done in specialised centres, as facilities based on cyclotrons or synchrotrons require mechanical constructions with large components, magnets and radiation shields. Laser-based accelerators would allow a more compact treatment, as the actual ion source can even be rotated around the patient. The current laser-based proton sources are about an order of magnitude below the particle energy required for therapy, and even have a large energy "spread", requiring collimating and energy-selective magnets to seize of the Bragg tip's treatment accuracy and ability to protect healthy tissue. And these lasers do not yet exhibit the necessary reliability and control either. In recent years the radiation pressure acceleration (RPA) mechanism becomes more confident on its the ability to create narrow energy spread including much more efficient proton energy scaling using laser energy than previously. Although theoretical models are still disputed, the acceleration mechanism is sufficiently well understood to allow an estimate of laser requirements. Scaling the existing PW lasers towards the required repetition rates is the biggest challenge at present, probably.

Particle accelerators typically generate beams of electrons or positive particle ions having closely the speed of light, consequently with high kinetic energy. The charge of isolated particles

allows them to be accelerated in electric fields. In accelerators of conventional use, the electric fields are confined in cavities, the name for hollow metal structures. The only way to increase the maximum particle energy is by building a longer accelerator. The result is the Large Hadron Collider (LHC), used for fundamental physics research at CERN, near Geneva, which is 27 km in circumference and cost several billion euros.

High-power laser systems of nowadays can generate tens of femtoseconds laser pulses. Such pulses can reach a power of tens to thousands of terawatts. To accelerate the laser plasma, the pulses are focused into a spot a few micrometers in size, comparable to the size of a bacterium. Concentrating on a small area such a high power creates the very high required intensity. (C1_1)

The aim of the PhD thesis is the investigation, in particular, of possible future experiments with graphene as an impact material. A tangible goal of our experiments is directed towards laser interaction with carbon ion plasma, very useful in particle therapy of hard-to-reach tumours.

Chapter 2

Dealing with the complex phenomena of interaction between coherent laser light and possible laser targets can only be done by numerical analysis methods, which implies the use of computer-programmable algorithms ("codes"), which make the best use of the available hardware computational resource through the most intelligent, refined method of composing the working instructions (software) given by the programmer to the computer.

Since the beginning of the computer's existence, a clear distinction has been made between the hardware part, i.e. electronic devices (transistors, integrated circuits, microprocessors) and the software part, i.e. the necessary instructions given to these electronic devices in order to carry out particular computing sequences, just as in elementary school we learned that operations in parentheses must be done before others or that multiplication must be done before addition, so the algorithm sets priorities.

To clarify the relationship between hard and soft, which will be useful in arguing for the need to know the theory before its technological handling, let us take up von Neumann's observation to Schrödinger's question, "what is life?", namely that metabolism and replication in the biological world, however great the entanglement (*fr intriqué*) between their connections, are logically separable. Therefore it is logically possible to postulate organisms composed only of hardware, capable of metabolism but incapable of replication. Also it is possible to postulate organisms made up of pure software, capable of replication but incapable of metabolism. And if functions of life are separated in this way, it is to be expected that the latter type of organism will become the obligate parasite of the former. Organisms that specialise in replication tend to be parasites, but hosts must exist before parasites. Host survival is a prerequisite for parasite survival. Someone has to feed and grow to provide a home for those that only reproduce. "In the world of microbiology, as in the world of human society and economics, we cannot all be parasites."

This observation applies entirely to the relationship between computer hardware and software, but, more importantly for our approach, also between the theoretical basis (hardware) and the technical/technological solutions that flow from it (software). Just as computer programming contains the analysis of the problem as hard, and its translation into a conventional language applicable to the computer (e.g. 32-bit, 64-bit, etc.) as software, the whole excursion here is to argue that, without a theoretical understanding, explaining the technological modalities remains a matter for the technician of the trade, no matter how skilled he or she may be. Therefore, this more "academic" chapter will be organised as follows.

In a first section the most important characteristics of the plasma are given, as the interaction of ultra-short, high-intensity laser pulse leads to immediate formation of plasma, whatever the target subjected to its bombardment. Even if some of the facts may seem arcane to specialists, their systematic and detailed organisation is not without its uses. As the late Professor Emeritus Octavian Stănăşilă used to say, "those who know something are not afraid to be trivial". If only for the fact that it offers the possibility of corrective replies to the speakers, thus contributing to the overall understanding of physical phenomena.

Immediately we turn to the collective effects of plasma electrons, including their acceleration, to reach the acceleration of protons in solid targets, the experimental concern we are involved in at ELI-NP. Thus, the TNSA and RPA mechanisms are properly detailed, with the whole court of physical effects due to the relativistic interaction of the laser with the plasma, at the level of intensities obtained by the PW laser at ELI-NP.

