Ultrafast Saturable Absorption in Single-Layer Graphene with Application to Broadband Mode-Locking

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Todas as correções determinadas pelo júri, e só essas, foram efetuadas.

O Presidente do Júri,

Porto, _____/_____/_______
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Resumo

Este projecto de investigação teve como objectivo explorar as características únicas de um novo e promissor material - grafeno - para mode-locking de banda ultra-larga em lasers de estado sólido vibracionais. Com esta abordagem, esperamos superar limitações atuais de outras técnicas de mode-locking de banda larga, em particular espelhos semicondutores com absorção saturável (SESAM) e mode-locking for efeito de lente de Kerr (KLM), no que diz respeito a estabilidade, eficiência e largura de banda.

Este trabalho mistidisciplinar, envolvendo ciência de matérias e tecnologia de lasers ultra-rápidos, foi desenvolvido ao longo de vários meses. Envolveu simulação, desenho e construção de cavidades laser ultra-rápidas, várias técnicas de caracterização de materiais (incluindo estudos intracavitários e extracavitários da absorção saturável não-linear em grafeno), e métodos de medição e compressão de impulsos ultra-curtos; várias amostras de grafeno produzidas por diferentes fabricantes foram usadas e estudadas durante este trabalho. Este trabalho culminou com a observação clara e reproductível de absorção saturável em grafeno mono-camada, e demonstração de um desenho viável de um laser de Titânio:Safira, apto para estudo em grafeno e outros materiais. É de notar que, tanto quanto pudemos apurar, este foi o segundo trabalho alguma vez feito sobre mode-locking com grafeno usando um laser de Titânio:Safira.

Estes resultados são também relevantes para o novo flagship de grafeno (pacote de trabalho sobre propriedades optoelectrónicas do grafeno) e estão na base de colaborações em fase de preparação neste momento, com os quais tencionamos avançar no estudo e aplicação de grafeno em novos dispositivos fotónicos.
Abstract

This research project was aimed at exploring the unique characteristics of a new and promising material - graphene - for ultra-broadband mode-locking of vibronic solid-state lasers. With this approach we expected to overcome current limitations inherent to other types of broadband mode-locking techniques, in particular those based on semiconductor saturable absorber mirrors (SESAM) and on Kerr-lens mode-locking (KLM), regarding stability, efficiency and operation bandwidth.

This multidisciplinary work, encompassing materials science and ultrafast laser technology, was developed over a period of several months. It involved ultrafast laser cavity simulation, design and construction, several techniques of material characterization (including intracavitary and extracavitary studies of the nonlinear saturable absorption of graphene), and methods of ultrashort laser pulse compression and measurement; several graphene samples, from different manufacturers, were studied and used in the experiments. The work culminated with the observation of clear and reproducible saturable absorption behavior in single-layer graphene, and with the demonstration of a viable Titanium:Sapphire laser design for intracavity studies of graphene and other materials. We should point out that, to our knowledge, this is the second work ever performed on graphene mode-locking of a Titanium:Sapphire laser.

These results are also relevant for the new Graphene flagship (optoelectronic properties of graphene workpackage) and are behind the collaborative work now being prepared within this context with which we intend to further advance on the study and application of graphene to new photonic devices.
# List of Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>BBO</td>
<td>Beta Barium Borate</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-Coupled Device</td>
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<tr>
<td>CW</td>
<td>Continuous Wave</td>
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<tr>
<td>FRAC</td>
<td>Fringe-Resolved Autocorrelation</td>
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<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
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<tr>
<td>GDD</td>
<td>Group Delay Dispersion</td>
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<td>GVD</td>
<td>Group Velocity Dispersion</td>
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<tr>
<td>HR</td>
<td>High Reflector</td>
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<tr>
<td>KLM</td>
<td>Kerr Lens Mode-Locking</td>
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<tr>
<td>NIR</td>
<td>Near Infrared</td>
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<tr>
<td>OC</td>
<td>Output Coupler</td>
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<tr>
<td>SAML</td>
<td>Saturable Absorber Mode-Locking</td>
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<tr>
<td>SESAM</td>
<td>Semiconductor Saturable Absorber Mirror</td>
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<td>SHG</td>
<td>Second Harmonic Generation</td>
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<td>SLG</td>
<td>Single-Layer Graphene</td>
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<tr>
<td>SPM</td>
<td>Self-Phase Modulation</td>
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<td>TOD</td>
<td>Third-Order Dispersion</td>
</tr>
<tr>
<td>TPA</td>
<td>Two-Photon Absorption</td>
</tr>
</tbody>
</table>
Contents

I  Introduction .................................................. 17

1  Ultrafast optics ............................................... 17
   1.1  Relevance and applications ................................. 17
   1.2  Context of this work ........................................ 18
   1.3  Aims for this thesis ........................................ 19

II  Theoretical Basis ............................................. 21

2  Multimode laser operation .................................... 21

3  Ti:Sapphire ................................................... 22

4  Laser pulse generation - Mode-locking ...................... 23

5  Methods of Mode-Locking ..................................... 27
   5.1  Saturable absorption mode-locking ......................... 27
   5.1.1  Cavity Master Equation .................................. 27
   5.1.2  Saturable Absorption and Solitonic Solution ............ 31
   5.1.3  Soliton Formation in Mode-locked Lasers - Dispersion-managed Mode-locking that 33
   5.2  Kerr Lens Mode-Locking .................................... 35

6  Saturable Absorption and Graphene .......................... 36
   6.1  Saturable Absorption Description ......................... 36
   6.2  Graphene .................................................. 41
       6.2.1  Graphene Band Structure ............................ 41
       6.2.2  Graphene Optical Properties ......................... 43
       6.2.3  Saturable Absorption in Graphene ..................... 43
       6.2.4  Graphene in the Current Mode-locking Scene .......... 45
   6.3  Pulse Measurement ......................................... 46
III Experimental Setup

7 Initial KLM Ti:Sapphire Setup

8 New Graphene Setup

9 Sample Characterization

10 Measurement Setups

IV Results and Discussion
11 Blank Substrate (“Dummy” Laser) 75

12 First Graphene Sample 77

12.1 Broadband Spectra 77

12.2 Multimode Oscillation 79

12.2.1 Oscilloscope Measurements 79

12.2.2 Spot Size measurements 80

12.2.3 Explanation 80

12.3 KLM 82

13 Second Graphene Sample 83

14 Saturable Absorption Measurements 84

V Conclusions 87
Part I

Introduction

1 Ultrafast optics

The field of ultrafast optics is a branch of nonlinear optics that studies ultrafast laser pulses. The “meaning” of ultrashort has changed with time and is currently applied to pulses with sub-picosecond duration, or less than $10^{-12}$s, which is quite impressive. Nowadays, pulses of the order of the femtosecond ($10^{-15}$s) can be produced and scientists are already accessing the attosecond ($10^{-18}$s).

Back in the 1960’s, when the laser first appeared, theoretical work had already predicted several ways to obtain picosecond pulses, making ultrafast optics one of the most active fields in laser physics. More than just the desire to hold the record of the world’s shortest pulse, there was a sense that this was the start of a new field of study in physics. And indeed, ultrafast pulses allow us to observe, control and measure phenomena that are only seen as an average with any other technique. As pulses grow shorter, new physical phenomena are being discovered and measured, and new applications in science, industry and medicine are being found every day. This makes ultrafast optics a very active field of study, with great interest from both the academic and industrial communities.

1.1 Relevance and applications

This technology opened new possibilities for research and applications. Pulsed lasers were first applied as measurement devices, allowing scientists to measure transient states of a number of systems. Phenomena on femtosecond scale include molecular reactions, semiconductor carrier relaxation times, magnetization phenomena and electronic gas cooling. In astrophysics, femtosecond lasers are used to calibrate spectrometers to unprecedented accuracy, allowing for measurements of the Doppler shifts of stellar objects with error approximately 1cm/s [1, 2]. Optical frequency combs produced by femtosecond lasers are used to help probe and manipulate the quantum state of gaseous atoms and molecules [3]. Today, pulses are short as 80 attoseconds have been produced and used for subatomic physics studies.

But ultrashort pulses are more than just short, they are also extremely intense. Since all the energy is being syphoned into a very small temporal window, pulse peak power (energy divided by pulse duration) is exceedingly high, even for moderate average powers. High intensities give rise to nonlinear effects, not easily studied without resorting to short pulse generation.

But even among what may be considered short, there are order of magnitude differences in pulse durations. The gap between nanosecond ($10^{-9}$s) and femtosecond ($10^{-15}$s) durations, is six orders of magnitude wide. Interaction between light and matter at those timescales is very different. Femtosecond pulses, as opposed to even “fairly short” nanosecond pulses, have such fast interaction with matter that thermal damage cannot occur. High power femtosecond lasers have very attractive industrial applications in micromachining, due to their very localized interaction, achieving precisions not possible with physical or chemical processes.
Figure 1: Laser ablation from nanosecond and femtosecond pulses. Interaction times with nanosecond pulses are long enough to create thermal shockwaves, resulting in debris. For femtosecond pulses, interaction is much more localized.

The absence of thermal damage is also very important for applications in sensitive materials, most notably living tissue. They are also used for in-vivo 3D imaging of the human retina, epidermis, and blood vessels [4].

1.2 Context of this work

Today, there are several ways of producing ultrafast pulses. The shortest pulses today are produced by mode-locking, either by the Kerr lens effect (Kerr lens mode-locking or KLM) or by saturable absorption (saturable absorber mode-locking or SAML). As shall be discussed further ahead, mode-locking is a laser regime where there is a well defined phase relation between all the oscillating modes of the cavity. This mode of operation is triggered by introducing nonlinear losses in the system, where more intense modes experience less loss than less intense ones.

A saturable absorber placed as an intracavitary element does just that. Saturable absorption is a nonlinear process where the absorption of a material decreases as the light intensity increases. Unfortunately, there are very few materials that can be used as an intracavitary saturable absorber, even more so when we aim to produce femtosecond pulses. Currently, femtosecond pulses can be produced using semiconductor saturable absorber mirrors (SESAM), but while SESAM can deliver good results, they also have a number of shortcomings. Being very complex multilayered structures, they are very fragile and have a short operational lifetime due to laser damage. Furthermore, they only work in a fairly narrow frequency band, which limits pulse duration, and cannot be manufactured for certain frequencies, making then unusable with some systems. There is a high interest in finding an alternative to SESAM that provides better results and less technical complications.

Making an appearance in yet another field of study, graphene has been demonstrated as a saturable absorber, and a very good one in fact. Graphene shows exceedingly fast carrier relaxation times and nearly constant absorption over a very broad frequency range, which are very desirable traits in a
saturable absorber, as we shall fully explain further ahead. Its achromatic absorption also means it can be used in broadband laser systems, even those for which no SESAM are available.

Graphene has already been used with great success in fiber lasers and solid state systems with uncommon emission frequencies. However, it has only resulted in fairly long pulses with narrow spectra, the broadest being 10 nm at FWHM. Broadband saturable absorption in graphene has not been thoroughly studied, as graphene has not been fully exploited in systems such as Ti:sapphire, which have emission bandwidths over 400 nm wide, centered at 800 nm. There is only one publication of a graphene-based SAML Ti:sapphire laser, producing pulses with 63 fs.

At femtolas (IFIMUP-IN), there is a home made Ti:sapphire oscillator capable of producing 10 fs pulses, which can be modified to accommodate and study graphene as an intracavity element. This system offers unique conditions to study graphene-based SAML, at unprecedented pulse durations. This will offer us a better understanding of the broadband nonlinear properties of graphene and SAML operation in general.

1.3 Aims for this thesis

In this work, we aim to use single layer graphene to produce femtosecond pulses. With this, we wish to study the broadband nonlinear optical properties of graphene and its behavior as a saturable absorber at unprecedented pulse durations.

The main challenge of this work is to design and implement a laser system where graphene works as a saturable absorber. This new system can also be used to study other materials inside the cavity, providing opportunities for future work, and should prove a valuable asset to femtolas.
Part II

Theoretical Basis

2 Multimode laser operation

Lasers are usually referenced and praised as a monochromatic light source. But when we want to produce short pulses, the emission spectrum must be as broad as possible. This is a consequence of the Fourier transform limit which states that the bandwidth of a coherent spectrum is inversely proportional to the minimum pulse duration it can produce, that is

$$\Delta \nu \propto 1/\Delta \tau_p$$  \hspace{1cm} (1)

where $\Delta \nu$ is the coherent spectral bandwidth and $\Delta \tau_p$ is the minimum pulse duration possible. The proportionality constant depends on the shape of the spectrum, but in the end the total oscillating bandwidth is what limits pulse duration.

Thus, it is important to discuss broadband coherent laser emission, starting with optical cavity modes and continuing to broadband laser media, in our case Titanium-doped Sapphire.

In the absence of a gain medium, a laser cavity is a passive optical resonator capable of supporting an infinite number of discrete frequencies, determined by a set of eigenvalue and eigenmode equations, corresponding to modes of the cavity.

Figure 2: (a) In the absence of a gain medium there is an infinite number of equally spaced oscillating modes (here shown cropped around a center frequency $\omega_0$). (b) Gaussian amplitude distribution around $\omega_0$ over a FWHM $\Delta \omega_L$.

Once a gain medium is placed inside the resonator, only the modes inside the gain profile will be amplified. Generally, lasers tend to oscillate in a large number of modes due to the fact that the frequency separation of the modes is usually much smaller that the width of the gain profile.
For a 1.5m long cavity with plane mirrors, the frequency separation between consecutive modes is $c/2L = 100$ MHz, where $L$ is the cavity length. This means that, for a spectrum spanning from 600 nm to 1100 nm (Ti:Sapphire bandwidth, which we shall discuss further down), there are more than one million modes in a 1.5 m long cavity.

When such a large number of modes is considered inside the gain linewidth, the gain difference between them becomes very small and thus a significant fraction is expected to be excited at sufficiently high pump rates.

