TUNABLE PHOTONIC MATERIALS AND RANDOM LASERS

Dottorato in Scienza e Tecnologia dei Materiali XVI ciclo

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31 Marzo 2004

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The work described in this thesis is financially supported by:
Istituto Nazionale di Fisica della Materia (INFM), Project PAIS-Randlas 2002 
and
Ministero dell’Istruzione, dell’Università e della Ricerca (MIUR), Project Coffin-Silicon Photonic Crystals 2002

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Chapter 1

An Overview of Photonic Systems

In this chapter an overview of the main optical properties of photonic systems is given. Dielectric materials can be assembled in an ordered or in a disordered way. In both cases an electromagnetic wave undergoes multiple light scattering. In the ordered case we can obtain structures that possess a band gap for the photons, similar to the electronic band gap of semiconductors. They are photonic crystals. For strongly dielectric disordered materials constructive interference phenomena give rise to Anderson localization for photons, analogous to the localization for electrons in disordered metals. Away from the localized regime the diffusion approximation is appropriate to describe the transport of light. If optical gain is added to a disordered system we obtain a device often referred to as a random laser, that uses the multiple scattering of light to reach the laser threshold.
CHAPTER 1. AN OVERVIEW OF PHOTONIC SYSTEMS

1.1 Light scattering in dielectric systems

The transport of light in "complex dielectric" materials is a rich topic of research. The term complex dielectrics refers to dielectric structures with an index of refraction that has variations on a length scale that is very roughly comparable to the wavelength. Such structures strongly scatter light. A possible building block for constructing a complex dielectric is a micro-sphere of diameter comparable to the wavelength and of a certain refractive index that is different from its surrounding medium. The single scattering from such a sphere has a rich structure due to internal resonances in the sphere, but its behavior is well-understood and can be calculated using the formalism of Mie-scattering [1]. A complex dielectric material can then be realized by micro-assembly of several micro-spheres. The spheres can be assembled in various ways with two opposite possibilities: a completely disordered packing or a fully ordered assembly (see fig. 1.1). Even though the same spheres with the same single scattering properties are used, their cumulative behavior after assembly will depend on the way the spheres are packed together. Light scattering occurs because the refractive index of the scattering particles differs from the index of the surrounding medium (usually air). We can define the multiple scattering regime when the average distance between two scattering events (the mean free path $\ell$) is much smaller than the sample dimensions.

In fig. 1.1 the two possible packing for a collection of spheres is shown. If the spheres are packed according to a crystal-like structure, then the interference will be constructive only in certain well defined directions, giving rise to Bragg refraction and reflection. In the disordered case the light waves will perform a random walk from one sphere to the other. The nature of interference effects is now less obvious to understand, however also in random systems interference effects turn out to be very important.

Interference of light in random dielectric systems influences the transport of light in a way that is similar to the interference that occurs for electrons when they propagate in disordered conducting materials. As a result, several interference phenomena that are known to occur for electrons appear to have
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In free space, the relation between the frequency $\nu$ and the wavelength $\lambda$ of light is simply

$$c = \lambda \nu ,$$

where $c$ is the speed of light. Defining the wave vector $k = 2\pi/\lambda$, we obtain the dispersion relation for free space

$$\omega = ck .$$

Figure 1.1: Ordered and disordered photonic structures derive from the same building block, which in this case is a single scattering sphere.

their counterpart in optics as well [2]. Interesting examples are universal conductance fluctuations of light [3], weak localization [4, 5], and Anderson localization [6-8]. In the case of Anderson localization the interference effects are so strong that the transport comes to a halt and the light becomes localized in randomly distributed modes inside the system.
The density of states $DOS$ of the electromagnetic field in a volume $V$ of the free space is

$$DOS(\omega) = \frac{\omega^2 V}{\pi^2 c^3}.$$ (1.3)

If we consider an uniform medium of refractive index $n$, the actual density of states will be eq. 1.3 in which $c$ is replaced by the phase velocity $v = c/n$.