In the situation of our work, we work with an ultra-short pulse laser, i.e. its duration is shorter than the longest relaxation time of the electron-to-grid energy transfer, as well as shorter with respect to heat conduction and hydrodynamic expansion (basically, $t_{puls} \approx 100 fs$). To have such an ultra-short laser-matter interaction, the pulse must have significant contrast ($\sim 10^9$) between its average intensity and that of the pre-pulse, so that there is virtually no pre-pulse or post-pulse in the time domain to produce phase changes that would affect those produced by the main pulse. Apart from the explicitly specified cases, where the pulse intensity in the focal spot could have a Gaussian distribution, the laser intensity is considered constant throughout the focal spot space (hence a rectangular, flat-top-hat distribution). To describe the interaction a set of parameters will be needed including wavelength, pulse energy and duration, spot diameter, assuming the focal spot as a circle. The concepts used are detailed in the Glossary. Also there are the characteristics of the laser beam.

We will mainly consider the interaction in strongly absorbing media, where the laser energy is absorbed in a thin layer of about tens of nm, much smaller than the focal spot diameter, so the 1D approximations we make will be valid in most of the cases considered. Since the laser pulse is considered shorter even than the expansion time, the laser-interacting material in the epidermal layer remains intact during the interaction and still long after the end of the pulse, even if the energy density exceeds that required for ablation. Thus, even the materials most strongly perturbed by the interaction remain to have a density close to the initial one (so that hydrodynamic motion can be ignored). However, at high intensities, material and optical properties change rapidly in the early phases of the pulse. In the following we will consider a self-sustained interaction, i.e. the two effects, the laser electric field on matter and matter on electric field, are considered to be simultaneous. Consequently, the coupled equations of the time-dependent field and matter describe all material transformations.

We start by identifying the physical phenomena that we need to explain when we encounter the ultrashort laser pulse, having intensity greater than $10^{18} W/cm^2$ to be sure of the existence of ionisation, with solid density targets. We know that, before the actual laser pulse, a so-called pre-pulse is transmitted, a non-collision manifestation of the laser, whose low intensity pedestal, together with the attack front of the actual pulse due to spontaneous amplified emission (ASE), leads to the formation of a pre-plasma. It follows that the main pulse encounters a pre-heated and strongly ionised plasma at the front of the target, in which the electrons will be accelerated to speeds approaching light speed by laser light field, causing the relativistic effects dominate their motion.

Large part of laser pulse energy is thus converted into relativistic electrons kinetic energy, these electrons being expelled from pulse focal zone because they are acted upon by the laser's

ponderomotive force, thus leaving behind them a space of positive ions charge near target's front surface. These electrons, which have acquired kinetic energies of several MeV, can propagate through the material of the entire target. Upon reaching the rear of the target, the electrons exit the target, thus generating a strong space charge separation field at the rear face. So there are two charge separations produced by energetic interaction of laser pulse with the target, at front and at back of the target. Both fields, born in the respective charge separation areas, vary on a time scale much longer than laser period dominating in this way electronic motion. It is precisely quasi-static fields that have the ability to accelerate ions to kinetic energies of MeV, despite their comparatively enormous mass compared to electrons.

It is now obvious that ion acceleration mechanisms understanding at two sides of the target requires knowledge of how the laser pulse interacts with laser plasma.

Chapter 3

We know of biological organisms that live only on Earth, a planet made of rocks, where the physical conditions allow molecules to exist organised in long chains, molecules made of individual atoms held together by Coulomb forces. With individual atoms close enough, bonding occurs, meaning that valence electrons of each atom can interact with potential hole of closest nucleus, this potential being energy comparable to the potential pit of its own atomic nucleus. The covalent bond means that valence electrons of two atoms simultaneously fill their valence bands in the bond. Consequently, binding energy of a biatomic molecular bond is comparable to the binding energy of the atom's valence electrons. For all known biological organisms, covalent carbon-carbon molecular bond forms the basis, having about 4 eV binding energy. In the same time individual atom bonded to its neighbour is also bonded to others, when larger molecular structures exist, using much less energy. E.g., in graphite, adjacent planes of carbon atoms are bonded by potential of about 0.05 eV/carbon atom.

Consequently, structures of large molecules can only remain structurally stable as state when low temperatures and pressures. The existence of life provide that Earth's surface, with average temperature of ≈ 300 K and average pressure of 0.1 MPa, is ideal for large and stable structures. We imagine matter that encounters us as neutral atoms are arranged in various stretched structures. Most of Universe visible matter is found at much higher temperatures and pressures. At those high temperatures or pressures, the large molecular structures needed by biology cannot exist. But there are also states of matter which, due to our poor experience, we consider 'exotic', such as plasma, which is in fact the ubiquitous material of the Universe.

We therefore call "**extreme conditions**", what is not in our existential habit, of course a mere extension of the arrogance specific to man, in fact humanity, Earth's biology, being the only extreme conditions of a cold and dark Universe.

Over the last half century humans have been able to create the physical conditions for high temperatures and pressures. Invention and development of nuclear weapons supported research of matter under extreme conditions. Much of research remained hidden for a long period of time. But later, parallel research conducted to major increase in finding out properties and behaviour of materials under extreme environmental conditions, and a new class of research in the natural sciences was needed.