3 Ti:Sapphire

Kerr lens mode-locking was first observed in Titanium doped sapphire (Ti:sapphire) at Wilson Sibbet’s group [5], and has since then become the predominant system in ultrafast optics. Excelling in traits such as gain bandwidth, energy level lifetimes and nonlinear refractive index, Ti:sapphire is one of the overall best gain media, both in performance and ease of implementation, compared to other media such as dyes. Ti:sapphire boasts the largest absorption and laser emission bands in the near infra-red (NIR) known today, only slightly less than a couple of materials with emission centered around 1.5 $\mu$m. This results in the shortest Fourier-limited pulses directly available from a laser. It is also convenient that the absorption and emission bands do not strongly overlap, since this causes residual parasitic absorption. With its absorption centered around 500 nm, Ti:sapphire lasers can be easily pumped by frequency doubled Nd-based lasers, resulting in great pump efficiency. This is one of the strongest points of Ti:sapphire. Pumping is a problem for some materials such as those mentioned above at 1.5 $\mu$m, that have absorption peaks in a region with no available laser sources, making for very elaborate pumping schemes. The small increase in bandwidth is not worth the additional setup complications.

In Ti:sapphire ($Ti : Al_2O_3$), $Ti^{3+}$ ions substitute the aluminum ions in the center of octahedron formed by oxygen ions. $Ti^{3+}$ only has one active electron in a 3$d$ shell, with the remaining ones in a closed-shell configuration. The 3$d$ electron interacts strongly with the oxygen ions, depending on

![Figure 3: The absorption and emission bands of Ti:sapphire [6].](image-url)
the orbital orientation. There are 5 angular momentum states, two of them (E doublet) pointing directly at oxygen atoms, and the remaining three (T triplet) not. This results in two energy levels separated by the energy of a green photon at about 500 nm. The top levels are further separated by the Jahn-Teller effect, where the Ti$^{3+}$ is displaced from the center of the octahedron, resulting in a broad absorption band at around 500 nm.

Furthermore, this displacement kicks the surrounding lattice leading to fast phonon scattering, resulting in nonradiative decay from B to C. Photon emission occurs from C to D, followed by a nonradiative decay to A. The broad emission bands come from the broad position distribution of the Ti$^{3+}$ ion at the bottom of the E band being coupled to a large spread of vibrational levels in the T band.

With the widest known NIR emission band, efficient pumping systems and the advantages of a full solid state system, Ti:sapphire has the most to offer when coupled with graphene to produce the shortest pulses possible.

4 Laser pulse generation - Mode-locking

Apart from the intrinsic pulses generated by flash-pumped lasers such as Ruby, shorter laser pulses can be generated in multiple ways, first achieved by Q-switching techniques [7], which can only achieve fairly long pulses (around the nanosecond mark), and later by mode-locking [8]. Q-switching relies on making a cavity unsuitable for laser action, causing the energy and population inversion in the gain medium to increase to very high values, since it can not be released by laser action. The cavity is then made suitable again, and all the energy is release as short laser pulse.
Mode-locking is a much more fundamental mode of operation than Q-switching, resulting from a fine relation between the longitudinal standing wave modes of the cavity. Inside a cavity, the laser will oscillate in a large number of longitudinal modes. Under ordinary circumstances, the phases of these modes will have random values and, for continuous wave oscillation, the beam intensity will show a very complex yet periodic behaviour. Figure 5 shows one such example, where 31 modes are present, each with the same amplitude $E_0$ and evenly separated by a frequency difference $\Delta \nu$ between consecutive modes.

![Figure 5: Time behaviour of the squared amplitude of the total electric field $|A(t)|^2$ for the case of 31 oscillating modes with equal amplitude $E_0$ and random phases [9].](image)

Being a superposition of $N$ frequency components, the seemingly random behaviour exhibits two properties, characteristic of a Fourier series:

1. The waveform is periodic with a period $\tau_p = 1/\Delta \nu$.

2. Each of the light pulses that compose the waveform has a duration $\Delta \tau_p \approx 1/\Delta \nu_L$, where $\Delta \nu_L$ is the total oscillating bandwidth, in this case $\Delta \nu_L = N\Delta \nu$.

For laser with very large gain bandwidths, such as solid-state, dye or semiconductor lasers, the duration of these pulses is very small, reaching sub-picosecond values. Since common photodetectors have response times much larger than pulse durations, the output seen is merely the average power, sum of the powers of each mode, hence proportional to $NE_0^2$.

Considering now a collection of $2n + 1$ longitudinal modes each with amplitude $E_0$, that unlike the random phase relation previously seen, are locked according to the relation

$$\varphi_l - \varphi_{l-1} = \varphi$$

where $\varphi$ is a constant. The resulting electric field can be written as

$$E(t) = \sum_{l=-n}^{+n} E_0 \exp \{i [(\omega_0 + l\Delta \omega) t + l\varphi] \}$$

(3)
where $\omega_0$ is the frequency of the central mode, $\Delta \omega$ the frequency difference between two consecutive modes and the phase of the central mode is set as zero, for simplicity. Equation 3 can be rewritten as

$$E(t) = A(t) \exp (i \omega_0 t)$$  \hfill (4)

with

$$A(t) = \sum_{l=-n}^{+n} E_0 \exp [il(\Delta \omega t + \varphi)]$$  \hfill (5)

These equations show the field $E(t)$ can be seen as a sinusoidal wave with frequency $\omega_0$ with varying amplitude $A(t)$. Changing the time reference $t'$ where $\Delta \omega t' = \Delta \omega t + \varphi$ and thus

$$A(t') = \sum_{l=-n}^{+n} E_0 \exp [il(\Delta \omega t')$$  \hfill (6)

This is nothing more than a summation of a geometric series. It can be easily performed to yield

$$A(t') = E_0 \frac{\sin [(2n + 1) \Delta \omega t'/2]}{\sin [\Delta \omega t'/2]}$$  \hfill (7)

Figure 6: Time behaviour of $A^2(t')$ for the case of seven oscillating modes with equal amplitude and locked phase relation [9].

$A^2(t')$ is proportional to the beam intensity and its form is shown in Figure 6 for the case where $2n + 1 = 7$. A mode-locked laser produces a train of evenly spaced pulses, separated in time by
Figure 7: The effects of the phase relation between cavity modes in the output profile. While random phase relation results in chaotic behaviour (left), locked phase relation produces a point of constructive interference which results in a very short pulse-like output.

\[ \tau_p = 1/\Delta \nu \]  

The width of each pulse (FWHM) is

\[ \Delta \tau_p = 1/\Delta \nu_L \]  

where \( \Delta \nu_L \) is the total oscillating bandwidth. The previous discussion addressed the case where all modes had equal amplitude which is clearly not the real-life scenario. Mode amplitude distribution will be dictated by the gain line shape of the active medium, which for a solid-state laser capable of femtosecond pulse generation (including Ti:Sapphire, as used for this work) has a Gaussian profile. The correction is simple to make and yields only a change in the pulse duration by a constant factor.

\[ \Delta \tau_p = 0.44/\Delta \nu_L \]  

Other line shapes occur but the result is always just a multiplicative factor in the pulse width: \( \Delta \tau_p = \beta/\Delta \nu_L \). A pulse whose duration satisfies this equality is said to be transform-limited. This is the minimum pulse duration obtainable for a given spectrum. Several factors such as dispersion will result in pulse stretching and must be minimized to ensure the shortest pulse possible is produced and maintained.

Mode-locking occurs when there is an element of nonlinear loss in the cavity, i.e. an element that introduces intensity-dependent loss. This can be understood by first considering the case where only linear absorption is present. In this scenario, recalling Figure 5, all the peaks will experience the same loss and gain, and the output intensity will grow to a constant value. If, on the other hand, there is an element which introduces loss that decreases with intensity, more intense pulses will experience less loss, and thus a higher net gain, than less intense pulses. As these stronger pulses are amplified, with the weaker suffering more loss, a snowball effect occurs. As more intense peaks grow, they increase in intensity and experience even less loss, thus even higher net gain. The opposite occurs for weaker pulses. In the end, this will result in what is seen in Figure 6.

Mode-locking can also be understood from a travelling soliton point of view. The phase relation needed for mode-locking can be seen as a travelling intensity pulse resulting from constructive interference between cavity modes. Figure 7 shows ML and CW operation from a mode interference point of view.
5 Methods of Mode-Locking

Mode-locking can be achieved by several methods, categorized as active mode-locking or passive mode-locking, depending on the nature of the nonlinear loss element.

Active mode-locking employs an element driven by an external source. The most widely used active mode-locking mechanism is amplitude modulation (AM mode-locking) [10], where a modulator is inserted into the cavity to produce a time-varying loss at a certain frequency. Other methods exist, such as phase-modulation (FM mode-locking) [10] and synchronous pumping [11]. Active mode-locking presents technical difficulties when trying to produce very short pulses, and is only suitable for production of picosecond pulses. Furthermore, a passive element is generally preferable as it gives rise to less complications and does not require active use: when correctly used, physics does all the work.

Today, passive mode-locking methods produce the shortest laser pulses, the main techniques being Kerr lens mode-locking (KLM), and saturable absorber mode-locking (SAML).

5.1 Saturable absorption mode-locking

The first successfully implemented passive mode-locking method was saturable absorption [12]. This technique relies on an element whose optical absorption decreases as it is irradiated with intense light, as discussed previously. There are two regimes for SAML: fast SAML and slow SAML. Fast SAML is when saturable absorber relaxation times are much smaller than pulse duration; in slow SAML relaxation times are much slower than pulse durations. Since fast saturable absorption produces shorter pulses, and when using graphene, due to its exceedingly fast carrier relaxation times, we are only interested in discussing fast saturable absorption regime.

We now shift to a more demonstrative plane to analyze the theory behind mode-locking using fast saturable absorbers. Saturable absorber mode-locking was the target of extensive theoretical study in the mid-70’s, notably by Haus [13]. We begin by discussing the assumptions made, proceed to obtain an equation to describe a laser cavity with general gain and loss elements, and then obtain a solitonic solution for the case where the loss element shows saturable absorption. After that, we will briefly discuss some of the corrections that must be made when pulse durations become shorter, causing peak power to increase and nonlinear propagation effects to become more relevant. This is called dispersion-managed mode-locking.

5.1.1 Cavity Master Equation

A few assumptions are made beforehand:

1. The relaxation time of the absorber is short compared to the pulse width.

2. The absorber experiences a small saturation with its absorption not varying greatly from the unsaturated value.

3. The relaxation time of the laser medium is long so that the laser gain is time independent.
4. The mode-locked pulse suffer only small modifications upon passing through any one of the system components.

5. The spectrum of the pulse occupies only a narrow portion of the laser linewidth.

Out of these assumptions, 1 and 5 are the most serious. In fact, regarding 1, pulses shorter than the relaxation time of the absorber can be produced while still in the fast saturable absorption regime. The explanation for this is twofold.

Firstly, assumption 1 is written as seen in [13] but as SAML yielded shorter pulses, it was found that it should be rewritten as:

1. (revisited) The losses of the absorber should present no significant dynamics in the pulse duration timescale.

Though this relaxes the assumption, it is still not enough to explain the extended validity of the fast SA regime. The second part of the explanation also concerns 5 and is actually not a small detail or correction, being a determining factor for very short pulses. As the pulse width becomes smaller with larger laser bandwidths, non-linear propagation effects are all but negligible. self-phase modulation (SPM) and group velocity dispersion (GVD) are the relevant features for short pulse propagation. When these are taken into account, the closed stationary soliton solution found in [13] must be corrected by studying dispersion-managed soliton formation. Sadly, this method does not deliver closed-form solutions and must be solved numerically for each specific case.

We shall start by obtaining a master equation for mode-locking, proceeding then to analyze its solutions and discuss corrections applicable for shorter pulses.

![Figure 8: Schematic of a laser cavity with a saturable absorber (for now just treated as a generic loss element, producing time dependent losses) [13].](image)

Figure 8 shows the setup for this study. The laser medium and saturable absorber occupy opposite ends of the cavity, with the absorber confined to a small fraction of the cavity length. The electric
field of the pulse after \( n \) round trips is given by \( E_n(t) \) and its Fourier transform \( E_n(\omega_k) \), the latter composed of a discrete spectrum spaced at \( 2\pi/T_p \), \( T_p \) being the period of the pulse train. From the left, after passage through the laser medium, the Fourier spectrum of the pulse is

\[
E_{n+1}(\omega_k) = \exp(-i\omega_k T_l) \exp[G(\omega_k)] E_n(\omega_k)
\]  

(10)

where \( G(\omega_k) \) is the frequency-dependent gain of the laser medium and \( T_l \) the time delay in the laser medium. Applying an inverse Fourier transform, we shift to the time domain

\[
E_{n+1}(t) = \exp \left[ G \left( \frac{d}{dt} \right) \right] E_n(t - T_l)
\]  

(11)

To obtain \( \exp \left[ G \left( \frac{d}{dt} \right) \right] \), \( \exp[G(\omega_k)] \) is expanded in \( i\omega_k \), with the \( n \)th power of \( i\omega_k \) replaced by \( d^n/dt^n \). After passage through the remainder of the cavity, including the saturable absorber, the field becomes

\[
E_{n+1}(t) = \exp[-L(t)] \exp \left[ G \left( \frac{d}{dt} \right) \right] E_n(t - T_l - T_{11})
\]  

(12)

where \( L(t) \) is the power-dependent absorption coefficient of the saturable absorber, also time-dependent under mode-locked operation.