The optical properties of atoms and molecules strongly depend on $DOS(\omega)$. As an example, let us consider the spontaneous emission of a photon from an electronic excited state of an atom or a molecule. We know that the spontaneous emission rate is proportional to $\omega \cdot DOS(\omega)$. Since spontaneous emission is the origin of the energy dissipation and of vacuum fluctuation of the radiation field, it suppresses the occurrence of laser oscillation. This dissipation is proportional to $\omega^3$, this is why high frequency lasers are not so easy to fabricate. So it would be very interesting to find a physical systems in which one can design and modify $DOS(\omega)$ [9]. Photonic crystal, proposed by Yablonovitch for the inhibition of spontaneous emission [10] and by John for another purpose [11], are the candidates for this modification.

Photonic crystals are a regular arrays of materials with different refractive indices modulated alternatively (see fig. 1.1). The spatial period of the modulation is called the lattice constant, equivalent to the lattice constant of ordinary crystal formed by a regular array of atoms. The relevant difference between ordinary crystals and photonic crystals is the scale of this constant. For ordinary crystals it is of the order of ångströms, while on the other side, for photonic crystals, it is of the order of the wavelength of the relevant electromagnetic wave. Due to the periodic modulation of the dielectric constant, photonic crystals exhibit a forbidden energy region for photons, called photonic band gap, similar to the electronic band gap for semiconductors that is caused by the periodicity of the atomic potential.

The first example of a complete photonic band gap material is reported by Yablonovitch et al. in 1991 [12]. They drilled three sets of holes at an angle of 35° off vertically into the top surface of a solid wafer, yielding an FCC lattice, as shown in fig. 1.2. The center of the gap was at a frequency
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Figure 1.2: A solid wafer was covered by a mask consisting of triangular array of holes. Each hole was drilled through three times, at an angle of 35° away from the normal and spread out of 120° on the azimuth. The result was a complete photonic band gap sample in the microwave region, today called Yablonovite [12].

of 15 GHz. This structure is today known as Yablonovite. In the last years calculations and fabrications of photonic crystals [13-17] were persecuted, with the goal to obtain complete photonic band structures in the near infrared and in the visible wavelength regimes. In a photonic crystal the parameter that determines the wavelength range in which destructive interference gives rise to the band gap is the normalized frequency $c/a$, where $a$ is the lattice constant. In the gap, $c/a$ is near to unity, which means that for microwaves $a \sim 1$ cm, while for near infrared or visible light $a < 1 \mu$m. Nowadays it is possible to grow ordered structures with small lattice constants, but at the beginning of 90’s this was not so easy. This is why the Yablonovite was first realized in the microwave regime.

Solving Maxwell’s equations with finite difference time domain (FDTD) simulation method [18], it is possible to predict how an electromagnetic wave propagates through a photonic crystal and so to calculate the density of states and the band structure. An example for a three-dimensional photonic crystal
is depicted in fig. 1.3. In (a) the band diagram is shown, where the normalized

![Diagram](image)

Figure 1.3: (a): Band diagram for a three-dimensional photonic crystal with an FCC structure. The band gap opens around $\omega a/2\pi c = 0.8$ and a main stop band is present around $\omega a/2\pi c = 0.5$. (b): For comparison with (a) the band diagram for bulk silicon is shown [19]. (c): The DOS of the same system presented in (a). Note that $DOS = 0$ in the band gap. The behavior is very different from the parabolic one in free space of eq. 1.3.

frequency is plotted in function of the $k$ vectors of the first Brillouin zone (here we report the symmetry points, not the values of $k$), for an ordered structure having an FCC lattice\(^1\). Such structure shows a complete photonic band gap around $1.5 \, \mu m$ ($\omega a/2\pi c = 0.8$ if $a = 1.2 \, \mu m$), which means that in this