Nowadays, the extreme conditions include beside high temperature and high pressure, high-radiation environments, large thermal loads, aggressive chemical environments and high electric and magnetic fields. Development of advanced technology such as high-power laser, nuclear reactors, aerospace applications require a better understanding of materials behaviour in extreme environments.

One important approach was to prototype and build different types of instruments, devices, which can focus energy in a controlled form that permits matter experimental investigation under extreme conditions. These include high-power lasers, particle accelerators etc. In parallel, diagnostic instruments have been developed that can measure physical processes in very short times and under hostile temperature/pressure conditions. Experimental investigations opened a new

horizon on physical processes different from ordinary experience, and much theoretical work has been devoted to understanding them. More important has been the combination of many physical processes with large complexity, which create notable challenges in mathematical modelling. Parallel development of high speed and performance computers, together with numerical and computational techniques of codes simulating combination of complex physical processes showed up. The synergy between experiment, theory and computation has led to a major technological advance in new areas of physics. For using "extreme conditions" term, we must decide which matter energy density should be classified as such. The scientific community accepted convention that "high energy" means energy density $> 100 \text{ kJ cm}^{-3}$, corresponding to pressure = 1 Mbar. It seems arbitrary and excludes "hot dense matter", (= matter at pressures less than 1 Mbar), but is nevertheless in different state from matter at standard temperatures and pressures ($T = 300 \text{ K}$ and $P = 1 \text{ atm} = 1 \text{ bar} = 100 \text{ kPa}$, STP state). In STP, electrons are bound in atoms and possess negligible specific electron heat compared to atomic specific heat, $3N_A k_B$, ($N_A = \text{Avogadro's number}$). We therefore prefer the term "**extreme physics**" for physics of matter properties and behaviour at much higher temperatures and pressures than STP. In this physics regime, internal energies are higher than typical binding energies, so atoms have some of their electrons expelled, or they have been compressed together so closely, that states of electron occupancy are different from the ones of atoms in isolated form. In case of extreme environmental conditions, we treat electrons and unbound ions as separate fluids, sometimes at different temperatures, concluding that electron specific heat is no longer negligible.

Plasma state is typically matter under extreme conditions, despite the fact plasma charged particles may exist in ordered form and have characteristics of a solid. The matter properties and behaviour are defined by interactions between plasma electrons and ions. Matter in extreme conditions includes Universe visible matter, remote from the surfaces of rock-formed planets, as well as all matter created by concentrated energy devices such as high-power lasers.

This is why we have previously analysed laser interaction with matter and plasma creation in the ELI-NP experiments, as we are in the area of "extreme conditions", "physics of extremes", which probably also needs new materials to be better understood. Hence the appetite for graphene, the material so praised for its mechanical, electrical and thermal performance, but still without significant applications.

Chapter 4

The main objective of experimental research work was focused on the identification and development of a cost-effective method for the synthesis of graphene films using GIC, suitable for high power laser applications. What is essentially of interest in our research is the realisation of an optimal method, in which the graphene sheets are of acceptable quality (the applications are not microelectronics, so the use of CVD would be unreasonable), for high power laser applications. In this aim, the environmental conditions cannot be other than standard (no vacuum chamber work), the time to obtain must be acceptably long (i.e. rather short), and the surface area of the foil, as well as the quantity of foil, must be larger than what can be obtained by CVD, since the graphene material is to be subjected to completely destructive experiments, the technological events, by their configuration, being expensive. Since in future applications, as well as in our experiments, conductivity remains an important parameter, as electronic properties lead to spectrometric characterisations that consider binding energies, we will give more attention to that property in the following. Two different GIC compounds (H_2SO_4 – GIC and FeCl_3 -GIC) have been investigated for identification of most reliable method for the development of graphene films. In this aim, special attention was paid on the selection of graphite precursors, intercalants (H_2SO_4 and FeCl_3) and exfoliation process.

Chapter 5

We have explicitly pointed out that the present work aims to contribute to the identification and even design of an optimal method that assembles certain scientific and practical requirements for achieving controllable and predictable interaction of PW power and femtosecond pulse lasers with graphene based materials. We justified the approach by two different considerations, namely:

1. The thesis should explicitly use experiments on this laser, ELI-NP, and not lasers in general. The graphene materials used must be produced by large-scale industrial processes, because the experiments are all destructive, but mainly because revolutionary applications are sought, with great impact on today's world.

2. The experimental conditions in the ELI-NP laboratories allow interaction of a certain type of laser radiation with graphene sheets, with carbonaceous materials. Therefore, the existing setup should be used for experiments to be designed in the near future.