So far, this only accounts for a one-way pass. To finish the round-trip, these exponential factors must be applied again. On top of that a factor \( \exp[-(\omega_0/2Q) T_R] \), where \( T_R = 2 (T_l + T_{11}) \) is the round-trip time and \( \omega_0 \) is the center frequency of the pulse spectrum. This accounts for the decay of the pulse and is thus related to the quality Q-factor of the cavity, \( Q \). Thus, after a round-trip

\[
E_{n+1}(t) = \exp \left( -\frac{\omega_0}{2Q} T_R \right) \exp \left[ G \left( \frac{d}{dt} \right) \right] \exp[-2L(t)]
\]

\[
\times \exp \left[ G \left( \frac{d}{dt} \right) \right] E_n(t - 2T_l - 2T_{11})
\]  

(13)

The gain is assumed to have a Lorentzian line shape around the center frequency \( \omega_0 \)

\[
G(\omega_k) = G(\omega_0) \left( 1 + i \frac{\omega_k - \omega_0}{\omega_L} \right)^{-1}
\]

\[
\approx G(\omega_0) \left[ 1 - i \frac{\omega_k - \omega_0}{\omega_L} - \left( \frac{\omega_k - \omega_0}{\omega_L} \right)^2 \right]
\]  

(14)

It is convenient to express the field as a slowly varying envelope \( v_n(t) \) and a fast oscillation at the center frequency \( \exp(i\omega_0 t) \), since the gain is expressed in powers of \( (\omega_k - \omega_0) \)

\[
E_n(t) = v_n(t) \exp(i\omega_0 t)
\]  

(15)
with the Fourier transform

\[ E_n (\omega_k) = v_n (\omega_k - \omega_0) \]  

(16)

Multiplying \( E_n (\omega_k) \) by \( i (\omega_k - \omega_0) \) corresponds to \( (\frac{d}{dt} - i\omega_k) \) in the time domain. Applying this to (16), results in the time derivative of \( v(t) \) alone. Using equations (13)-(16), and expanding the exponentials to the first order, we obtain

\[ v_{n+1} = \left[ 1 - \frac{\omega_0}{2Q} T_R - 2L(t) + 2G(\omega_0) \left( 1 + \frac{1}{\omega_L^2} \frac{d^2}{dt^2} - \frac{1}{\omega_L} \frac{d}{dt} \right) \right] v_n (t - T_R) \]  

(17)

Some convenient notation can be introduced. We can write the gain normalized to the decay loss, as

\[ g = \frac{2G(\omega_0)}{(\omega_0/2Q) T_R} \]  

(18)

and the quality factor as

\[ \frac{Q}{Q_A(t)} = \frac{2L(t)}{(\omega_0/2Q) T_R} \]  

(19)

where \( Q_A \) is the amplitude - hence time - dependent inverse \( Q \) produced by the saturable absorber.

Finally

\[ v_{n+1} (t) = v_n (t - T_R) - \frac{\omega_0}{2Q} T_R \]

\[ \times \left[ 1 + \frac{Q}{Q_A(t)} - g \left( 1 + \frac{1}{\omega_L^2} \frac{d^2}{dt^2} - \frac{1}{\omega_L} \frac{d}{dt} \right) \right] v_n (t - T_R) \]  

(20)

This final expression clearly shows that the \((n + 1)st\) pulse is a delayed version of the \(n\)th pulse, modified by the operator

\[ -\frac{\omega_0}{2Q} \left[ 1 + \frac{Q}{Q_A(t)} - g \left( 1 + \frac{1}{\omega_L^2} \frac{d^2}{dt^2} - \frac{1}{\omega_L} \frac{d}{dt} \right) \right] \]  

(21)

This first term inside the parenthesis represents linear cavity loss, the second is the saturable absorber. The last term accounts for the laser medium, with gain and dispersion. Inside the innermost parenthesis, the first term represents the laser gain, the second is a diffusion operator and the third a time delay of \( \omega_0 g / 2Q \omega_L \).

In the steady state, a closed solution requires the pulse to reproduce itself after one pulse period \( T_P \). The pulse period may not be equal to the cavity round-trip time \( T_R \), as changes to the pulse envelope may lead to additional delays or advances.

As such, we obtain

\[ \text{30} \]
\[ v_{n+1}(t) = v_n(t - T_R + \delta T) \]  

(22)

where \( \delta T \) is the effect of pulse envelope modulation. For small values of \( \delta T \), \( v(t + \delta T) = v(t) + \delta T \frac{dv}{dt} \). Applying this closure condition to (21) we finally obtain

\[
\left[ 1 + \frac{Q}{Q_A(t)} - g \left( \frac{1}{\omega_L^2} \frac{d^2}{dt^2} \right) + g + \delta \frac{d}{dt} \right] v = 0
\]

(23)

where

\[
\delta = \frac{\omega_L \delta T}{(\omega_0/2Q)T_R}
\]

(24)

This is the final steady-state pulse envelope master equation for a cavity with a gain medium and a time dependent loss element.

5.1.2 Saturable Absorption and Solitonic Solution

So far, the saturable absorber has only been treated as a generic loss element. In this section, we shall address the term \( \frac{Q}{Q_A(t)} \), vital in creating a solitonic solution. We will now accommodate saturation into (23) and show that this results in a pulse-like solution. The rate equation for the population \( n \) difference between the lower and upper levels of the absorber is

\[
\frac{\partial n}{\partial t} = -\frac{n - n_e}{T_A} - \frac{\sigma_A |v(t)|^2}{h\omega_0 A_A} n
\]

(25)

\( |v(t)|^2 \) is the term responsible for the intensity dependence of the absorption. \( T_A \) is the relaxation time of the saturable absorber, \( n_e \) is the equilibrium population difference, \( \sigma_A \) is the optical cross section of the absorbing particles, and \( A_A \) is the cross section of the beam in the saturable absorber. If the relaxation time \( T_A \) of the absorber is fast compared with the rate of change of the intensity, the population difference is an instantaneous function of intensity. The time-dependent population difference \( n \) is then approximately

\[
n = n_e \left( 1 - \frac{|v(t)|^2}{P_A} \right)
\]

(26)

where the saturation power of the absorber is defined as

\[
P_A = \frac{h\omega_0 A_A}{\sigma_A T_A}
\]

(27)

After a single pass through the absorber, the absorption is
\[ L(t) = \sigma_A \theta A n_e \left( 1 - \frac{|v(t)|^2}{P_A} \right) \]  
(28)

where \( \theta A \) is the length of the absorber. The parameter \( Q/Q_A \) defined by (19) can now be written as

\[ \frac{Q}{Q_A}(t) = q \left( 1 - \frac{|v(t)|^2}{P_A} \right) \]  
(29)

with

\[ q = \frac{2 \sigma_A \theta A n_e}{(\omega_0/2Q) \tau_R} \]  
(30)

Thus, finally, when the element shows fast saturable absorption, the master equation for the pulse envelope becomes

\[ \left[ 1 + q + (g + \delta) \frac{1}{\omega_L \frac{d}{dt}} - g \left( 1 + \frac{1}{\omega_L^2 \frac{d^2}{dt^2}} \right) \right] v = q \frac{|v(t)|^2}{P_A} v \]  
(31)

It can be shown that no periodic solutions exist when \( g + \delta \neq 0 \). It is a fairly long demonstration we shall skip, but can be understood in [13]. This simplifies the equation to

\[ \left[ 1 + q - g \left( 1 + \frac{1}{\omega_L^2 \frac{d^2}{dt^2}} \right) \right] v - q \frac{|v(t)|^2}{P_A} v = 0 \]  
(32)

The solution to this equation is pulselike and symmetric in time, given by

\[ v(t) = \text{vosech}(t/\tau_p) \]  
(33)

with

\[ q \frac{v_0^2}{P_A} = \frac{2g}{\omega_L \tau_p^2} \]  
(34)

and

\[ 1 + q + g = \frac{g}{\omega_L \tau_p^2} \]  
(35)

There is an interesting yet logical detail in this solution. A hyperbolic secant function has exponential tails. Such tails are characteristic of passive mode-locking, as the system behaves linearly in the tails since the intensity is smaller. A second order differential equation such as Eq.(32) requires any bound pulselike solution to be exponential. It is also worth noting that \( g < 1+q \), from (35). This means that in the linear regime, before absorber bleaching kicks in, the laser is below operation threshold, with
the gain not compensating the unsaturated loss. This is actually a very important point, otherwise small noise fluctuations between pulses would experience gain, resulting in an unstable solution.

5.1.3 Soliton Formation in Mode-locked Lasers - Dispersion-managed Mode-locking

As mentioned before, ever shorter pulse durations edge closer to the validity of closed-solution formulations. As pulses become shorter, we enter the area of dispersion-managed mode-locking. A problem of this nature must be solved numerically for each case but an overview of its general results is in order.

When dye lasers started to appear in the 80’s, it was realized that the group velocity dispersion (GVD) and self-phase-modulation (SPM) caused by the Kerr effect of the laser elements could not be ignored. As pulses duration decreases, peak power increases, inferring additional importance to nonlinear propagation effects. The group velocity of light on a given transparent medium depends on its frequency, in what is called group velocity dispersion. This is true even for coherent broadband waves such as a laser pulse, and causes the frequency components that form the pulse to be temporally separated. An obvious and very serious complication of GVD is pulse broadening, since the various frequency components that were once superimposed are now separated.

![Figure 9: A pulse (top curve) propagating through a medium undergoes a self-frequency shift (bottom curve) due to self-phase modulation. The front of the pulse is shifted to lower frequencies while the back is shifted to higher frequencies. In the centre of the pulse the frequency shift is approximately linear.](image)

To balance this, another nonlinear propagation effect comes in. Due to Kerr effect, high intensity beams alter the refractive index of the mediums where they propagate. In pulses, this nonlinear intensity dependent change in refractive index causes a nonlinear phase delay felt by the pulse itself. This causes the instantaneous frequency of the pulse, producing what is called a chirped pulse. As the beam propagates, frequency components are spread apart by GVD and rearranged inside the
pulse by SPM, eventually creating a stationary pulselike solution, when balance conditions are met. Together SPM and GVD, are responsible for solitonic solutions at a fs scale.

To accommodate this, SAML master equation (32) is modified to [14]:

\[
\left[1 + q - g + \left(\frac{g}{\omega_L^2} - iD\right) \frac{d^2}{dt^2}\right] v - (q + i\delta_K) \frac{|v(t)|^2}{P_A} v = 0
\]  

(36)

where \(D = \beta'' L/2\) is the dispersion parameter, \(\beta\) is the propagation constant in the medium and \(\beta''\) its second derivative. \(\delta_K = (2\pi/\lambda) L/A_{eff}\) is called the Kerr coefficient. These relate to GVD and SPM, respectively.

As seen in Figure 10, after the initial pulse formation, a gain window due to saturation is formed. Since the pulse peak is more intense than the wings, it will experience more gain and as all the energy is syphoned into a narrower temporal, the leads to further pulse shortening. SPM contributes to pulse chirp and together with negative GVD, leads to pulse compression. A final balancing between both pulse shortening and broadening will lead to a solitonic solution, shorter than what would be expected from the analysis carried out in [13].

To achieve this balance, it is necessary to introduce negative dispersion inside the cavity, to counter the dispersion of the cavity length itself. This is usually done by using a pair of high-quality prisms, which spacially spread the pulse frequencies, causing higher frequencies to travel a longer distance than lower frequencies, giving the latter opportunity to “catch up”. Thus dispersion can be adjusted to whatever value produces the shortest pulse by varying prism insertion. Dielectric chirped mirrors can also be designed to introduced specific negative dispersion curves inside the cavity, with the advantage of being reflection based as opposed to transmission based, thus introducing less loss in the cavity.
Figure 11: Nonlinear loss exploiting the optical Kerr effect. Nonlinear loss can be introduced by a physical aperture or pump-mode matching inside the gain medium. The intracavitary lens seen in the image is the result of Kerr lens effect, not an actual physical lens.

5.2 Kerr Lens Mode-Locking

First observed in 1991 [5], mode-locking via the Kerr effect uses the laser medium as the source of the intensity-dependant loss. It should be made clear beforehand that the laser medium does not exhibit saturable absorption as described before, although it produces results similar to SAML using an absorber with instantaneous response time. KLM is only possible with solid state lasers.

When a highly intense light beam passes through a physical medium, the refractive index of the medium changes and is written as:

\[ n = n_0 + n_2 I \]  

(37)

Both \( n_0 \) and \( n_2 \) are constants for the particular medium, but the total refractive index \( n \) varies with the intensity of the light traversing the medium. This is caused by deformation of the electronic cloud due to the intense electric field. One should note that \( n_2 \) is a very small coefficient, which is why this effect is only seen when using coherent high intensity sources.

Suppose now that a beam is incident on a medium showing the Kerr effect, with a given transverse profile, Gaussian for instance. The intensity of the beam in the center is higher than in the edges, causing the nonlinear part of the index to vary in space. For a Gaussian profile: \( I = I_0 \exp\left(-2(r/w)^2\right) \) where \( w \) is the beam spot size. The phase acquired by the light due to the nonlinear part of the index over a length \( l \) is

\[ \delta \phi = 2\pi n_2 il/\lambda = (2\pi n_2 I_0 l/\lambda) \exp\left(-2(r/w)^2\right) \approx \left(2\pi n_2 I_0 l/\lambda\right) \times \left[1 - 2(r/w)^2\right] \]  

(38)

In this first order approximation, being parabolic in \((r/w)^2\) means that this is equivalent to introducing a spherical lens inside the medium. This is called the Kerr lens effect.

More intense modes will be focused more strongly and, by using an aperture, intensity-dependent losses can be introduced in the cavity. The resulting scenario is analogous to mode-locking with a very fast saturable absorber. It is also possible to design the cavity so that high intensity modes are better matched with the gain volume created inside the laser medium by the pump mode. Thus, high intensity modes will experience more gain that their low intensity competitors, without the need of a physical aperture.
Achieving KLM in Ti:sapphire systems was a revolutionary milestone in laser physics. A typical Ti:sapphire KLM system only has 2 intracavitary elements: the crystal, and prism pair for introducing negative dispersion. This makes commercial systems very easy to build and led to a great growth in the number of groups equipped with femtosecond sources, even some with little experience in ultrafast optics.

There is one downside to KLM lasers when compared to SAML. Using SAML, especially when produced by SESAM, the mode-locking can be optimized separately from the cavity and employed in many different cavity geometries in which KLM does not work. While KLM delivers equal performance with easier implementation, it lacks in flexibility.

6 Saturable Absorption and Graphene

So far, we have addressed laser pulse theory and pulse generation. The effects of a saturable absorber inside a laser cavity have been discussed, arriving at a periodic pulse solution. We now shift towards solid state physics and material science to better understand how saturable absorbers work and how graphene can be a game changer in yet another branch of physics and technology.

6.1 Saturable Absorption Description

Although saturable absorption is a fairly complicated process, it can be completely described using a two-level system [9]. After understanding the two-level system, we can move to understanding the role of the band structure of a given material and nonlinear optical properties that result from different band structures.

We start off with a two-level system composed of a ground state (level 1) with energy $E_1$, populated by $N_1$ atoms per unit volume and an upper state (level 2) with energy $E_2$, populated by $N_2$ atoms per unit volume. We define beforehand some useful quantities: the total number of atoms per unit volume $N = N_1 + N_2$, the difference in occupation $\Delta N = N_1 - N_2$, and the energy difference between the levels $\Delta E = E_2 - E_1$. The system can be affected by 4 major phenomena of relevance to this work: 1) Spontaneous Emission; 2) Stimulated Emission; 3) Absorption; 4) Non-radiative decay.