\(^1\)The calculations were performed at the University of Toronto
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wavelength range any light wave with any $\mathbf{k}$ vector is reflected back by the sample. In fig. 1.3 (c) the $DOS$ versus the normalized frequency is shown for the same sample. The two arrows connect the band diagram and the $DOS$ diagram for the photonic band gap (around $\omega a/2\pi c = 0.8$) and for the main pseudo-gap centered around $\omega a/2\pi c = 0.5$. Pseudo-gap means not complete, so in this wavelength range for some $\mathbf{k}$ vectors of the Brillouin zone light waves are transmitted by the crystal. The DOS is zero in the photonic band gap, and very low in the pseudo gap. This is the main property of a photonic crystal, a system in which the spontaneous emission is drastically suppressed in the photonic gap. Fig. 1.3 (b) shows, for comparison, the electronic band diagram of bulk silicon [19], where the electronic band gap is shown. Obviously the two crystals, electronic and photonic, have different behaviors, starting from the particles involved that have a charge, a mass and a spin value of $1/2$ for the electrons and no charge, no mass and a spin value of $1$ for photons. In spite of that there are a lot of analogies between these two crystals, starting from the Shrödinger and waves equations, as we will see in chapter 3, and hence the name photonic crystals is very appropriate.

1.2.1 The photonic crystal world

Photonic crystals are not so common in nature with respect to electronic crystals, but some examples can be made. The oldest and best-known example is the opal, a sedimentary gem that has a crystalline structure where the periodicity is of the order of hundreds of nanometers instead of ångströms. It is made of tiny spheres of silica packed together. The diffraction of light through this arrangement produces a characteristic play of colors, the nature of which is determined by the size and the distance of the spheres. This gem inspired artificial opals, where sedimentation of dielectric spheres is used to build up a three-dimensional photonic crystal.

At the University of Sydney, Parker et al. have discovered that photonic crystals exist also in the animal world [20], specifically for the “sea mouse”, a small worm. The sea mouse, shown in fig. 1.4 (a), is covered with long
threads and spines that produce a brilliant iridescence. A scanning electron microscope (SEM) image for a spine is depicted in fig. 1.4 (b). It reveals a periodic microstructured pattern with hexagonal symmetry. This is an example of a two-dimensional photonic crystal that possesses a pseudo-gap. Other examples of photonic crystals can be found in some butterflies possessing blue iridescence. Blue pigments are, in fact, very rare in nature.

After that, we can concentrate on artificial photonic crystals used to manipulate and modified the flow of light. Photonic crystals can be classified into three main groups, that is, one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) systems, according to the dimensionality of the structure that forms the crystal. We can have structures that go from the microwave regime to visible wavelengths. Decreasing the wavelength means increasing the difficulties to produce them, because precise miniaturization processes have to been involved. Examples of photonic band gap structures are presented in fig. 1.5. 1D crystal is obviously the simplest that exists, and relatively easy to fabricate; in its simplest form it is a dielectric mirror. In
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Figure 1.5: (a): Coupled microcavities as an example of 1D photonic crystal in which intentionally defects were introduced (University of Trento, project INFM-PAIS 2002). (b): 2D macroporous silicon with a triangular elementary cell (University of Trento, project INFM-PRA 2002). (c): 3D structure as a 5 woodpile layers of GaAs (from SANDIA National Laboratory). (d): 3D self-assembled direct opal of SiO$_2$ with a crack in the center (Polytechnic of Turin, project MIUR-COFIN 2002).

In fig. 1.5 (a) the more interesting coupled microcavities structure is shown. The structure is formed by distributed Bragg mirror (DBR), that is a 1D photonic crystal and by some defects (microcavities) that trap the electromagnetic field inside the sample [21]. Nowadays such multilayer structures are obtained by chemical vapor deposition (CVD) or by using porous silicon [22], grown by hydrofluoric acid (HF) etching.

Increasing the dimensionality more problems arise in the fabrication. In fig. 1.5 (b) the state of art of 2D structure is shown. The sample is made of macroporous $Si$, where micrometric air columns are drilled by reacting ion etching, with the help of a lithography mask [23]. 2D photonic crystals are very promising for optics components used in telecommunications. For
example in an optical fiber the standard glass cladding can be replaced by a 2D photonic crystal with an appropriate design. These photonic crystal fibers have extremely low losses because the light travels predominantly in the hollow core [24].