Apart from these requirements, general conditionalities, we have to deal with the present conditions of the research moment, namely the incompleteness of the evaluation of what a laser of such a configuration could do in real life, as well as the scarcity of solutions (if not the complete lack) in giving applicative value to (theoretically) exceptional materials, generically called graphene. The impossibility of precisely defining the applications envisaged also seems to stem from the hypnosis that the multiple graphene qualities provoke in the researcher, so sensational are they that they seem to be applicable to a plethora of concrete applications, but in fact, despite the short years since the explosion of interest in the material in question, worldwide successes are less than modest. For all these reasons, we are looking in our excursus for a middle way that neither ruins any possible revolutionary application by restricting the treatment of the material's properties, nor offers a real chance of practical achievements beyond the realm of speculation. The acute problem is to construct a useful program from what has been obtained, and at the same time to make it a blueprint for the future for obtaining the desired experiments under the right conditions. In this context, the need to understand as deeply as possible in both areas of the experiment, the emission of well-identified laser radiation, as well as the behaviour of a certain type of matter (graphene) for the benefit of applications in the process of being identified, becomes mandatory. This can be done by knowing better the general laser-matter area of interaction, as well as by a careful, rigorous research of the field of graphitic materials, including the performance of own experiments, those that allow to build confidence in relevant and professional observations in the literature. The above assertion justifies the insistence on what has been presented theoretically in Chapters 1, 2 and 3, but simultaneously outlines an agenda for the future. At its core, the paper promotes the justification of some general ideas that follow.

1. Useful applications require solving industrial challenges.

As we want to produce usable products, we must respect two fundamental principles of industrial technology:

- an exponential increase in size must be matched by a polynomial increase in complexity (material, process, etc.);

- in order to benefit from the (even exceptional) properties of a material/product, it must be correctly incorporated into a host device.

In the case of graphene made in the form of wafers with a large aspect ratio and a large surface area, no matter how good the quality, if these nanowafers are not correctly distributed in the final formulation under consideration, no significant benefit will be obtained. This general feature is propagated down to the general properties, which we present below according to their importance in the industrial applications under consideration.

Producing graphene of high quality by using procedures that are reliable, repeatable, environmentally friendly and inexpensive is a pre-condition for achieving the fascinating properties of this material in industry. Production methods have been described based on the use of non-covalently intercalated compounds in graphene, subjected to expansion conditions such as microwave shocks, followed by exfoliation, leading to few-layer graphene materials. We are able to obtain either aqueous graphene mixture, free powder, or suspension, whether we use a certain exfoliation step approach.

Surfactants can help disperse forming in this way inks of graphene. For scaling up to mass production, process parameters must be simple, efficient and cheap. However, the methods presented in the literature, including patent literature, are only good in the laboratory and are not applicable on an industrial scale. Scaling up to a large scale is hardly conceivable with complicated procedures, with reactions in many stages, especially as in some cases certain methods are dangerous in themselves, and may even cause explosions, requiring additional protective measures, which increase costs. But there are also many experimental chemistry issues, one particularly important one being the content of oxygen species (e.g. graphene oxide) in the intercalated compound.

2. Even ELI-NP will not use graphene devices produced in its own labs, nevertheless a real expertise of what is going on with those materials must be in the ELI-NP researcher's lot. Thus the experimental effort presented in the thesis is understandable.

As the PhD thesis is today part of a process of accentuated, niche learning, not a certification of the innovator's qualities of the maker, the maker is obliged to turn the work towards much theoretical part and analysis of the exorbitant literature, avoiding innovation and petty speculation in the margins of some articles, useful perhaps to the PhD student of industrial firm producing graphene-based devices. We are talking about our own experiments, carried out largely on inspiration from the available literature, hence the need to present in-extenso their theoretical basis.

From our study the following general observations emerge, which at the same time form the basis of a future program of continuation of the present research:

1. Laboratory methods cannot apply to mass production (for graphene materials) as they contain too many step reactions with complicated procedures.

2. The expansion coming out of exfoliation presents form of thermal instability, leading to changes in electronic and mechanical properties along the crystallographic axis c that are pretty significant. Usually the thermal instability occurs within a fluid heated from the bottom up, i.e. a horizontal layer of fluid has a hotter bottom than the top. And the ground state is at rest, with the

fluid slightly below the heavy one (obviously very similar to the treatment that microwave interlayer undergoes). Having a temperature difference across the layer large enough, we may overcome the stabilising viscosity effects as well as thermal conductivity by destabilising buoyancy, consequently reverse instability results as thermal convection form. The present convective instability might be different from free convection, that is the case of vertical plate that is hot, where hydrostatic equilibrium is impossible. In fact, a free convection flow base may itself be unstable. Dealing with unstable phenomena is a problem of exceptional difficulty. This is why theoretical and computational modelling is necessary, without which we remain at the level of heuristic explanations. This results in significant changes in electrical and mechanical properties along the crystallographic *c* direction, even if the phenomenon is used to advantage in some practical applications. In addition to the sample thickness instability, there is also the intercalant concentration instability. It was found that the exfoliation is reversible for dilute non-compounds. Anyway, in case of concentrated compounds, there might be large and violent expansion during exfoliation that are accompanied by considerable deformation becoming permanent, consequently on subsequent cooling the compound remained expanded. Thus, the reversibility of exfoliation depends on the concentration of the intercalant. The reversibility of dilute compounds allows many practical applications of the exfoliation phenomenon.