Spontaneous emission occurs when an atom is in level 2. Since $E_2 > E_1$, the atom will tend to decay to level 1. This can be done by emitting a photon with energy equal to $\Delta E$, with frequency

$$\nu_0 = (E_2 - E_1)/h$$  \hspace{1cm} (39)

This results in a change of population proportional to the population $N_2$:

$$\left(\frac{dN_2}{dt}\right)_{sp} = -AN_2$$  \hspace{1cm} (40)

$A$ is a positive constant called the spontaneous emission rate. Spontaneous emission can also be characterized by a lifetime $\tau_{sp} = 1/A$. It is important to note that $A$ (and as such $\tau_{sp}$) depends only
on the particular transition.

For stimulated emission, a similar expression can be written:

\[
\left( \frac{dN_2}{dt} \right)_{st} = -W_{21}N_2 \tag{41}
\]

where \( W_{21} \) is the stimulated emission rate. There is however one very crucial difference. Stimulated emission is, as the name indicates, a stimulated process and as such it depends not only on the transition but also on the intensity of the incident electromagnetic wave that stimulates the process.

\[
W_{21} = \sigma_{21}F \tag{42}
\]

where \( F \) is the photon flux and \( \sigma_{21} \) is the stimulated emission cross section. Like \( A_1 \), \( \sigma_{21} \) depends only on the transition.

Much like stimulated emission, absorption is a stimulated process and again, we write:

\[
\left( \frac{dN_1}{dt} \right)_{a} = -W_{12}N_1 \tag{43}
\]

Again:

\[
W_{12} = \sigma_{12}F \tag{44}
\]

where \( \sigma_{12} \) depends only on the transition and is called the absorption cross section.

Figure 12: Two-level system interacting with a high intensity e.m. wave [9].

It was shown by Einstein that \( \sigma_{12} = \sigma_{21} = \sigma \) and \( W_{12} = W_{21} = W \) when the two levels are non-degenerate.

Lastly, non-radiative decays account for any manner of decay from level 2 to level 1 which does not involve the emission of photon. It can be the result of electron-electron scattering, electron-phonon scattering (lattice scattering) and other similar processes. Being a spontaneous process, it does not depend on the incident field and is described in a similar way to spontaneous emission:
\[
\frac{dN_2}{dt}_{nr} = -\frac{N_2}{\tau_{nr}} 
\]

\(\tau_{nr}\) depends not only on the transition but also on the characteristics of the surrounding medium.

Well all the above are considered for our two-level system, we obtain:

\[
\frac{dN_2}{dt} = -W(N_2 - N_1) - \frac{N_2}{\tau} 
\]

where

\[
\frac{1}{\tau} = \frac{1}{\tau_{sp}} + \frac{1}{\tau_{nr}} 
\]

Using the notation defined beforehand:

\[
\frac{d\Delta N}{dt} = -\Delta N \left( \frac{1}{\tau} + 2W \right) + \frac{1}{\tau} N_t 
\]

In the steady-state: \(d\Delta N/dt = 0\) and we obtain:

\[
\Delta N = \frac{N_t}{1 + 2W\tau} 
\]

In order to remain in steady-state and maintain this population inversion, the material needs to absorb a constant amount of power per unit volume given by:

\[
\frac{dP}{dV} = h\nu W\Delta N = h\nu \frac{WN_t}{1 + 2W\tau} 
\]

The system is said to be saturated when the incident photon flux \(F\) is so high that the stimulated emission and absorption rates \(W = \sigma F\) are vastly superior to the spontaneous decay rate (radiative and non-radiative) \(1/\tau\). Hence at saturation:

\[
W\tau \gg 1 
\]

And (50) becomes:

\[
\left( \frac{dP}{dV} \right)_s = \frac{h\nu N_t}{2\tau} 
\]

Upon closer inspection, the power per unit volume needed to maintain the system saturated is equal to the power lost by the material due to the decay of the upper state population when \(N_1 = N_2 = N_t/2\).

This is to be expected, since the absorption and stimulated emission coefficients are equal. This means that when these processes occur much more frequently than spontaneous decay, the latter can be neglected, and the former equal each other leading equal level population. This is in fact why laser
action cannot occur in two-level systems, where $N_2$ can never be greater than $N_1$ and thus population inversion necessary for laser action is never achieved.

There is a more convenient way to express equations (49) and (50). First, we write $W = \sigma I / h\nu$, since $F = I / h\nu$, and now (49) and (50) can be rewritten as:

$$\frac{\Delta N}{N_i} = \frac{1}{1 + (I/I_s)} \quad (53)$$

$$\frac{dP/dV}{(dP/dV)_s} = \frac{I/I_s}{1 + (I/I_s)} \quad (54)$$

where we define the saturation intensity:

$$I_s = h\nu/2\sigma\tau \quad (55)$$

Studying how the population is affected by saturation, will enable us to understand how saturation affects absorption, since the absorption coefficient of a material is defined as (for $N_1 > N_2$):

$$\alpha = \sigma \Delta N \quad (56)$$

So far, we have been very simplistic with the transition frequency: we have assumed that only photons with the exact energy of the transition can interact with the system and cause stimulated processes, i.e. $\sigma \neq 0$ only when the incident photon frequency $\nu$ equals the transition frequency $\nu_0$. In reality, the system will interact with photons with frequencies around $\nu_0$ with varying intensity, result in $\sigma$ being described by a distribution around $\nu_0$:

$$\sigma \propto g(\nu - \nu_0)$$

where $g(\nu - \nu_0)$ is called the lineshape of the system and applies for both absorption and stimulated emission. This is called line broadening and comes in two varieties: homogeneous and inhomogeneous broadening.

Homogeneous broadening occurs when the absorption line of each atom is broadened in the same way. An example of homogeneous line broadening mechanism is collision broadening, where collisions between atoms (in gases) or atoms and phonons (in solids) introduce random phase shifts in the electric fields of the atoms. Since relative phase is important in interaction processes, the incident field will not be viewed by the atom as monochromatic. Homogeneous broadening results in a Lorentzian lineshape.

Inhomogeneous broadening corresponds to distributing the atomic resonance frequencies of the atoms over a range of frequencies. This results in broadening of the overall line of the system. In solid state laser, this is mainly caused by material inhomogeneities which cause local variation of the electric field producing, via Stark effect, a local variation of the energy levels and thus of the transition frequencies. This is particularly relevant for ionic glasses. For gaseous media, the Doppler effect will induce a shift in the frequency seen by an atom moving with a particular velocity, relating the
absorption lineshape to the velocity distribution of the medium. Inhomogeneous broadening results in a Gaussian lineshape.

The full derivation of $\sigma$ requires extensive quantum electrodynamics deduction, and we shall only cite the final result:

$$\sigma = \frac{2\pi^2}{3n\varepsilon_0 c h} |\mu|^2 \nu g(\nu - \nu_0) \quad (57)$$

Using (56) and (57), we obtain:

$$\alpha = \frac{2\pi^2}{3n\varepsilon_0 c h} |\mu|^2 \Delta N \nu g(\nu - \nu_0) \quad (58)$$

To evaluate how saturation affects absorption, we imagine an ideal pump-probe experiment. Pump-probe experiments involve two beams: the pump beam with very high intensity $I(\nu)$, which interacts with the system; and the probe beam with much lower intensity $I'(\nu') \ll I(\nu)$ so as to not perturb the system and measure how the system is altered by the pump beam. In this case, the pump beam is used to saturate the material, while the absorption of the probe is measured. To ensure that the probe beam interacts only with the saturated region, the beams must be made collinear.

Looking at (53) and (58), we can write:

$$\alpha = \frac{\alpha_0}{1 + I/I_s} \quad (59)$$

where

$$\alpha_0 = \frac{2\pi^2}{3n\varepsilon_0 c h} |\mu|^2 N_1 \nu' g(\nu' - \nu_0) \quad (60)$$

Equations (59) and (60) show two very important results. Firstly, as expected, when the pump intensity increases, the probe absorption coefficient decreases (this much was expected from saturable absorption). Yet, it was not obvious beforehand that the lineshape of the absorption remained unaltered, but it is seen that the absorption line $g(\nu' - \nu_0)$ is not affected by $I_s$. Figure 13 shows absorption coefficients for three values of $I/I_s$. 

40
6.2 Graphene

In this section we discuss the optical properties of graphene, especially its nonlinear properties. We will then talk about the place graphene holds in the current pulse generation scene, comparing it with its main competitors, the SESAM, and review how graphene has been used in pulse generation and what remains to be done and studied.

6.2.1 Graphene Band Structure

Postulated in 1947 [15], and awarding a Nobel prize in 2010 [16], graphene is a crystalline form of carbon, forming a nearly 2D hexagonal lattice of carbon atoms. This 2D gas of Dirac fermions shows notable transport properties, an amazingly high electrical conductivity [17] and a constant low intensity absorption over a very broad range of frequencies [18]. More importantly here, it has been demonstrated to be a saturable absorber [19, 20, 21, 22].

When first produced by exfoliation of highly-ordered pyrolytic graphite (HOPG) in 2004 [16], graphene could not be produced in large scale samples, but the first reports on graphene properties initiated an extensive search for scalable graphene production techniques. Among these techniques are chemical vapor deposition (CVD) [23, 24], thermal decomposition of SiC [25] and other chemical methods [26]. The size and the quality of graphene flakes obtained using these methods have opened a way to verify experimentally theoretical predictions on the properties of two-dimensional (2D) systems.

Figure 14 shows the direct and reciprocal lattice structures of graphene. The primitive cell contains a carbon atom at each of two sublattice sites labeled A and B, separated by a bond length of $d = 1.42\text{Å}$. The outer shell of carbon atoms contains 4 electrons, 3 of which are tight bonded, forming the $\sigma$-bonds with neighboring atoms. The fourth electron is involved in the $\pi$ and $\pi^*$ bonds. These weaker bonds are responsible for most the optical and electronic properties of graphene. In the tight-binding approximation, the dispersion of the valence and conduction bands can be calculated as [27]:

![Graphene Band Structure](image-url)

Figure 13: Probe absorption coefficient for various values of pump intensity. Note it exhibits a Lorentzian shape for all values of $I$ (typical for homogenous broadening)
Figure 14: (a) Crystal lattice structure of graphene. (b) Reciprocal lattice structure of graphene.

Figure 15: Electron dispersion of graphene in the first Brillouin zone. Detail on the right shows the Dirac cone around the $K$ point. Image from Centro de Física do Porto (www.faraday.fc.up.pt).

\[ E(k_x, k_y) = \pm \gamma_0 \left[ 1 + 4 \cos \left( \frac{\sqrt{3}}{2} k_x a \right) \cos \left( \frac{1}{2} k_y a \right) + 4 \cos^2 \left( \frac{1}{2} k_y a \right) \right]^{1/2} \]

where $\gamma_0$ is the nearest-neighbour hopping energy and $a = \sqrt{3}d = 2.46\text{Å}$ is the lattice constant. The "+" and "−" correspond to electrons and holes, respectively. This dispersion relation is plotted in Figure 15.

One of the most notable aspects of graphene is its linear dispersion in the vicinity of the Brillouin zone edge, i.e., at the $K$ and $K'$ points. At these points, the top of the valence band and the bottom of the conduction band meet, forming a dual cone structure touching at the Fermi energy $\epsilon_F = 0$. Around these points the dispersion for holes and electrons is described by the Dirac equation:

\[ E \left( \vec{k} \right) = \hbar v_F \left| \vec{k} \right| \tag{61} \]

where $v_F \approx 10^6 m/s$ is the Fermi velocity in graphene. This linear dispersion along with zero bandgap, give graphene unique electric and optical properties.
Figure 16: Graphene shows very constant absorption in a very broad frequency range, decreasing slightly for shorter wavelengths. Graphene’s absorption is nearly constant in the 700-900 nm range, the main part of the emission spectrum of Ti:sapphire.

6.2.2 Graphene Optical Properties

Electrons in the vicinity of the $K$ and $K'$ points determine the optical properties of graphene in the visible and infrared regions of the spectrum. Since graphene shows no bandgap and linear dispersion, absorption of any frequency is possible. Moreover, as long as electrons near the $\Gamma$ point (center of the Brillouin zone) are not involved the absorption process, the absorption coefficient of graphene is independent of the frequency over a very wide spectral range and equal to [28, 29]

$$\pi \alpha \approx 2.3\%$$ \hspace{1cm} (62)

where

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}$$ \hspace{1cm} (63)

is the fine structure constant. Linear dispersion also causes graphene to show exceedingly high optical nonlinearities [30]. While centrosymmetric media such as graphene show no second-order susceptibility $\chi^{(2)}$ (nor any even order susceptibilities), graphene shows an amazingly high $\chi^{(3)}$, which is responsible for saturable absorption [31] and intensity dependent refractive index (Kerr effect). Very high higher order $\chi$ in graphene also result in very efficient high harmonic generation [32].

6.2.3 Saturable Absorption in Graphene

Figure 17 shows the process of saturable absorption in graphene. In a similar fashion to other semiconductor materials, saturable absorption in graphene results from Pauli blocking. In (b), electrons are excited from the valence to the conduction band by an incident pulse, creating a non-equilibrium ensemble of electrons and holes centered at half of the excitation photon energy with
Figure 17: The saturable absorption of graphene near the Dirac point. (a) The low-energy band structure of graphene. Blue cone is the valence band. Red cone is the conduction band. (b) A photon with energy $E = \hbar \omega$ excites an electron from the valence band to the conduction band. (c) Electrons excited into the conduction band lose energy and momentum to the crystal lattice and to electron-electron scattering; the holes they left behind behave similarly. This allows new electrons to be excited to this same energy level and contributes to intraband relaxation time of the absorber. (d) At high enough peak intensities and pulse fluences, enough electrons have been excited into the valence band that there are no open states of lower energy in the conduction band. Absorption and stimulated emission reach a steady state and the absorber is saturated. [33]

respect to the Dirac point. After the excitation, in (c), a fast $(7 - 120 \text{fs} \ [34])$ electron thermalization through electron-electron scattering takes place, resulting in a hot Fermi-Dirac distribution. A slower (picosecond) electron-phonon scattering will then further cool the electrons. After that (not shown in the figure), electron-hole recombination will dominate until the equilibrium electron and hole distribution (as seen in (a)) is restored. The electron-hole recombination gives rise to a broadband photoluminescence [35].