The greatest problems are present in 3D samples. Simulations on 3D photonic crystals show that such structures can possess a full photonic gap in three dimension, but until today no proof of a complete photonic band gap have been experimentally obtained. In fig. 1.5 (c) a woodpile photonic crystal is shown. This type of structure, as for the Yablonovite, has a complete gap for microwaves [25] but only pseudo-gaps in near-infrared and in the visible [26]. The design uses layers of parallel one-dimensional rods of rectangular cross section, disposed in space as a woodpile. The growing technique is very time consuming, because it consists of layer-by-layer deposition of semiconductor materials. The main problem in this case is that it’s very difficult to grow a sufficient number of layers to obtain the full photonic gap. 4-5 layers represent the state of art, because beyond the woodpile rods exhibit misalignment [27]. Note that 4 layers form one unit cell for this crystal; almost 7 unit cells are necessary, and so 28 layers, to open the gap.

In fig. 1.5 (d) another 3D sample is depicted. It is the opal structure. Opals are usually made of dielectric spheres as $SiO_2$ or polystyrene, grown by spontaneous sedimentation [28]. This is the main difference between opals and the other photonic crystal structures: opals use self assembly to generate an FCC crystal. This is an advantage because it is not so difficult to obtain a crystal. The main disadvantage is that sedimentation cannot be controlled as in a layer-by-layer or chemical etching technique and usually opals present cracks as shown in fig. 1.5 (d). There are two main reasons on the origin of cracks:

- Polydispersity of the spheres. If $R$ is the mean radius of the spheres, the deviation for each sphere from this mean value is $\Delta R$. $\Delta R/R$ is the polydispersity of the spheres. To obtain “good” samples in which one can find an area of $\sim 50 \times 50 \, \mu m$ of quasi-perfect crystal, this dispersion
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has to be typically lower than 4%.

- The surface roughness. The surface of each sphere is not completely smooth.

In opals there are not fundamental limitations on the number of layers as in woodpiles. The more promising structures are the inverse opals, inverse means that we invert the systems, so instead of spheres of dielectrics and air between the voids, we have dielectrics in the voids and air spheres [17]. The advantage is enormous because calculations show a larger band gap with respect to the direct case. Inverse structures are also relatively easy to obtain, it is necessary to infiltrate the direct one with another dielectric material and remove the constituent of the spheres in a chemical way.

Nowadays the state of art for 3D photonic crystal is not high enough to obtain full photonic band gap materials, as happens for 2D and 1D photonic crystal.

1.2.2 Negative refraction

A new class of systems emerged recently, called left handed materials. They were predicted by Pendry et al. in 1999 [29] and they possess negative electric and magnetic permeability. The first discussion on such systems is dated 1968, when Veselago [30] introduced the concept of “left handed” systems, emphasizing the fact that the intensity of the electric field \( E \), the magnetic intensity \( H \) and the wave vector \( k \) were related by a left handed rule. This can easily seen by writing Maxwell’s equations for a plane monochromatic wave

\[
\mathbf{k} \times \mathbf{E} = \frac{\omega \mu}{c} \mathbf{H} \quad \text{and} \quad \mathbf{k} \times \mathbf{H} = -\frac{\omega \epsilon}{c} \mathbf{E}.
\]  

(1.4)

If \( \epsilon \) and \( \mu \) are both positive, then \( \mathbf{E}, \mathbf{H} \) and \( \mathbf{k} \) form a right set of vectors. In the case of negative \( \epsilon \) and \( \mu \), these three vectors form a left set.

In left handed materials some physical effects behave differently with re-
spect to classical right handed ones. The Poynting vector

$$ S = \frac{c}{4\pi} E \times H $$

(1.5)

does not depend on the sign of the permittivity and permeability of the medium. Then $k$ and $S$ are parallel in right handed and antiparallel in left handed. Consequently the phase and the group velocity of an electromagnetic wave propagate in opposite direction in left handed. This means for instance that the Doppler and Cherenkov effects are reversed [30].

Both negative $\epsilon$ and $\mu$ imply also a negative refractive index $n$ [31]. If an electromagnetic wave passes through an interface formed by a right handed and a left handed we observe negative refraction. Experiments on negative refraction has been performed [32, 33] and today are subject of a controversially debate.

Negative refraction allows the fabrication of a perfect lens [34] that is maybe the most challenging property of a left handed material. In principle such lens, constructed from a material with $\epsilon = \mu = -1$, can work without any limit imposed by diffraction. But the existence of perfect lenses seems to be in contradiction with fundamental physics laws, as discussed in some papers [35].