3. There is a need to explore more precise experiments that bring together the lessons learned about the treatment of precursors (natural graphite flakes, HOPG, GO), acceptor interactions, intercalation methods (chemical, electrochemical), expansion (microwave irradiation). The proposed improvements for each of the categories listed are presented below as a preliminary action programme.

4. It is also necessary to develop a platform for the analysis of different techniques using results, which can give a consistent characterisation of the properties of the intercalated and exfoliated material. The above synthesis of the conclusions of the work allows the validation of the actions to be taken leading to the identification of the optimal solution for the graphitic materials required for ELI-NP experiments, in the form of technological procedures for synthesis, analysis and characterization. Thus, in agreement with point 2 listed above, a more thorough theoretical approach is mandatory to adequately master at least some of the possible events occurring in the thermal instability established during GIC expansion. Point 4 shows us that the unification of experimental outcome analyses will be the main direction in determining which characterisation techniques we will address, in which order, with which parameters, so that data aggregation follows what is strictly necessary to qualify the experiments. The first point requires the refinement of laboratory procedures accompanied by computational analyses, so that a viable method can be developed in an industrial system that focuses on yields and costs.

As for the third point, we detail it below, precisely because the PhD thesis allows the identification of clarifying steps that should continue the present experiments. Before, it is worth of summarising the final conclusions of both experimental results.

So that, for identifying the optimal method of graphene film production according to the starting problem set-up, two GIC compounds have been thoroughly investigated: based on H₂SO₄

and FeCl₃. Three main processes have been studied accordingly: precursor, intercalant and exfoliation.

H₂SO₄-GIC experiment

1. Developing a cost-effective method used available materials with low environmental impact, fully suitable for high-volume production.
2. The chemical synthesis method starts with graphite containing more *sp*² hybridisation than (*sp*³+CH) and having a lower concentration of oxygen.
3. The exfoliation is prepared in one-step synthesis of graphite intercalated by H₂SO₄ (H₂SO₄ - GIC), with KMnO₄ as oxidising agent and H₂O₂ reactive species.
4. We found out there is a limit of carbon shift contributions above which chemical intercalation-exfoliation becomes difficult. Thus, the sample with *sp*²/*(sp*²+*sp*³+CH) of about 77% and with a lower concentration of oxygen in the sample (< 12%) provided an observed minimum quality for intercalation exfoliation to occur easily.
5. Then we improved the exfoliation process using ultrasonication in concentrated hydrogen peroxide (H₂O₂ 30%). The selected samples were optimised as exfoliation process parameters: sonication time, GIC solution concentration (by controlling the amount of hydrogen peroxide and ultrapure water), number of dilutions and successive sonication steps.
6. Thus we developed a predictable and reproducible way to perform exfoliation that is also in good control of the process (key element is the fast phase transition, achieved by exposing GIC to microwave radiation, energy being delivered directly to target via light-speed radiation, with more control treatment of exfoliation).
7. SEM microscopy confirms the morphology of the graphene sheets obtained after microwave treatment as almost transparent. AFM showed individual graphene sheets with 1.9 - 2.6 nm thicknesses between double/triple layers.

FeCl₃-GIC experiment

8. In this experiment, we have evaluated two industrially and chemically important parameters, specific surface area and expansion volume. In thermal method, increase in surface area and porosity is a reflection of expansion of gaseous quantities and the exfoliation of graphene sheets - the pressure generated by gaseous interlayers being the major driving force leading to rapid and explosive expansion. Different factors should be considered in microwave irradiation expansion.
9. Alternating changes in electric field produce rotations, vibrations and oscillations of the dipole moments, which in turn generate energy and heat, allowing a state of activation of the molecules in a very short time. It is from the combination of these effects that the explosive expansion of GICs under microwave irradiation results.
10. At intercalation step we could not find FeCl₃, even some of its elemental decomposition. Accordingly, we explain that exfoliation is based on the intercalation-expansion with the ions of *HSO*₄⁻ from the sulphuric acid used in the synthesis. We provide also a speculation about what may happen due to possible reversibility of not-complete exfoliation, that should be evaluated in further experiments.

11. If we continue along this chemical route, we must find a solvent (a) capable of dissolving "enough" anhydrous FeCl_3 , (b) being a weaker base than graphite surface, so that FeCl_3 can spontaneously move from the solvated complex onto the graphite surface, and (c) compatible with any strong oxidant we should use to generate charges on the graphite surface. Most probably we have to switch to gas phase, since liquid FeCl_3 has a very narrow range of stability at room temperature without using a pressurised system, and solid FeCl_3 is not of use in this case.

Despite the relevant outcome of both experiments, it is quite premature to choose one route against the other, since deeper clarifications are expected to be obtained after modelling the respective processes. Consequently, theoretical and practical program of continuation is provided in closing the present work. Accordingly, we retain important immediate subsequent steps. The process will be based on:

- the use of precursors as graphite flakes, HOPG and GO;
- the intercalate will be of the acceptor type: H_2SO_4 and FeCl_3 ;
- the synthesis methods will be based on chemical and electrochemical oxidations;
- the expansion of the synthesised GIC will be done using microwave radiation;

In this configuration, the subsequent actions aim at:

A. improved dispersion after exfoliation, its stability including dispersibility in solvents, achieving good dispersion and conductivity simultaneously by avoiding oxidation of the GIC basal plane. These require pre-treatment of the precursor, e.g. by functionalising the graphite edges prior to intercalation (edge-selectively oxidised graphite).