This, however, is just the case for linear absorption when under low intensity. As the the intensity increases, so will the carrier pairs concentration and it will eventually be much greater than the intrinsic concentration. This causes the states near the edge of the conduction and valence bands to fill, blocking further absorption as seen in (c). If the intensity is maintained at a high enough value, it will compensate for the scattering and recombination, reaching a stationary state.

Other effects occur when graphene is subjected to high intensity, the most relevant for our purposes being two-photon absorption (TPA) [36]. This is another high intensity effect where the material interacts with two photons $\omega$ at once, resulting in a $2\omega$ transition. This typically occurs for intensity values higher than the saturation intensity, and results in an absorption increase after the decrease due to saturation. This can compromise mode-locking efficiency for high intracavitatory intensities. Quantum perturbation theory predicts this effect to be 100 times more intense in bilayer graphene [36] and is a good experimental indicator of the quality of a monolayer sample. Figure 18 shows the effect of TPA in saturation absorption measurements.
Figure 18: Absorption saturation measurements performed in [37]. While the main figure shows regular absorption saturation, the inset shows a rollover in the high fluence region. This is due to TPA and causes transmission to drop.

6.2.4 Graphene in the Current Mode-locking Scene

Currently, SESAM are the most widely used device for SAML. SESAM have the advantage of being very compact and customizable. They can be tailor made according to design specifications and can also be optimized separately from the cavity. This means that the cavity dynamics can be changed with no change to its geometry.

But specificity is also the source for their main flaws. SESAM are very complex and expensive multilayer devices with a lengthy fabrication procedure, and can not be designed for some central emission frequencies. Being based on Bragg reflectivity, they only work on a fairly narrow frequency band, which limits pulse duration. Also, being very complex, they are very susceptible to damage, having short work lifetimes when used in high repetition rate lasers. While SESAM have produced notable results, there is great interest in finding an alternative that provides better results and less technical complication.

With very intense nonlinear properties, nearly achromatic linear absorption and extremely fast carrier dynamics, graphene appears to outperform current saturable absorbers. The remarkably large absorption of graphene results in lower saturation intensity than traditional semiconductor materials such as gallium arsenide (GaAs). The 2.3% absorption of a single layer of graphene is more than twice that of a 10nm thick GaAs quantum well. Due to its nearly constant absorption over a wide spectral range, graphene can be saturated in a wide frequency range. This is important for mode-locking laser with exotic central wavelengths, where there are no efficient mode-locking solutions. So far, graphene has been used to mode-lock tunable optical fiber lasers with great success [38, 39, 40] and exotic lasers with unconventional emission frequencies, for which there are no available SESAM [41, 42, 43].

Being used mostly in fiber systems and exotic lasers, pulse durations produced using graphene fall short of what can be obtained by the most competitive laser systems, namely Tisapphire lasers.
Titanium:sapphire has one of the widest emission bands known today and is the ideal system to study the properties and effects of graphene in ultra-broadband systems. Prior to this work, only one group had produced results with graphene in a Ti:sapphire setup. Constant broadband absorption is also key for Ti:sapphire lasers, where a small absorption window would limit the width of the emission band and thus limit the minimum pulse duration.

Carrier relaxation times are also a very important factor for SAML, as these will dictate duration of the gain window where the pulses form. If these are too long, the medium will remain saturated for a long time after the initial saturation, leading to a long net gain window and long pulses are formed, regardless of how broad the emission band is. For fs pulse generation, the fast electron-electron scattering is what counts and graphene shows an exceedingly short fast relaxation constant, at 7 – 120fs [34], depending on sample quality. These times are on par with today’s fastest SESAM devices [44].

Furthermore, graphene’s modulation depth, i.e. the maximum change in absorption by incident light with a given wavelength, is vastly superior to its direct competitors SESAM; both in value, at 66.5%; and in bandwidth, where the optical properties of graphene are nearly independent of frequency, while SESAM only work in a fairly narrow band.

Graphene is also durable enough to withstand high repetition-rate systems [45], and can be deposited on optical-quality low loss substrates, making it much more practical to use and maintain.

6.3 Pulse Measurement

Having a pulse short enough to sample any event we wish to measure has its problems. How can we measure and characterize what we hope to be the shortest event our lab can produce? Common
measurement devices such as oscilloscopes become unsuitable for even relatively long pulses around picoseconds in duration.

Suppose we measure a pulse with a certain abstract device. This device is characterized by a spectral response \( H(\omega) \) or, equivalently, its impulse response function \( h(t) \). Assuming a linear system, what will in fact be known from the measurement is not the pulse amplitude itself \( a(t) \), but rather a signal \( s(t) \) given by the convolution

\[
s(t) = a(t) \otimes h(t)
\]  
(64)

Convolution operations state that \( \psi(t) \otimes \delta(t) = \psi(t) \), where \( \delta(t) \) is the Dirac delta function. Important conclusions come from this. If \( h(t) \) is much shorter than any feature of \( a(t) \), it can be approximated by a Dirac delta function and the measurement yields \( a(t) \). However, when dealing with short pulses, it is the other way around: \( a(t) \) is much shorter than the impulse response of any common measurement devices and thus the measurement yields only \( h(t) \).

But there is one thing as fast as the pulse we want to measure: the pulse itself. By using nonlinear detection systems, there are several options for self-referencing measurements.

### 6.3.1 Second Order Autocorrelation

The most straightforward and widely used measurement is the second-order autocorrelation. Figure 20 shows a basic setup for a pulse autocorrelator. An incident pulse is split by a 50/50 beam-splitter into two sub-pulses, each propagating through one arm of a Michelson interferometer. They are then focused onto a nonlinear detector consisting of a frequency doubling crystal, a high-pass filter to remove the original frequency signal, and a photodiode with a bandgap greater than the photon energy to make two-photon absorption possible.

By varying the length of one of the interferometer’s arms, the difference between pulse arrival times is varied. When the arms length match, the detected signal reaches its maximum, decreasing symmetrically around this point, as the field seen by the detector is the coherent addition of the two sub-pulses. The intensity of the signal registered by the detector during a time \( 2T \) is proportional to

\[
\frac{1}{2T} \int_{-T}^{+T} \left( |E(t) - E(t - \tau)|^2 \right)^2 dt
\]  
(65)

This signal is called the fringe-resolve interferometric autocorrelation (FRAC). When the integration time \( T \) is much larger than the field period, this signal is proportional to the second-order autocorrelation function of the complex electric field:

\[
G_2(\tau) = \int_{-\infty}^{+\infty} \left| \tilde{E}(t) - \tilde{E}(t - \tau) \right|^2 dt
\]
Figure 20: Typical autocorrelation configuration

\[ G_2(\tau) = \int_{-\infty}^{+\infty} \left[ \tilde{E}^2(t) \tilde{E}^*(t) + \tilde{E}^2(t) \tilde{E}^* (t - \tau) + \tilde{E}^2 (t - \tau) \tilde{E}^* (t) + 2 \tilde{E}(t) \tilde{E} (t - \tau) \right] d\tau \]

Expanding this expression:

\[ G_2(\tau) = \int_{-\infty}^{+\infty} \left\{ \tilde{E}^2(t) \tilde{E}^* (t) + \tilde{E}^2(t) \tilde{E}^* (t - \tau) + \tilde{E}^2(t - \tau) \tilde{E}^* (t) + 2 \tilde{E}(t) \tilde{E} (t - \tau) \right\} d\tau \]

\[ = \int_{-\infty}^{+\infty} \left\{ I^2(t) + I^2(t - \tau) \right\} d\tau \]

This final form has four terms, each with a specific significance.

1. \( \int_{-\infty}^{+\infty} I^2(t) + I^2(t - \tau) d\tau \) is a constant background

2. \( \int_{-\infty}^{+\infty} 4[I(t) + I(t - \tau)] \text{Re} \left[ \tilde{E}(t) \tilde{E}^* (t - \tau) \right] d\tau \) is the sum-of-intensities weighted interferogram of \( \tilde{E}(t) \)

3. \( \int_{-\infty}^{+\infty} 2\text{Re} \left[ \tilde{E}^2(t) \tilde{E}^* (t - \tau) \right] d\tau \) is the interferogram of the second harmonic

4. \( \int_{-\infty}^{+\infty} 4I(t) I(t - \tau) d\tau \) is the autocorrelation of \( I(t) \)
The interferometric autocorrelation simply combines several measurement of the pulse into one (admittedly complex) trace. Conveniently, however, they occur with different oscillation frequencies: 0, \omega and 2\omega.

![Graph showing interferometric and intensimetric autocorrelation](image)

Figure 21: Simulated intensimetric and interferometric autocorrelation of the same pulse.

When the two sub-pulse beams are superimposed in the detector in a non-collinear fashion, \(G_2\) is reduced to terms 1. and 4. in what is called a non-collinear intensimetric autocorrelation. One advantage in non-collinear autocorrelation is that, if SHG is used as the nonlinear process, the background term can be totally suppressed, since phase-matching results in the signal being emitted in a different direction with respect to the input pulses, resulting in a background-free autocorrelation. On the other hand, intensimetric autocorrelation has the disadvantage of a lower peak-to-background ratio. When the sub-pulse arrive with a large delay (when \(\tau = \infty\)) only the background term is left, and equal to 2 \(\int_{-\infty}^{\infty} I^2(t) \, dt\). For the peak value, at \(\tau = 0\), intensimetric autocorrelation counts only terms (67) and (70) to yield 6 \(\int_{-\infty}^{\infty} I^2(t) \, dt\) while interferometric comes in with all four terms to yield 16 \(\int_{-\infty}^{\infty} I^2(t) \, dt\). Thus, interferometric autocorrelation has a peak-to-background ratio do 8:1 while intensimetric autocorrelation only has 3:1, which is certainly a big advantage but not the only one.

The most important parameter of an AC trace is its FWHM, \(\Delta \tau\). From there, a suitable pulse shape needs to be selected, then an expected signal is computed from the autocorrelation and both are compared. For different expected shape pulses, different deconvolution factors are applied to go from the FWHM of the AC signal \(\Delta \tau\) to the FWHM of the pulse \(\Delta t_p\). Table 1 shows the factors for the important cases of Gaussian and sech\(^2\) shaped pulses.

<table>
<thead>
<tr>
<th>Pulse shape</th>
<th>(I(t))</th>
<th>(\Delta \tau /\Delta t_p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaussian</td>
<td>(\exp \left(-4 \ln (t \Delta t_p)\right)^2)</td>
<td>1.414</td>
</tr>
<tr>
<td>Hyperbolic secant</td>
<td>(\text{sech}^2 \left[2 \ln \left(1 + \sqrt{2} t / \Delta t_p\right)\right])</td>
<td>1.543</td>
</tr>
</tbody>
</table>

Table 1: Autocorrelation to pulse width conversion factors

The main flaw of FRAC is the lack of reliable phase information. While that may not be a big
issue for long pulses (longer than 20fs) since long pulses tend to have less structure features and their relative effect is smaller. Still, GDD and third order dispersion (TOD) are impactful in the pulse shape, resulting in different pulses for the same frequency spectrum. More recent techniques overcome this problem, being able to retrieve full envelope and phase information. Such an example is the dispersion scan or “d-scan” technique, recently developed at IFIMUP-IN [46]. This technique consists in measuring the spectrum of the second-harmonic of the pulse as a function of dispersion. Dispersion is varied by using two glass wedges and varying their insertion. The spectrum of the second-harmonic is dependent on the dispersion but also on the phase of the electric field. A 2D plot is obtained for spectral intensity vs. dispersion and a phase retrieving algorithm is used to best recreate the data measured, calculating the spectral phase.
Part III

Experimental Setup

The objective of this work is to create a laser system where ultrashort pulses are produced by saturable absorption in graphene.

Designing and building a laser cavity from scratch is an endeavour far beyond the context of a MSc thesis. To make this work possible, we opted to take apart an already working laser system and modify it, saving both time and resources (as only a small number of parts had to be purchased or made).

But while it is certainly easier than starting with and empty table and a set of boxed components, modifying an already existing system poses its own set of challenges. This means we have to work around and already existing setup, being as little invasive as possible.

A laser system built to study the effects of graphene as an intracavity element can also be used to study other materials as intracavity elements. We are building a system that can be used for further work after this, providing unique study conditions for samples such as thin films. There are other 2D materials besides graphene, whose optical properties have not been extensively studied. With this setup, we have the opportunity to build upon the work done here and produce results with materials other than graphene.

Measurements of saturable absorption were performed on two graphene samples, using sub-10fs pulses. The setup for these measurements was very complex, involving pulse compression using ten chirped mirrors and tight focusing on the sample, and will also be extensively analyzed.

7 Initial KLM Ti:Sapphire Setup

Work started on a homemade Ti:Sapphire KLM oscillator. While there are many commercial systems for KLM Ti:sapphire oscillators, namely Rainbow by Femtolasers (used to feed a chirped pulse amplifier in another setup at IFIMUP-IN), this system was designed and built to offer higher levels of performance and flexibility. Extensive cavity modifications are possible, since it is not the standard “enclosed in a box” system. Figure 22 shows the setup of the cavity. It was originally designed and built by professor Helder Crespo during his PhD work in Lisbon [47]. It was brought to FemtoLab and re-assembled by Alexandra Amorim for her PhD work [48].

The crystal used was custom ordered to Crystal Systems, tailor-made for this setup according to provided specifications. Every mirror used is dielectric and an intracavity prism pair is used for dispersion compensation, very important for dispersion-managed mode-locking. An external compression system is also used, to compensate for the stretching the pulse suffers once it leaves through the output coupler. Extracavitary compensation is important and adds much to the laser’s flexibility, as the pulses can be used for a number of applications and experiments, and will most likely travel different distances when used with different
Figure 22: Initial KLM setup as used in [48]. The setup includes one additional prism pair to compensate the dispersion (and hence temporal stretching) the pulse experiences after exiting the cavity. After exiting through the output coupler, the beam is reflected on the far left, crossing the left bottom prism, followed by the right bottom prism. On the bottom right, the beam is elevated using a periscope, reversing its path but now crossing the top prism pair. It finally passes above the mirror where it was first reflected as it existed the output coupler.