As for the first experiments on photonic crystal, the proof of perfect lens effect and negative refraction was given only in the microwave regime, where it is easy to obtain samples with the desired properties. In one of the last experiments performed the sample used was a 2D photonic crystal [33]. It was found that photonic crystals, in some frequency regions (outside from the band gap), have a negative refraction controllable by the band structure. This property gives in this way an additional application to photonic band gap materials. This application, obviously, will be more appreciable when near-infrared or visible wavelengths are involved.
1.3 Anderson localization

Anderson predicted in 1958 a transition in the diffusive transport of electrons in metals, in particular, in lattices where disorder was introduced as impurities [36]. The transition changes the electrons transport from classic diffusion (what happens in a copper wire for example) to the absence of diffusion. Experimental evidence of this prediction was found in the following years when studying this transition in conducting materials. The electric conductivity $\sigma$ decayed exponentially with the length of the system when the Anderson localization regime was reached [37]. The Anderson transition means that a conductor becomes an insulator, because the wave function of electrons is localized inside the sample, stopping the classic diffusion. The origin of this effect is the multiple scattering of the electrons by defects in solids.

The same effect is present for photons in strongly disordered dielectrics [2], with the great advantage that no interaction is present for photons with respect to electron-electron interaction in the electronic case. This fact can make photonic systems more suitable for studying Anderson localization than electronic ones. On the contrary obtaining the same scattering efficiency with respect to electronic solids is not so easy in dielectrics. The proposal of John for photonic crystals [11] derived from the necessity to design a strongly scattering dielectric system to study Anderson localization of photons.

Experimental proofs for the existence of localization of light in the near-infrared was given in 1997 by Wiersma et al. [7], where GaAs powder, with particles dimension of $\sim$ 300 nm was used. To obtain localization in a 3D sample, the transport mean free path $\ell_t$ (the length over which the light has lost its original direction completely) is subject to the Ioffe-Regel condition [38]

$$k\ell_t \leq 1.$$  \hspace{1cm} (1.6)

Localization means that the diffusion mechanism of photons is stopped, and the light is trapped inside the sample. The transmission of the sample
Figure 1.6: Anderson localization is caused by constructive interference of time reversed waves if the Ioffe-Regel criterion is fulfilled in a 3D system. The diffusion is stopped and the light is localized in loops.

\[ T = T_0 \exp\left(-\frac{L}{\xi}\right), \]  

(1.7)

where \( L \) is the length of sample and \( \xi \) is the localization length, that represents the critical dimension for a sample to have localized states. Fig. 1.6 shows schematically what happens to photons in the localized regime. If \( S \) is a point source inside a strongly scattering medium, subject to the Ioffe-Regel condition, two waves that propagates in opposite directions along this loop will acquire the same phase shift and so they interfere constructively. Far from the localization, loops of this type have very low probability to exist and classical diffusion dominates.

### 1.4 Disordered systems: random lasers

The light propagation in disordered multiply scattering systems, that for the moment we can suppose to be dielectric to avoid light absorption, has been studied in last years. Out from the Anderson localization regime the light propagates diffusively in first approximation. The physical condition to have light diffusion is simply \( \lambda \ll \ell_t \ll L \), meaning that we have to stay away
from Anderson transport and also that the sample dimensions $L$ have to be longer with respect to transport mean free path to be in the multiple scattering regime. From a diffusive sample we can perform measurements from which we extract the transport mean free path, using the coherent backscattering technique [4, 5], or we can measure the diffusion constant $D$ with a time-resolved experiment [39]. These two quantities, that in general depend on frequency, are related if one supposes to have isotropic diffusion in three dimensions by

$$D(\omega) = \frac{1}{3} v_e(\omega) \ell_t(\omega).$$

$v_e$ is called energy velocity (it describes the transport of the electromagnetic energy). It can be of the order of the phase velocity $c/n$ for many dielectric systems, but can be also $10^{-5} c$, as happens for a cold cloud of rubidium atoms [40].