B. GIC enhancement by using heating temperature and GNS post-treatment;

C. Moving the oxygen-containing functional groups from GO by microwave irradiation in a hydrogen atmosphere;

D. Enhancement of the perfection of the exfoliation process by better alignment on the crystallographic axis c ;

E. A comparison of the electrochemical method addressed to the two mentioned interlayers to facilitate the decision making process of identifying the industrial method.

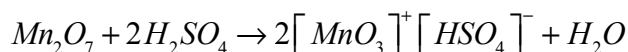
These directions are not simply future directions, but are presented here in sequence.

So, detailing the above

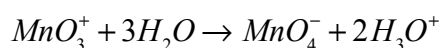
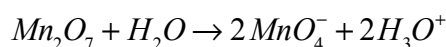
A. "Sealing" the edges of graphite to be free of oxygen in the basal plane (= defects) - oxidation at the edges before intercalation and (edge-selectively oxidised graphite = EOG). We will discuss below an idea helpful in making large quantities of graphene sheets. The physical exfoliation method stimulates production of large quantities of defect-free graphene in many situations. On the other hand, the solution using GO, highly dispersible carbon monolayer (2D) containing oxygen functional groups, improves the dispersibility of GO in solvents (due precisely to the oxygen functional groups), but in the same time leads to a decrease in rGO performance in basic applications. The edge-selectively oxidised graphene (EOG) method would be the way to improve stability of dispersion after exfoliation.

Obviously, carboxyl groups are mainly generated by GO on the edges, and hydroxyl groups and epoxide groups are mainly generated by the basal plane of the graphene oxide. Consequently, by introducing carboxyl groups at graphite edges and using resulting higher edge reactivity compared to basal plane, then stability of the dispersion could be improved without destroying the conjugation state. In a pioneering work it was shown that the Hummers method of obtaining graphene oxide can be divided into two sequential steps by using oxidation materials and liquid media in each step. Here's how:

Oxidation step I



Oxidation step II



Potassium permanganate (KMnO₄), introduced into sulphuric acid, is converted to manganese heptoxide (Mn₂O₇) and manganese trioxide ion (MnO₃⁺). These manganic oxides oxidise the whole graphite and produce GO during the first oxidation step. After the addition of water, the oxidants from the first oxidation step are removed and the permanganate ion (MnO₄⁻), which is the main oxidant of oxidation step II, is formed in an acidic aqueous environment. The identification of these distinct oxidation steps made it possible to verify that one could omit step I of Hummers method and apply only step II for a few hours on the raw graphite. The results suggest that the 2nd oxidation step isn't producing additional graphite oxide from raw graphite, since the not exposed inner graphite layer does not oxidise during this step. The phenomena thus occur due to the change of oxidant from dimagnesium heptaoxide (Mn₂O₇) to permanganate ion (MnO₄⁻) and the solvent medium from H₂SO₄ to H₃O⁺ and H₂O. Changing medium of oxidation to lower acidity and de-intercalating H₂SO₄ causes the occurrence of oxidation at graphite edges, which are more reactive than the basal plane. This observation permits a new strategy, omitting the first oxidation step, which favours the complete oxidation of the graphite (Hummers method) precisely to avoid inner part of the graphite oxidation. Experimental realisation of the Hummers method modified in this way involved isolating the influence of the second oxidation step in obtaining GO, for which the conditions of step I and of main oxidation, before water addition, were strictly controlled to be same over whole sample: two hours at 35^o C. The experimental variables only controlled were the duration of the oxidation time of step II and its temperature. When comparing the two oxidation steps (I and II) it was observed that the trend in GO damage was the same. On the other hand, structural change and exfoliation production showed different aspects in steps I and II. Therefore, it was concluded the two oxidation steps participate in the control of GO characteristics by different mechanisms. Based on these experimental results, it is suggested that two mechanisms exist during the 2nd oxidation step of the Hummers method: oxidative cleavage of C=C double bonds with

permanganate, producing carbonyl functional groups (ketone and carboxylate derivatives), and acid catalyzed hydrolysis of epoxides, producing hydroxyl groups. Permanganate ions dissociate C=C double bonds into C=O carbonyl groups via the cyclic manganese ester compound as an intermediate (although not technically separable) at very low pH, although they oxidise C=C into vicinal diols (= organic compound containing two hydroxyl groups) at moderate or high pH. This mechanism ensures carboxylic acids at GO sheets edges by cleaving C=C double bonds or enols. Oxidation condition of step II is highly acidic, often prolonged at high temperature, thus fulfilling very well the criteria for occurrence of oxidative cleavage mechanism.