Figure 23: Periodic pulse output (left) and spectrum (right) obtained with the initial setup by Alexandra Amorim [48]. A slit was placed between the intracavity prisms, where the spectral components of the pulse are spatially separated (as we shall discuss ahead), allowing for laser tuning.

setups. There is no physical aperture in the cavity, mode-locking is achieved by pump mode matching. This system produced notable spectra and pulses and was used in two PhD works, regarding its design and characterization [47] and supercontinuum generation in optical fibers [48].
Figure 24: Supercontinuum generation in a hollow fiber (part of the PhD work of Alexandra Amorim) [48]

8 New Graphene Setup

After looking at the results obtained using the already built Ti:sapphire setup, the step to take apart and significantly alter it was a well-thought step with plenty of planning and simulation. This section is divided into two sections. This first section addresses the calculations and simulation done to determine the new design. These were carried out using a laser cavity simulation software, WinLase. The second deals with more technical aspects, focusing on the implementation of the optimal conditions obtained in the first section.

8.1 Preparation

8.1.1 Beam Focusing and Spot Size

The most important point when designing a laser mode-locked using saturable absorption is ensuring saturation occurs. As mentioned before, saturation intensity varies modestly between samples, and a reference value of 0.53MW/cm$^2$ [49] was used. To reach such high values of intensity, the beam must be focused in a small area of the graphene layer.

Firstly, simple calculations were performed to determine an estimated value of the area needed to deliver these intensities. Intracavitary power is calculated using the output power of the laser and the reflectivity of the output coupler. The output coupler of the system has a reflectivity of 96.75%, and considering a modest output power of 300mW, we calculate an intracavitary power of 9.23W. For a gaussian beam, peak intensity is calculated as

\[ I = \frac{1.88P}{\pi w^2} \]  

(71)
where \( P \) is the intracavitary power and \( w \) is the beam waist at the spot. Using (71), we estimate saturation to occur when beam waist is smaller than 32.3 \( \mu \)m.

The focusing system chosen was a dielectric spherical chirped mirror pair, with the graphene placed in the focal point between them. The beam waist at the focal point is determined by the focal distance of the mirrors

\[
w_0 = \left( \frac{2\lambda}{\pi} \right) \left( \frac{f}{D} \right)
\]

where \( f \) is the focal distance of the lens and \( D \) is the beam diameter incident on the lens. Smaller focal distances will provide the smallest beam waist at the focus but they also pose setup constraints, so the largest focal distance that still guarantees saturation is the goal. We found three commercially available suitable mirrors, with focal distances \( f \) of 2.5 cm, 3.75 cm and 5 cm. Smaller focal distances allow for smaller beam waist at the focal point, but may be impossible to implement in setup, due to space constrictions. Figure 25 shows a simulation of the spot size on the face of the substrate as a function of the substrate position for the \( f = 3.75 \) cm focal length mirror pair. The results are well below the 32.3 \( \mu \)m required for saturation. The \( f = 3.75 \) cm pair was chosen as the compromise between obtainable spot size and ease of implementation.

Figure 25: Spot size at the sample surface as a function of substrate position. The distance is measured from the first sample sub-cavity mirror, i.e. the one between the sample and the crystal sub-cavity. Figure produced using WinLase.
8.1.2 Loss and Aberration

As usual, to minimize reflection losses, the substrate containing the graphene must be placed at a Brewster angle with the beam path between the two mirrors. The Brewster angle depends on the refractive index of the substrate, made of fused silica, $n_{\text{silica}} = 1.453$ at 800nm. It was calculated that

$$\theta_B = \arctan \left( \frac{n_{\text{silica}}}{n_{\text{air}}} \right) = 55.5^\circ$$  \hspace{1cm} (73)

Brewster angle placement has one inconvenience: it introduces astigmatism in the cavity. There is a break in symmetry between the sagittal and tangential planes of propagation. As seen in Figure 26, when the beam enters the silica plate placed at Brewster angle, it is refracted and becomes wider when inside the medium. For gaussian beams, divergence decreases with increasing beam waist. Since this beam broadening only occurs in the sagittal plane, the beam becomes less divergent in this plane than in the tangential plane. This affects the stability region, causing the stability maxima to be misaligned.

To compensate for this, we used off-axis reflection in the dielectric mirrors at a specific angle, which introduces symmetric astigmatism. The correction angle depends on the focal length of the mirrors and was also a determining factor in choosing the mirror pair.

8.1.3 Other Considerations

Matricial optics state that afocal systems, such as a the graphene sub-cavity, can be designed to produce a unitary matrix. This means that the rest of the cavity can remain unaltered, which is vital. We must ensure that the cavity is stable when $X+Y$ (seen in Figure 29) equals $Z$ (seen in Figure 22). This will ensure our system is stable without the need for further alterations in the placement of other already existing cavity elements.
Figure 27: Cavity stability region with respect to the distance between the first sub-cavity mirror (cystal side) and the graphene layer. Both images show stability astigmatism, due to incorrect mirror angles. Undercompensation in the left (7°), overcompensation in the right (9°). Figures produced using WinLase.

Figure 28: Proper astigmatism compensation with both mirrors tilted at 8°. The stability maxima of the sagittal and tangential planes have been made to coincide in the left stability region. This is the region where the laser will operate. Figure produced using WinLase.
8.2 Implementation

In this section, we will discuss more technical aspects of the cavity construction process. Modifying an existing cavity instead of designing one from scratch certainly saves some time and provides a comfortable safety net. On the other hand, having to work around an already built design can be a major impairment when it comes to implementing the calculated optimal design. It is also important to have adjustments for the most important parameters inside the new sub-cavity, such as mirror separation and graphene position. With such a small separation between the mirrors and working around already existing work, implementing the new design took some creative thinking. In the end, the cavity took shape as seen in Figure 29.

8.2.1 Previous Work

Only one work has been published using graphene to mode-lock a Ti:sapphire laser [37]. While holding the record for shortest pulse produced by graphene SAML, there are a few aspects of the setup that can be improved.

As is usual, this setup includes an intracavitary prism pair for dispersion compensation. However, placing it just before the output coupler means the pulses exit the cavity with spatial chirp, i.e. with its frequency components spatially separated. While this may not be a problem for narrow bands, separation becomes more severe as the spectrum broadens.

The focusing system is different from what was used in this work. Replacing one of the already placed cavity mirrors for a spherical mirror was not a possibility. Furthermore, while this configuration has fewer elements, having a spherical mirror as the high reflectivity mirror makes the cavity more sensitive to misalignments than a plane mirror.

Also, the mirrors used in [37] were all regular dielectric mirrors. In our setup, both the crystal
Figure 30: Cavity design used by In Hyung Baek et al., capable of producing 63fs pulses.

Figure 31: While introducing negative dispersion to correct temporal pulse chirp, prism pairs introduce spatial chirp where the frequency components of the pulse are spatially separated, as seen on the right.

and graphene sub-cavities were equipped with chirped mirror pairs, which will be discussed further ahead. These introduced negative second order dispersion in the system, compensating for the GDD introduced by the graphene sample. Again, for longer pulses this may not be crucial, but dispersion-managed mode-locking becomes very important as durations decrease, as previously discussed.

Still, this design resulted in the shortest pulses ever produced with graphene, at a notable duration of 63fs.
Figure 32: Results obtained by [37]. The spectrum obtained shows a very symmetric and smooth shape. This goes to show that complex and structured spectra are not typical of graphene SML.

### 8.2.2 Graphene sub-cavity construction

Focusing a micrometric laser spot in a single layer of carbon atoms is no easy feat. Intracavitary focusing systems, commonly called sub-cavities, are very sensitive to fine alignment. The stability region when changing the mirror distance is only 1.5 mm wide and working on the edge of the stability region is not ideal, so the optimal working region is a fraction of a millimeter. Being very important in minimizing losses, the angle of incidence in the graphene also affects the distance the beam travels inside the substrate. The position of the substrate along the beam path inside the cavity is crucial, as this will determine the spot size at the graphene layer. In real life, graphene is not a perfectly homogeneous and crystalline Carbon honeycomb, and local defects can render some areas of the sample useless for our purposes. Thus it is also important to be able to control the area of incidence.

We must be able to finely vary: sub-cavity mirror distance, graphene placement along the beam path, horizontal angle and vertical tilt of the substrate and the area of incidence in the substrate. All this in a 7,22 cm length. A custom mount equipped with micrometric platforms angled at Brewster was assembled to move the graphene. One translation stage moves the graphene along the beam path, while the other, perpendicular to the sample surface, allows us to select an area of incidence without compromising position along the propagation. On top of these, the sample is placed in a substrate holder with fine vertical and horizontal angle adjustments.

There are two possible configurations for a focal system of this type: z-style and x-style. A z-style configuration is less invasive on the cavity, as the output coupler only needs to be slightly moved to the side. As seen previously, the off-axis incidence angle in the mirrors is very small, and this OC displacement would also be very small, and the alignment between the cavity and the exterior compression system would not be severely damaged. Unfortunately, spatial constraints make a z-style sub-cavity impossible to implement, as seen in Figure 33. While the substrate itself actually fits, it must be placed on a mount equipped with fine adjustments, which would obstruct the beam path. The sub-cavity was assembled in x-style and is shown in Figure 34.
Figure 33: Z-style (top) and X-style (bottom) sub-cavity comparison, design using autoCAD. The substrate fits between the beams in the Z-style but sadly does not float mid-air. The space is too small to fit a mount with the adjustments needed such as angle and position adjustment. Using an X-style sub-cavity, it is still a tight fit but feasible.

Figure 34: Graphene sub-cavity implementation. The red line is an approximate trace of the beam path. This figure illustrates the precision needed to make the configuration possible.
8.2.3 Mirrors

Since intracavity losses, even when very small, have a deep impact on laser performance, mirrors used inside laser cavities must have exceedingly high reflectivities and must also be able to withstand high intensities. Common metallic mirrors are generally out of the question. Laser cavity mirrors are almost always dielectric mirrors. Dielectric mirrors are made of many layers of different optically transparent materials. Even if the Fresnel reflection coefficient from a single interface between two materials is small (due to a small difference in refractive indices), the reflections from many interfaces can, in a certain wavelength range, constructively interfere to result in a very high overall reflectivity of the device, above 99.97%. Since they only reflect a certain range of frequencies, they are often transparent to the pump beam (this happens for Ti:sapphire lasers), which is very convenient.

Dielectric mirrors can be designed to have very specific characteristics, most importantly for pulse generation they can be used to introduce tailored negative dispersion in the cavity. These are called chirped mirrors. By varying the layer thickness, the Bragg wavelength is varied, and different frequencies travel further inside the mirror before being reflected. Using very complex designs and sophisticated nanofabrication techniques, chirped mirror can be constructed with a specific GVD curve, as seen in Figure 37. Chirped mirrors show severe oscillations in the GVD over $\lambda$ function as
Figure 36: Sub-cavity mirror reflectivity as a function of wavelength. Reflectivity is higher than 99.9% from 650nm to 950nm.

seen in Figure 37, that cannot be removed. These are due to a Fresnel reflection at the face of the mirror and coupling between the counterpropagating waves inside the mirror. While they can not be removed, by using a mirror pair they can be designed to cancel each other’s oscillations and thus produce a smoother curve. This technique is called dispersion matching.

The mirrors used for this work were made by Layertec, borrowed from Madrid (courtesy of Professor Rosa Weigand at the Universidad Complutense in Madrid). Chirped mirrors, being such complex structures, have a lengthy manufacturing process, especially when the dispersion curve is custom made. It was a stroke of good luck that Professor Weigand had a chirped mirror pair made with nominal GVD of $-150\text{fs}^2$ at 800nm. Fused silica introduces $36.6\text{fs}^2/\text{mm}$. For a 3mm plate, placed at the Brewster angle, we have around 135$\text{fs}^2$ which is very closely compensated by the mirror pair. This GVD balance is very important if we hope to create few femtosecond pulses, as previously explained when we addressed dispersion-managed mode-locking.

9 Sample Characterization

Over the course of this work, three substrates were placed in the new sub-cavity. First, a fused silica substrate with nothing deposited was used to optimize the CW regime and study the new cavity without the effects of saturable absorption. After that, a sample of single layer graphene deposited on an identical substrate was used. The results obtained were unsatisfactory and it was believed to be due to insufficient sample quality. Raman analysis revealed the sample to be of low quality, much lower than what is require for our purpose. This led to the acquisition of a second single layer graphene sample, including with the order a Raman analysis to ensure the desired quality.
Figure 37: Negative GVD introduced by the sub-cavity mirrors as a function of wavelength. While each mirror has significant fluctuations that can not be removed, when working with a pair it is possible to design the GVD to a certain extent. The overlay curve is plotted as an average for comparison with the single mirror curves. In reality, the single mirror curves are additive, resulting in a total that is the double of the overlay plotted in the figure.

Samples were characterized by Raman spectroscopy, as vacuum methods such as electron microscopy were considered to invasive and potentially dangerous for the monolayer graphene. Furthermore, Raman spectroscopy is a very powerful tool and supplies enough information to assess the quality of a graphene sample. This analysis was made at IFIMUP. The light source was the polarized He-Ne line at 514.5 nm. The scattered light was analyzed by a T64000 Jobin-Yvon spectrometer operating in triple subtractive mode, and equipped with a photon-counting device. Using 1800 lines/mm holographic gratings and taking into account the 3 mm x 640 mm focal length, the spectral resolution is 0.15 cm$^{-1}$.

\section{9.1 Graphene Raman Spectra}

It is important to briefly discuss the information that Raman spectroscopy can provide about a particular graphene sample. Being a very convenient and powerful tool, Raman spectra of graphene have been extensively studied, looking for tell-tale signs of layer number, defect and impurity presence and substrate interaction. \cite{51, 52}

Figure 38 shows a single-layer graphene Raman spectrum. The main features features of the spectrum (from left to right) are the D, G and 2D bands.