Thinking about applications for random dielectric systems, one can add optical gain to these systems to obtain an optical device. What we have in this way is a random amplifying medium or what is called today a random laser. Random laser effect was predicted by Letokhov in 1968 [41], but the first experimental evidences of this effect are dated 1993-1994 [42, 43].

A random laser is a sort of mix of a standard laser and a light bulb. Fig. 1.7 shows the comparison between a “classic” laser and a random laser. On the left side a traditional laser cavity is depicted. It is simply formed by two mirrors and by an active medium that amplifies the light. The output is a coherent beam, monochromatic and directional. On the right side of fig. 1.7 a random laser is shown. The cavity does not exist and the gain medium is dissolved in the scattering dielectrics. It is the multiple scattering that in a certain way replaces the optical cavity. The light is trapped inside the medium by multiple scattering and during the scattering it is amplified by the gain medium. The output radiation can be roughly monochromatic, but without coherence and it is emitted over the whole solid angle.

The emission properties of random lasers are not so different from the traditional ones. In particular random laser exhibit a threshold behavior. When
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the gain overcomes the losses the system goes above threshold. The losses are proportional to the total sample surface and the gain to its volume, so the threshold criterium can be expressed in terms of a critical volume $V_{cr}$ above which the system lases [41].

There are many ways to obtain a random amplifying medium. At the beginning particle suspensions of TiO$_2$ was dissolved in methanol plus Rhodamine 6G (laser dye) [43], or laser crystals were powdered to have both gain and scattering as Nd:YAG [42] or Ti:Sa [44]. Today many other systems are studied, such as porous glasses in which liquid crystals plus laser dye are infiltrated [45], Zinc oxide powder for high scattering and high gain [46] and many others. From the point of view of the random laser the crucial parameter is the transport mean free path, that is a measure of the scattering strength of the system. Most of the systems studied are in the diffusive regime, where $\lambda \ll \ell_t \ll L$.

Some experiments were also performed in the Anderson localization regime. Cao et al. [46] used a high scattering semiconductor powder (emitting around 380 nm) as a random laser. The emitted light had the same behavior as a diffusive random laser, except for the fact that the spectrum exhibited ultranarrow spikes. They argue that such spikes are caused by a resonant feedback generated by localized states, which act as standard laser cavities. The debate
is very controversial on this argument, similar to what is happening for left handed materials [47].

Ultra-narrow spikes were also observed for a random laser in the diffusive regime, but they are caused by the amplification of the photon noise [48]. From Monte Carlo simulations, where one can follow the random walk for each photon, “rare” lucky photons can make a very long path inside the gain region and be amplified much more than others. These lucky photons generate ultra-narrow spikes. One photon is enough for a laser spike.

1.5 Tunability of photonic devices

In both the systems described, ordered systems as photonic crystals and disordered dielectrics in the form of random lasers, the important parameter is the scattering strength of the system, which determines the opening of a complete photonic band gap for the first and an efficient diffusive feedback for the latter. Obviously when one builds up a photonic system the scattering strength is fixed. As for standard electronic devices, where a bias voltage control allows one to change the diffusion of electrons, we need for photonic devices something that could permit us to change the scattering strength.

In 1999 Busch and John [49] suggested infiltrating a 3D photonic crystal with a nematic liquid crystal, to use the birefringency of the nematic phase and the alignment of the nematic director with an external electric field to change the dielectric contrast\(^2\) of a photonic crystal.

Usually liquid crystals in the nematic phase possess two indices of refraction differing of \(\sim 0.2\). If no electric field is applied we can speak about of an average refractive index \(n_{\text{ave}}\). Typically \(n_{\text{ave}} \sim 1.6\), so replace air (\(n_{\text{air}} = 1\)) with liquid crystals is not so useful in a photonic crystal, because we are reducing the refractive index contrast. It means that the scattering and hence the width of the photonic gap decrease. When we apply an electric field, the situation changes. The liquid crystal molecules align following the field and

\(^2\)The dielectric contrast is simply defined as the ratio between the refractive indices of the two materials that form the photonic crystal.
the incoming light experiences different refractive indices for different polarization vectors. It means that changing the polarization of light we can tune the scattering strength of a photonic crystal.