EOG has a reduced ID/IG ratio (up to 0.33) on basal plane; ID/IG ratio (1.08) at edges, these wholly differing from FOG (full oxidized graphene) ~1.05, for the whole surface and ~0.05 at the raw graphite. Thus, by the presented innovative method of selective edge oxidation of graphite sheets, oxidation of the ground plane was avoided, generating functional oxygen groups only at the graphite edge. This is a pre-treatment before the intercalation process.

B. High-quality GNS can be produced using microwave irradiation of solid-state for mixture GO - GNS in hydrogenate atmosphere. In such a mixture, GNS acts as an effective susceptor, having a large specific surface area and a corresponding C/O ratio. The hydrogenate atmosphere is good for increasing the quality of GNS, as it promotes GO reduction and prevents the formation of defects in the GNS. MW irradiation synthesis of solid state is fast, clean, convenient and ultimately a scalable process for manufacturing high quality GNS.

C. Improving the quality of graphene sheets means, if they are used in applications other than microelectronics, excluding as far as possible functional groups containing oxygen. This can be done by MW irradiation of a mixture of graphite oxide and graphene sheets, in solid state, in a hydrogen atmosphere. The mixture graphene sheets act as an effective microwave susceptor, providing sufficiently rapid heating to exfoliate the GO. The hydrogenate atmosphere plays the important role of reducing the oxide, preventing the formation of defects in the graphene. The most commonly used susceptor materials for cladding microwave devices are various forms of carbon (carbon, graphite, etc.) and silicon carbides (SiC) which can withstand temperatures above 2000^o C. Susceptors are used in plate or powder form. During thermal exfoliation of GO, the GO functional groups can decompose into CO₂, this gas leading to expansion between graphene sheets, producing real exfoliation. Why is rapid heating important for successful thermal exfoliation of GO? At heating rate above 2000^o C/min, the decomposition of oxygen-containing functional groups (GOs) rate exceeds the evolved gases diffusion rate, thereby leading to sufficiently rapid increase in pressure that can overcome the vdW forces between GO graphene sheets. Why is hydrogen atmosphere important? Hydrogen atmospheres tend to form H₂O instead of CO₂ (due to the GO oxygen-containing functional groups), which prevents formation of vacancies and defects that would occur as a result of the loss of carbon atoms.

D. Extensive studies have shown that crystallographic *c*-axes alignment of the different grains minimises the interface between the grains if each grain elongates along *c*. Without alignment, the stress exerted by the grain on another is enough to make exfoliation impossible, as observed by seeing the compounds based on isotropic graphite and graphitic fibres behaviour. An

interesting comparison of the exfoliation behaviour between pyrolytic graphite and highly oriented pyrolytic graphite (HOPG) shows that there is 380% expansion in pyrolytic graphite and 850% in HOPG. Hence, the tendency towards exfoliation increases with increasing grain alignment perfection along the *c*-direction.

E. Comparison from electrochemistry - Comparative behaviour of H₂SO₄/FeCl₃ intercalated species in graphite. These species were chosen for intercalation, as they are known to produce the lowest domain structures (i.e. the thinnest possible graphene sheets) and the best stability. Without re-explaining the GIC synthesis methods (vapour transport, thermal method, chemical oxidation and electrochemical technique), we only highlight, in passing, the important characteristics that define them, differentiating them.

The thermal method is usually carried out in sealed glass vials, in which the graphite and the intercalant are placed separately. Sufficient activation energy is obtained to trigger intercalation at a high temperature vapour pressure - due to the harsh chemical conditions of preparation, the duration, the difficulties in obtaining homogeneous products in large quantities, the method is not practical for industry, despite obtaining well-defined stages of GIC.

Chemical oxidation involves either species-intercalated oxidation in solution or using a specific oxidising agent as an auxiliary agent. The resulting GIC often consists of non-uniform stages, due to poor intercalation efficiency and uncontrollable stoichiometry.

For the time being, the most suitable technique for synthesising GIC, from a quality and quantity perspective, remains electrochemistry. This is because it gives rise to uniform structures obtained for various stages, fast reactions of any degree that could be easily controlled by refining the electrochemical parameters.

The two GIC variants analysed in the paper are both of the acceptor type, and in the cases presented the electrochemical process can be divided into three relatively distinct steps: oxidation of graphite at the anode, introduction of intercalates between the graphite layers, formation of the scaffold, of the intercalated structure. The GIC thus synthesised follows the expansion stage, expansion in the direction of the thickness of the material (crystallographic axis *c*), achieved either by rapid heating or by irradiation with microwave radiation. The expanded GIC is obtained by expelling interlayers and thermal shock. The underlining is especially useful, since in our own experiments with FeCl₃, the final detection of the intercalate elements was practically impossible, due to the small quantities revealed by the apparatus, creating momentary perplexity. The result of the treatments is a porous, spongy, accordion-like expanded graphite (EG), which can then be exfoliated into graphite nanoplatelets (GND) or nanographene sheets. The successful synthesis of such sheets is assessed globally by investigating the graphene sheets aspect ratio (directly dependent on the performance of expansion and exfoliation), with the respective synthesis steps in turn affected by GIC staggering, intercalated species and expansion techniques.