The G-band is the primary mode in graphene and graphite. It represents the planar configuration $sp^2$ bonded carbon that constitutes graphene. The band position is independent of excitation laser frequency, making it different from the other graphene bands that will be discussed. The position of the band and to a certain extent the shape can provide some information. One common application for the G-band is to aid in determination of graphene layer thickness. As the layer thickness increases, the band position shifts to lower energy representing a slight softening of the bonds as the layer thickness
increases. On the other hand, G-band position is also very sensitive to doping and strain. This needs to be considered when attempting to use the band position of this band to determine graphene layer thickness, hence G-band positioning alone is not sufficient to determine layer thickness.

The D-band is known as the disorder band or the defect band. It represents a ring breathing mode from \( sp^2 \) carbon rings, only active when the ring is adjacent to a graphene edge or a defect. The band is the result of a one phonon lattice vibrational process. The band is typically very weak in graphite and is typically weak in graphene as well. If the D-band is significant, it indicates that there are a lot of defects in the material.

Finally the 2D-band, sometimes referred as G'-band when discussing carbon nanotubes. The 2D-band is the second order of the D-band and results from a two phonon lattice vibrational process. Unlike the D-band, it is not indicative of defects and is always intense, even when no D-band is present. This band is very indicative of the layer thickness of the sample, as show in Figure 39.

While there is a general shifting to higher wave numbers as the layer thickness increases, the more noticeable changes have to do with the band shape, relating to changes to the active components of the vibration. With single layer graphene, there is only one component to the 2D-band, but with bilayer graphene, there are four components to the 2D-band. This band is also very sensitive to folding. When looking for high quality SLG, this band should be very intense, symmetric and structureless.

### 9.2 First Graphene Sample

This sample was purchased before this work started, along with a multilayer graphene sample, both used for third harmonic generation in graphene. It was manufactured by Graphene Supermarket on a supplied substrate, identical to the blank substrate. This analysis was initially scheduled for the closing weeks of this work, but initial results were underwhelming and there were reasons to believe these were due to poor sample quality. That shall be made clear further on when analyzing results. It was deemed necessary to disassemble the subcavity to perform Raman spectroscopy.
Figure 39: Evolution of the 2D-band with the number of layers. It is seen that as the layer number increases, the peak becomes wider and more structured.

Figure 40: Raman spectrum of the first graphene sample
Figure 41: Raman spectrum of the second graphene sample used, deposited by Graphenea. This Raman spectrum was measured by Graphenea to ensure sample quality.

Figure 40 shows the Raman results for our first sample. The spectrum clearly evidences a poor quality a graphene. The D-band, which should be as small as possible is quite intense and broad. It is broad enough to have distinctive features, indicating a high defect density in the sample. Both the G-band and the 2D-band are broad and very featured, indicating a varying number of layers, along with folding. The sample was studied at various surface points, with the results not varying significantly. Due to the presence of significant noise, instead of an average of the spectrum taken from several points, we present the one we found to be most representative of the group.

Whether these results are due to poor manufacturing quality or sample degradation over time, we do not know. But from this analysis, it became clear the sample was unfit for our needs.

9.3 Second Graphene Sample

After dismal conclusions about the first sample, great care was exerted when trying to find a supplier for a new sample. A new pair of substrates was ordered, as graphene deposition companies do not supply optical grade substrates. After a recommendation from a colleague in Madrid, Rosa Weigand, Graphenea was selected to produce the sample. To ensure the desired sample quality, order details included a Raman spectrum of our sample, instead of the standard batch quality testing.

Figure 41 shows the spectrum measured by Graphenea. It is a noticeable improvement from the previous sample, with a nearly suppressed D-band and very intense and symmetric G and 2D bands. This points to a very high quality SLG sample.

10 Measurement Setups

In this section, we will discuss the various measurement systems used throughout this work.
10.1 Autocorrelation

To perform temporal measurements of the pulses, a commercial autocorrelation block was used: FemtoMeter commercialized by FemtoLasers. Data acquisition is handled by a custom LabView software, FemtoAQ. This software enables real time autocorrelation measurements as well as spectral measurements. When a spectrum is acquired, the program can estimate pulse duration in real time, as the autocorrelation trace is being performed. FemtoAQ was also serves as the interface for the spectrometer most used throughout this work.

10.2 Spotsise measurement

Since the intensity on the sample depends on the spot size, it is important to measure the spot Using a charge-coupled device (CCD) camera with a proper imaging system. We can measure the spot at the surface of the sample by measuring its scattering. This technique offers a simple setup, fast in implementation and analysis, which was important due to time restriction. It also has an important advantage: since we are measuring the scattering from the sample surface, the spot can only be overestimated. Thus, if the measured spot radius is smaller than what is needed for saturation, we need not worry about experimental errors, since it can only be smaller than what is measured. A $2f - 2f$ imaging system was used to create a 1:1 image of the spot in the sample.

To analyze the results, the image obtained from the CCD is imported as an numerical array to a Python program. The spot is then fitted using gaussian functions both vertically and horizontally, and the width is calculated at $1/e^2$, seeing as we are measuring an intensity.
10.3 Saturable absorption measurement

To complement the intracavitary studies of graphene, extracavitary measurements of absorption saturation were performed. With this, we aim to study the response of our samples to ultrafast pulse, by measuring the absorption of the sample as a function of the pulse fluence instead of an average power. Pulse fluence is given by

\[ F = I_{\text{peak}} \times \tau = \frac{1.88 P}{\pi w^2} \tau \]  \hspace{1cm} (74)

Usually measured in \( \mu\text{J/cm}^2 \), it is a measurement of the energy density a pulse transmits to an incident surface. Though fluence increases with pulse duration, peak power decreases with pulse duration. More than short pulses with high peak power, we are interested in very energetic pulses, tightly focused in a small area. For this study, a commercial Ti:sapphire oscillator, Femtolasers Rainbow was used. This oscillator usually feeds a hollow fiber amplifier and is used for pump-probe experiments. While having less output power than the home made system used throughout this work, it is capable of shorter pulse durations, of around 7fs.

These measurements proved a great technical challenge and the setup used suffered several changes to overcome various setbacks. Initially, the beam was focused on the sample surface and the intensity varied by attenuating the beam. This method yielded no results, even when the attenuation and focusing systems were changed. With this, we decided to change our approach and use a z-scan method, where the beam power is fixed, and the sample is moved along the propagation direction, changing the spot area, and thus the intensity. With this approach, we were able to observe absorption saturation.

10.3.1 First setup - \( \lambda/2 \) Plate and Polarizing Cube and Focusing Lens

The initial setup used for these measurements is shown in Figure 45.

To achieve high intensities, the beam must be tightly focused on the sample surface, just as with
Figure 44: Spectrum of the Femtolasers Rainbow laser oscillator used for these measurements

Figure 45: First absorption saturation measurement system. This system features focusing lens and a polarization-based intensity variation block
<table>
<thead>
<tr>
<th>Component</th>
<th>Material</th>
<th>GDD / length [fs²/mm]</th>
<th>Thickness [mm]</th>
<th>Piece GDD [fs²]</th>
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<tr>
<td>Free propagation (~3m)</td>
<td>Air</td>
<td>0.0204255</td>
<td>3000</td>
<td>61.28</td>
</tr>
<tr>
<td>$f = 200\text{mm}$ plano-convex lens</td>
<td>BK7</td>
<td>44.6518</td>
<td>4</td>
<td>178.61</td>
</tr>
<tr>
<td>$f = -50\text{mm}$ plano-concave lens</td>
<td>BK7</td>
<td>44.6518</td>
<td>3</td>
<td>133.96</td>
</tr>
<tr>
<td>$\lambda/2$ plate</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>71</td>
</tr>
<tr>
<td>Polarizing cube (17.5mm)</td>
<td>Calcite</td>
<td>39.6427</td>
<td>17.5</td>
<td>693.75</td>
</tr>
<tr>
<td>$f = 35\text{mm}$ plano-convex lens</td>
<td>BK7</td>
<td>44.6518</td>
<td>3.7</td>
<td>165.21</td>
</tr>
</tbody>
</table>

Table 2: GDD values for the components of the absorption saturation measurement system. The total value is 1304 fs².

intracavitary saturation. Focusing is done using a $f = 35\text{mm}$ spherical planar-convex. Just as before, smaller focal lengths produce smaller spots, but a minimum usable focal length is set by design constraints. Using a polarizer cube after a $\lambda/2$ plate, beam intensity is varied. Since the beam exits the cavity with horizontal ($p$) polarization, the $\lambda/2$ plate will rotate the polarization, keeping it linear. Since the polarizer cube only transmits $p$ polarization, by varying the angle of the easy axis of the $\lambda/2$ plate, we vary the amount of power transmitted by the cube.

Beam power is measured at two points, before and after the sample. To this effect, a beam splitter was placed after the polarizer cube. Since we are interested in measuring the intensity incident on the sample while losing as little intensity as possible, transmission should be very high, and as such a 95/5 beam splitter was used. The 5% power is measured using a very sensitive Thor Labs PM100USB powermeter. To measure the intensity after the beam crosses the sample, a Thor Labs DET210 photodiode is used, connected to a Stanford Research Systems SR830 DSP lock-in amplifier. Filtering is done by a mechanical rotating chopper at 133Hz. This will allow for stable and precise measurements, reducing optical noise.

Since we are trying to measure an intensity, it is also important to measure the spot size on the sample surface. In this case, it is not necessary to use an imaging system like the one discussed in the previous section. We can simply heavily attenuate the beam using neutral density filters and place a CCD camera on the laser spot.

Peak power and therefore pulse duration are crucial, thus it is necessary to ensure the pulse arrives at the sample as short as possible. Seeing as the pulse will have to travel a great distance and cross several dispersive components, it is necessary to use chirped mirror pairs to compensate for the GDD introduced by these components, which severely stretches the pulse. Calculations were made beforehand to determine the amount of GDD introduced, accounting for each individual component and the air distance travelled. Table 2 shows the GDD of each material and the thickness of each component.

Due to a large number of highly dispersive components, this total value of 1304 fs² would result in a pulse with picosecond duration, much higher than the initial 7fs. The available mirror pairs, manufactured by Venteon introduce a negative GDD of $-120$ fs² per pair. To compensate for such a high positive GDD, 11 passes are needed, meaning that with only 5 pairs available, several reflections in each mirror are needed. For this kind of GDD compensation, it is best to overcompensate the calculated dispersion, then use a pair of glass wedges, one of them being movable, to introduce variable positive dispersion in order to achieve maximum pulse compression. As such, a total of 13 passes
Figure 46: Setup used for second harmonic generation to fine tune pulse compression

were used.

To accurately measure compression, a 5mm-thick Beta Barium Borate (BBO) crystal is used to generate broadband second harmonic, placed where the graphene samples would be, since it is there that we wish the pulse to be shortest. By looking at the second harmonic spectrum and intensity, it is possible to infer pulse duration, since SHG depends on the peak intensity, and thus on the duration of the pulse. By varying wedge insertion, the net GDD of the system is varied and maximum second harmonic intensity is achieved when this value is zero, decreasing when there is either positive or negative GDD. A visual qualitative analysis is used to find the best combination of peak intensity and emission width, since we are interested in the total power, which depends on the integral of the intensity over the emission band. A more complex version of this principle is used in the already mentioned dispersion scan pulse diagnostic technique.

The pulse compression measurement setup is shown in Figure 46. A very sensitive spectrometer, HR4000 by Ocean Optics, was used in these measurements.

10.3.2 Second Setup - Variable Neutral Density Filter and Focusing Spherical Mirror

Using the initial setup, no saturation was observed with neither samples and the reason was not clear at first. As can be seen by the SHG, the pulse is properly compressed and we expect it to be near the Fourier limit. Though the lenses used for the spot reduction and focusing on the sample introduce great loss, reducing the power from the initial 170mW to just 70mW, this value should be sufficient for saturation to occur.

A saturation fluence between $10^3 \mu J/cm^2$ and $10^2 \mu J/cm^2$ is expected [37]. Using Eq.(74) with $P = 70$ mW, $w = 30 \mu m$ and $\tau = 10$fs, we have $F = 4.56 \times 10^3 \mu J/cm^2$, which is well above the expected saturation fluence. Still, only linear absorption was absorbed for both samples.

The first step was to remove all the lens from the setup and replace then for spherical silver mirrors with the same focal distances. Sadly, due to lack of components, it was not possible to build a
Figure 47: SHG spectra obtained with different wedge insertion. The bottom spectrum, due to its higher intensity and broader band, is generated with a more compressed pulse than the top spectrum.
Figure 48: Second absorption saturation measurement system. This system features focusing spherical mirror and a neutral density filter-based intensity variation block.

4× reducing telescope using mirrors. Nevertheless, the $f = 40\text{mm}$ plano-convex lens used to focus the beam in the sample was swapped by a $f = 50\text{mm}$ spherical silver mirror. Reflective systems have the advantage of introducing less loss and no dispersion in the system. And while GDD can be compensated by chirped mirrors, third-order dispersion (TOD) is a much trickier problem. TOD may not be very important for pulses longer than 20fs or 30fs, but it has significant impact on sub-10fs pulse. This could lead us underestimate the actual pulse duration, and consequently the saturation fluence.

It should be clear by now, that lenses are not exactly laser-friendly components, introducing heavy loss and dispersion (both GDD and TOD) in the system. But a much more serious problem than these is chromatic aberration, when a lens fails to focus all the frequencies to the same convergence point. For ultra broadband pulsed lasers, this results in a spacial separation of the frequency components of the pulse. More than just distorting the spot in the focal plane, chromatic aberration also results in different frequencies being focused at different distances from the lens. This makes unviable for short pulse focusing. At the time of the first setup, this fact was disregarded, while we concerned ourselves only with loss and GDD, which turned out to be the least of our concerns.

By exchanging the lens for a silver spherical mirror, there was a noticeable increase in beam power at the sample, from 70mW to 85mW. Adjustments were made to the GDD compensation system, with the number of mirror pair passes reduced from 13 to 11, and some minor adjustments to the glass wedges.

A grave problem was also discovered in the intensity variation system. The polarization of beam exiting the cube, instead of being fixed $p$ polarization as expected, varied as the $\lambda/2$ plate was rotated. Since the transmission of the beam splitter depends on the polarization and is only 95% for pure $p$ polarization, this polarization rotation renders our system unusable, since we cannot accurately measure the input power on the sample.
To resolve this, a variable neutral filter was used. While neutral density filters are very reliable and efficient attenuators, this variable filter has the downside of having a discrete number of attenuation settings, 11 in total, limiting the number of points we can measure. This filter also introduces far less GDD than the λ/2 plate and polarizer cube, resulting in a further reduction of mirror passes, from 11 to 5.