The other advantage in using liquid crystals as tunable systems is that their refractive indices are very sensitive to temperature. The nematic phase exists only in a limited range of temperatures, after that the liquid crystal returns to the “classic” liquid phase. The nematic-isotropic phase transition can be used to tune the DOS of the photonic systems [50, 51].

Starting from this idea to tune with temperature and with external electric field the mean free path of an ordered system, we can apply it also for the disordered case, to try to change the diffusive transport of light in a random laser. The tuning of photonic systems is one of the main argument of this thesis and in chapter 2 we will see the main properties of liquid crystals, considering them as versatile instruments for photonic devices.

Other ways are under investigation to obtain tunability for a photonic crystal. One of the more promising and interesting is a theoretical prediction, which shows that a three-dimensional semiconductor photonic crystal can be switched on a femtosecond scale through two-photon excitation of free carriers [52]. Beyond this particular case, the ability to change the scattering properties of a photonic systems is the crucial point if one wants flexible photonic devices.

1.6 The outline of this thesis

In chapter 2 the main properties of liquid crystals will be presented, such as surface anchoring and birefringency. These properties are fundamental in understanding the liquid crystals infiltration in opal photonic crystals of chapter 3 and the emission properties of the polymer dispersed liquid crystal random laser in chapter 4. In chapter 3 we will show reflectivity measurements on opal photonic crystals. In particular for inverse opals made of silicon we will point out the non Bragg behavior of the diffracted peaks.

In chapter 4 the polymer dispersed liquid crystal random laser will be stud-
ied. This system reveals interesting features regarding the transport of light. The random laser can be turned on and off by the nematic-isotropic phase transition. Upon electric field application the emitted spectrum is spatially anisotropic and also polarized. At the end, in chapter 5, 1D random multilayer systems will be studied. The states of the multilayers result of two types: localized states and necklace states. The latter are very important because they contribute dominantly to the resistance of the samples. Besides that, we will also study the emission properties of a 1D random laser formed by silicon multilayers.
Bibliography


Chapter 2

Liquid Crystals

Discovered at the end of the last century (1888-Reinitzer), liquid crystals were considered an oddity with only pure academic value until 1960, when they were first considered for use in display technology. For 20 years, most of the effort was devoted to the understanding of the bulk properties (surface effects were oversimplified by the strong anchoring hypothesis). In the 1980s the attempts to mix liquid crystals with plastic materials gave rise to a new class of materials, called polymer dispersed liquid crystal (PDLC), in which small random droplet of liquid crystal were arranged. In this chapter we present the main properties of nematic liquid crystals such as elastic properties, interactions with external surfaces, birefringency and diamagnetism.

2.1 The three phases of liquid crystals

Today around us many devices such as monitors, digital cameras and others use the liquid crystal knowledge for the display technology. But when one looks through a LCD (liquid crystal display), can ask to himself how can a thin liquid crystal film (~50 μm) reproduce such good quality images? The answer stay in one of the main optical property of liquid crystals: the dielectric
anisotropy. High resolution images are possible because an external electric field can change the alignment of nematic liquid crystal molecules.

The mechanical and symmetry properties of liquid crystals are intermediate between those of liquids and those of solids. This is the reason for which we call them liquid crystals. Liquid crystals are systems in which liquid-like order exists at least in one direction of space and in which some degree of anisotropy is present. In nature three types, or better three phases, of liquid crystals exist and they depend on the molecular order of the system (see fig. 2.1).

- **Nematic phase** happens if the positional order is in one dimension.

- **Smectic phase** happens if the system can be viewed as a set of two-dimensional liquid layers stacked on each other with a well defined spacing.

- **Columnar phase** can be described as a two-dimensional array of liquid tubes, which corresponds to a two-dimensional ordered system in three dimension.

Usually nematics and smectics are made of elongated objects (as shown in fig. 2.1) and columnars are made of disk-like molecules. The temperature range in which the liquid crystal phase exists, depends on its chemical properties. Out of this range we can have traditional solid (if the temperature is decreased)
or liquid (if it is increased). In this thesis the interest in liquid crystals is restricted to nematics, so in next sections only the properties of such a phase will be described.