In the characterisation phase, the standard techniques used are:

- XRD for the determination of the GIC scale index;
- SEM for sample morphologies at different synthesis steps;
- HRTEM for particle size and thickness analysis of the obtained sheets;

- BET analysis for surface area and pore volume (N adsorption techniques).

In XRD diffractograms, for the same stage 5 of both GIC compounds, a sandwich thickness $d_s = 7.95 \text{ \AA}$ was obtained for H_2SO_4 (literature value = 8 \AA), while for FeCl_3 $d_s = 9.63 \text{ \AA}$ (vs. 9.40 \AA). In order to make a proper comparison, we need to understand the effects of staggering on the expansion behaviour of GIC (recall that the effect called staggering is described by the regular stacking sequence of intercalates in graphitic galleries, domain 5 meaning that the intercalate occupies galleries every 5th graphite layer). It is precisely the expulsion of intercalates upon heating that causes the GIC to undergo a dramatically anisotropic expansion, leading to a porous structure formation, like the bellows of a lute accordion, an object with a large surface area. So the lower the GIC domain index (hence more frequent interlayering), the greater the surface area and the greater the pore volume. Because besides the pore volume there is another parameter relevant to the porosity of the material, the expansion volume. We will compare the behaviour of H_2SO_4 -GIC and FeCl_3 -GIC on the basis of: a) effect of intercalation, b) effect of expansion techniques.

a) Based on the experimental results, at the same level of scaling, graphite expanded with FeCl_3 had a larger surface area and pore volume than EG with H_2SO_4 . This means a possible better exfoliation of FeCl_3 -GIC. Where does this difference come from? In H_2SO_4 -GIC, what was intercalated was acid in the form of liquid layers containing the ions HSO_4^- randomly oriented. The density of the intercalate was found to be higher than that of the original sulfuric acid, so the 2D layer of acid was "squeezed" between the graphite ones, its condensation producing a decrease in its volume at the same dispersed mass. So the height of the layer was lower (8 \AA). But in FeCl_3 -GIC it was found that the chloride structure remained practically the same as in the original FeCl_3 -GIC, the density did not increase, the thickness of the FeCl_3 sandwich $d_s \sim 9.4 \text{ \AA}$ higher than in H_2SO_4 -GIC.

On the other hand, before intercalation, the natural graphite surface was smooth with rounded edges and no separation between the graphitic layers along the edges was visible. After intercalation, in both cases of intercalation, the GIC showed much rougher basal planes: with steep edges and "delaminated" (delaminated) from each other. And here the difference between the two GICs can be seen explicitly, as the basal plane of FeCl_3 -GIC is rougher, as a result of partial exfoliation occurring precisely because of the larger d_s distance. Better exfoliation of FeCl_3 -GIC produces transparent (i.e. thinner) graphene sheets, where steep edges without parallel lines were found indicate the existence of uni-layered graphene.

b) Regarding the expansion techniques, we may say that both the changes in specific surface area and expansion volume for EG depend linearly on the furnace temperature (at heat treatment), however, using the microwave oven, at a power of 650W the highest efficiency of these parameters was found. And comparing the two techniques, the one using microwave irradiation showed the most significant increase in specific surface area and expansion volume.

One of the most widely accepted theories today is that these increases are a reflection of growth, expansion of gas cavities and exfoliation of graphene sheets. In the thermal method, the driving force for the rapid expansion is given by the pressure generated by the gaseous interlayer. But in expansion under the action of microwaves there are several factors to consider. Namely that intercalated H_2SO_4 molecules are dipolar, with vibrational frequencies similar to the microwave

vibration of the electromagnetic field. It is precisely these alternating changes in the field that can produce rotations, vibrations and rapid oscillations of the dipolar moments, which generate heat and energy, allowing the molecules to be activated in a short time. These combined effects lead to more explosive expansion than blast furnace heating. The strong impact of the expansion causes the brittle parts of the EG to be separated, resulting in a larger surface area with a corresponding overall reduction in particle size.

The thesis topic was treated under the challenging and simultaneously severe conditions of the fact that the ELI-NP laser, of unprecedented power, is currently being evaluated for the applications it could have, improve or serve. The material discussed, graphene, does not yet have industrial applicability, despite its exceptional theoretical and experimental qualities. The research programme is not aimed primarily at the development of certain specified materials or immediately implementable applications.

Hence the need for an optimal approach, in which everything that is known and evaluated should be given equal probability, while other considerations should be weighted in line with current expectations.

In such a set-up, specific experiments and theoretical analyses have been carried out on the ELI-NP laser-matter interaction, with the results presented. Fortunately, these allow the drawing up of a future programme to advance along the line considered, without excluding any variant of success, but confined to procedures that have a real chance, on the grounds of a scientific literature that urges in those directions.

The future action programme has been detailed and contains both theoretical components of great importance and immediate practical objectives linked to the results obtained.

From these points of view, the PhD thesis is a document of constant efforts to decipher a field that is, if not uncertain, at least insufficiently assessed and predicted, while also providing a roadmap for the achievement of precise goals useful for any further development of the field.