Finally, we borrowed another optical power meter from INESC, which allowed us for a simpler measurement setup, dropping the photodiode and lock-in amplifier. Now, we are using the PM100USB to measure the power after the beam crosses the sample and an extremely precise (picowatt precision) Newport 818-ST power meter to measure the 5% of the beam reflected at the beam splitter.

10.3.3 Z-scan measurements

As a last resort, we had a paradigm shift. If we cannot reliably vary the incident power, then we do not vary it at all. By keeping the incident power constant and moving the sample along the propagation path, around the focal point, the spot size in the sample changes, and with it the intensity, which was the initial objective.

The sample is mounted in a fine translation stage, and the transmitted intensity is measure as a function of sample position. We expected to observe a maximum in transmission as the sample crossed the focal point, and this is exactly what was observed. With this setup we observed saturable absorption for both graphene samples. These results obtained with each sample shall be discussed further ahead.
Part IV

Results and Discussion

This part is divided in three sections, relating to the results obtained with the different samples used throughout this work. Firstly, a fused silica substrate with no material deposited was used to obtain Kerr lens mode-locking for correct comparison to SAML, seeing as the geometry of the cavity was significantly altered. Using the first graphene sample, we were able to obtain KLM, but SAML was not observed. Multi-mode broadband emission was observed but confirmed pulsed operation was only obtained with KLM.

11 Blank Substrate (“Dummy” Laser)

After modifying the cavity to its new configuration and first observing laser action, the plan was to optimize CW output power and then try to obtain broadband KLM. However, KLM was surprisingly easy to obtain with fairly broadband spectra and for a wide array of output powers.

KLM regime relies on pulsed operation being more efficient than CW operation. In the standard KLM setup, as pump power increases, CW gain increases and it becomes harder to perturb the CW and initiate KLM. Even if KLM starts at high pump powers, there is usually a CW peak in the spectrum corresponding to a baseline countinous power, that grows as pump power increases and eventually CW operation becomes more favorable and takes over.

However these sort of instabilities were not seen in this setup. KLM was observed for a wide range of pumping powers. It was also more easily initiated than in the old setup, and no CW peaks were observed though the pumping power was increased to its maximum value. Also, output power was much higher than expected, given the added loss of the substrate and the more complex cavity, harder to optimize alignmentwise.

This is due to the higher complexity of this cavity, which results in higher sensitivity to mechanical perturbations. Thus the laser did not have to operate so close to the edge of the stability region to initiate KLM, resulting in high output powers. It also made it harder for the CW instabilities to grow and take over, leading to a very stable KLM behaviour with a smooth broad spectrum shown in Figure 50.

The sample sub-cavity mirrors are also very important. Since they were designed to compensate the GVD of a substrate similar to the one used, the balance necessary for KLM and dispersion managed mode-locking was not significantly lost, with only minor adjustments to the intracavitary prism pair needed.

Results obtained using KLM with the new design were quite positive, with broad and stable spectra. The CW peaks that usually plague KLM cavities were nowhere to be seen as pulses as short as 27fs were produced (see Figure 51).

Some of the dielectric mirrors inside the cavity, such as the folding mirror and the high-reflector, were
Figure 49: Laser slope efficiency. Output power was measured with the laser in KLM for all points.

Figure 50: Spectrum obtained by KLM using a blank substrate in the sub-cavity.
changed to silver mirrors. Ti:sapphire lasers are tunable in a very broad band of frequencies, from 600 nm to 950 nm. However, our laser could not be tuned below 725 nm nor were frequencies below this value present in any spectrum obtained. This led us to believe these frequencies were possibly being cut off by some of the mirrors. While not being as reflective, metallic mirrors have broader reflection bands than most dielectric mirrors, so there was a chance to gain some bandwidth at the expensive of output power.

However, this brought no improvements to the spectrum, only reducing the output power and severely attenuating longer wavelengths, as seen in Figure 52. The first dielectric mirrors were returned to the cavity.

Since we do not wish to obtain KLM when using the substrate containing graphene, after studying the KLM behaviours of the cavity, its parameters were optimized for CW power in the center of the stability region. This provides the best chance for saturation, while minimizing the chance of falsely identifying KLM or graphene-assisted-KLM as SAML.

12 First Graphene Sample

12.1 Broadband Spectra

After studying the new subcavity without the effects of saturable absorption, and setting up the cavity parameters for optimal intracavitary power and spot size, it was time for graphene to make its appearance.
 Shortly after the sample was switched, the beam spot right outside the output coupler lost the speckled pattern and showed a smooth appearance, typical of mode-locking operation. Right afterward, our first graphene broadband spectrum was measured, shown in Figure 53. While very structured and not very broad, it is clearly broadband emission. This regime was self-starting, ruling out the possibility of KLM. Spectral structure showed strong dependence in pump power and sample position inside the cavity, as we would expect from an intensity dependent regime.

After some optimization, Figure 54 shows the broadest spectrum obtained.
As pump power is increased, spectral structure is significantly altered, most notoriously by the appearance of a peak at around 860nm. We first identified this as a solitonic spectral peak [53], a spectral peak coherent with the rest of the spectrum, though being an isolated structure. Solitonic spectral peaks are formed as a consequence of dispersion-managed mode-locking, as the laser distributes the power it receives from the pump through the spectrum. In this case, soliton efficiency was not shown, because the broadband spectral profile varies greatly in intensity, unlike what happens in KLM.

12.2 Multimode Oscillation

After obtaining self-starting broadband emission with the graphene sample, we started to work on autocorrelation measurements, to measure the pulses being produced. Autocorrelators can be tricky to align, in a time consuming process. But even so, measurements were yielding no results despite having observed broadband emission. This made us resort to other diagnostic techniques and led to the discovery of a temporal regime which, to the best of our knowledge, has not been described in the literature.

12.2.1 Oscilloscope Measurements

After no results were obtained using the autocorrelator, a DET210 photodiode (manufactured by ThorLabs) connected to a Tektronix oscilloscope was used to measure the laser output. While oscilloscopes can not measure pulses, they can be used to verify a periodic pulse output function. Results were dismal in contrast to a very promising start. Figure 55 shows these measurements.

These results were very unexpected. We expected a train of pulses like the one seen in Figure 23, separated by the round trip time.
Figure 55: Measurements of the temporal profile of the output intensity, using a photodiode. A periodic output was measured,

Since this occurs only with the substrate containing the graphene: after these results, the samples were switched again solely to confirm this. This is very important as it means that the graphene is actually doing something that results in a broad emission band but does not yield pulses.

12.2.2 Spot Size measurements

To ensure these results did not come from setup flaws, the spot size in the graphene layer needed to be measured, confirming the focus was tight enough for saturation to occur. Using the spot size measuring system previously discussed, spot size is measured both vertically and horizontally. Measurement results and shown in Figure 57. The measured width values of 18 $\mu$m in the sagital plane and 24 $\mu$m in the tangential plane are well below the 32$\mu$m needed for saturation to occur. This rules out design flaws as the source of the problem.

12.2.3 Explanation

Firstly, as said before, this behaviour is caused by the graphene layer. No similar behaviour was observed with the blank substrate. It was also confirmed that the beam was focused tightly enough for saturation to occur, with a sufficient margin from the threshold. Saturable absorbers can have other effects on the cavity, beside SAML, such as saturable absorber Q-switching [54], but these result in pulses with nanosecond duration. The microsecond time scale behaviour seen in the oscilloscope is actually rather odd, since there are few processes that occur in that time scale.

The answer lies in the structure of the spectra. Comparing the spectra obtained when using graphene
Figure 56: Laser spot size as viewed by the CCD camera and imported to a Python color map.

Figure 57: Spot size measurements along the sagittal (left) and tangential (right) planes. The data is fitted using a Gaussian curve and the width is measure at $1/e^2$ of the maximum, since we are measuring an intensity.
Figure 58: Broadest KLM spectrum obtained using the first graphene sample. This spectrum is noticeably narrower than those obtained with a blank substrate.

with the KLM obtained with the blank substrate, there is a significant difference in smoothness. Even when compared with the results obtained by Baek et al [37], the spectra we obtained are much more featured. So this is not expected from the geometry of the cavity nor from the SAML regime.

We believe this is caused by poor selectivity of the more intense oscillating modes. Seeing as the behaviour observed is very intensity and graphene-position dependent, saturation must be involved. However, it may not be discriminative enough, causing several modes to survive independently and oscillate uncoherently. This would explain why the spectra observed were a collection of connected peaks.

This behaviour was suspected to be caused by poor sample quality, this assumption being confirmed by the Raman analysis previously discussed. Nonetheless, we intend to further explore this temporal regime in a future work.

12.3 KLM

After no results were obtained with SAML, we decided to optimize the cavity for KLM operation and compare the results to that of the “dummy” laser. The results obtained, even after extensive optimization efforts fall very short of those obtained using the blank substrate. The broadest spectrum obtained showed only 15nm (FWHM).

We are still unsure of the cause of this, since the geometry did not change from the previous section. This can be due to dispersion, which even in very small amounts can ruin dispersion-managed mode-locking. Also, the additional loss introduced by the graphene layer will force us to use more pump power to obtain the same output power. High pumping power can compromise mode-locking by making CW operation more viable.
Figure 59: Though it can be hard to see in a photograph, a large number of fairly large dust particles is present on the sample surface, including the graphene layer.

13 Second Graphene Sample

After obtaining uncoherent broadband oscillation using the first graphene sample and finding out that it was degraded or of poor initial quality, we naturally had high hopes for a higher quality sample. Judging from the Raman spectrum (Figure 41), the sample purchased from Graphenea appeared to be nearly flawless single-layer graphene. However, visual inspection revealed flaws not detectable by Raman spectroscopy - something as simple as dust. Dust particles are a severe issue when present on intracavitary elements, acting as a scattering center, thus introducing significant loss. And considering we are focusing the beam in a 18 μm spot, comparable to a dust particle cross-section, we see that a single dust particle can block the majority of the beam, hindering laser action.

This was directly observable when moving the sample along the Brewster angle. This caused the output power to vary significantly, as the focal point passed over dust particles. As a result, though the cavity proved stable for CW operation as it was with the other graphene sample and substrate, we were unable to obtain KLM or SAML using this sample.

Figure 60 shows the only broadband spectrum obtained using this sample. The spectrum was very unstable. SAML relies on a small difference in absorption of the order of 1%, but since the absorption modulation depth of the dust particles is much larger than this, mode intensity selectivity became negligible.

Although the back of the substrate was thoroughly cleaned with methanol, the graphene layer may be too fragile to withstand standard optical cleaning procedures. At first we were reluctant to clean the sample surface, but as results were not obtained either way, we are now considering performing an analysis of the possible damages induced by cleaning in a small test section of the sample with the help of Raman spectroscopy. Should we succeed, we will attempt to clean the whole sample and
Figure 60: Only broadband spectrum obtained with the second graphene sample.

test it again inside the laser cavity.

14 Saturable Absorption Measurements

Though we were not able to produce mode-locking, we still obtained broadband emission which was clearly due to the presence of graphene. Additional work was required to fully understand the role of graphene in the behaviour of our cavity. For this a set extracavityary experiments was designed to study saturable absorption in graphene, complementing the intracavity work already performed.

As previously discussed, after the first two setups failed, we used the z-scan method and successfully observed absorption saturation using the first graphene sample, manufactured by Graphene Supermarket, as seen in Figure 61 and Figure 62. As the surface sample approaches the focal point, there is clear increase in transmission, as the beam intensity increases with the decreasing spot size. Figure 63 was measured first with incident power of 92mW and, observing saturation over a wide range of sample positions, we decided to reduce the incident intensity to 75mW and, as expected, the length of the saturation region decreases. This region length decrease along with the rough symmetry of the results are clear evidence that the transmission increase is due to saturable absorber and not due to inhomogeneities in the sample surface.

The saturation profile is not as symmetric as other previous results [55], but it is to be expected since we were not prepared beforehand to make this kind of measurement, which require fine characterization of the beam profile. As seen before, off-axis reflection and propagation through an angled plate introduce astigmatism, which results in different focal points for the sagittal and tangential plate, which could account for the rough symmetry.

With the second graphene sample, manufactured by Graphenea, saturable absorption was not ob-
Figure 61: Z-scan measurements of graphene with 92 mW of incident power.

Figure 62: Z-scan measurements of graphene with 57 mW of incident power.
served. Just as when it was used as an intracavitary element, the dust on the sample surface make it too inhomogeneous for saturable absorption to be observed beyond doubt. As the sample was moved along the axis, transmission would greatly fluctuate (upwards of 30%), due to the sample surface quality. When compared to the 0.7% which we expect from saturable absorption, it is clear that no reliable measurements can be obtained.

As mentioned before, we are now planning to study the cleaning-induced damages on the graphene layer, and depending on the results obtained, we expect to repeat these extracavitary measurements in a near future.
Part V

Conclusions

In this work, we have explored the potential of single-layer graphene films, deposited on laser-quality fused-silica substrates, for new methods of mode-locking of broadband vibronic lasers, specifically Titanium Sapphire lasers, based on the promising saturable absorption properties of graphene.

A new type of laser cavity containing a second intracavity focus suitable for placing the graphene sample was designed and successfully built. Two different graphene samples from different manufacturers were tried, their saturated absorption was measured, and their quality inferred using complementary techniques, in particular Raman spectroscopy. From this analysis we concluded that the two samples had very different quality.

We were able to obtain broadband laser action with considerable average output power (approximately 250 mW) using the higher quality sample, although the observed regime was not as expected for pure mode-locking operation, being more consistent with multi-mode (but phase incoherent) operation. The better sample was significantly contaminated with external particles, and a proper cleaning method will have to be tried prior to further attempts at obtaining mode-locking. We also performed extracavity experiments, using a few-cycle (7 fs) ultrashort pulse laser, aimed at characterizing the saturable absorption properties of the graphene samples.

Using a z-scan setup, we clearly observed absorption saturation for energy fluences starting at around 1 millijoule per square cm. These results are in very good agreement with those reported in the literature and are also relevant for the new Graphene flagship (optoelectronic properties of graphene workpackage) with which we intend to further advance on the study and application of graphene to new photonic devices.
References