### 2.2 Elastic properties of nematics

Nematic liquid crystals, depicted in fig. 2.1(a), show some order in the direction of the molecules. They tend to be parallel to a common axis labelled *nematic director* $\mathbf{n}$. This means, for instance, that optically a nematic is an uniaxial medium with the optical axis along $\mathbf{n}$. The states of director $\mathbf{n}$ and $-\mathbf{n}$ are indistinguishable (nematics are not dipolar ferroelectric). Another remarkable property is that nematics flow like liquids. The nuclear magnetic resonance (NMR) spectrum shows line spitting caused by the uniaxial symmetry, and, at the same time, such lines are narrow enough to identify rapid molecular motion (like for conventional liquids).

Nematics formed by rod-like molecules exhibit spontaneous quadrupolar ordering. If $\boldsymbol{\alpha}$ is a unit vector along each rod molecule, the polar order $<\mathbf{\alpha}>$ averaged an all molecules is zero since the nematic is not dipolar ferroelectric. To define the mean orientation we need to look at the mean quadrupolar order defined by:

$$\frac{3}{2} < \mathbf{\alpha} \mathbf{\alpha} - \mathbf{I}/3 >,$$

where $\mathbf{I}$ is the identity tensor. We find that this molecular average is a tensor oriented along the director $\mathbf{n}$ ($n^2 = 1$), which can be written as

$$\frac{3}{2} < \mathbf{\alpha} \mathbf{\alpha} - \mathbf{I}/3 > = \frac{3}{2} S < \mathbf{n} \mathbf{n} - \mathbf{I}/3 >,$$  \hspace{1cm} (2.2)

where $S$ is the scalar uniaxial parameter [1]. In what follows we use the traceless tensor order parameter [2]

$$Q_{i,j} = \frac{3}{2} S (n_i n_j - \delta_{i,j}/3)$$  \hspace{1cm} (2.3)

having a quadrupolar structure. If $Q_{i,j}$ is position-dependent, as in the clas-
sical theory of elasticity, it is possible to write an elastic energy density. Let $F$ be the free energy density of the nematic phase, we can write:

$$F = F(Q_{i,j}, Q_{i,j,k}),$$

(2.4)

where $Q_{i,j,k} = \partial Q_{i,j}/\partial x_k$ are the spatial derivatives of tensor order parameter elements. If we suppose that $Q_{i,j}$ changes slowly in space, $Q_{i,j,k}$ are small quantities. So we can rewrite eq. 2.4 as

$$F(Q_{i,j}, Q_{i,j,k}) = F_u(Q_{i,j}, 0) + F_e(Q_{i,j,k}),$$

(2.5)

where $F_u$ is the free energy density of the uniform nematic, whereas $F_e$ represents the elastic contribution to the total free energy density. The uniform part of $F$ depends only on the temperature, and contains information for the nematic-isotropic phase transition [3]. If we suppose that nematic liquid crystal distortion is completely described by $Q_{i,j,k}$, $F_e$ can be expanded in power series of the deformation tensor $Q_{i,j,k}$. In the harmonic approximation one obtains:

$$F_e(Q_{i,j,k}) = A_{i,j,k} Q_{i,j,k} + \frac{1}{2} B_{ijklmn} Q_{i,j,k} Q_{l,m,n} + O(3).$$

(2.6)

The tensors $A$ and $B$ describe the elastic interactions. If $A \neq 0$, the ground state is deformed. In this case nematic liquid crystals are called cholesteric because the structure undergoes a helical distortion. We are interested in pure nematics, so we can put $A = 0$; if we impose $S = \text{cost.}$, we obtain the well-known Frank expression [4]

$$F_e = \frac{1}{2} [K_{11} (\text{div } \mathbf{n})^2 + K_{22} (\mathbf{n} \cdot \text{curl } \mathbf{n})^2 + K_{33} (\mathbf{n} \times \text{curl } \mathbf{n})^2],$$

(2.7)

where $K_{i,j}$ represent the components of the elastic deformation tensor. The Frank expression is derived from the continuum theory, where the main hypothesis is that $Q_{i,j}$ varies over distances $\geq 1 \mu m$, much larger than typical molecular dimensions $\sim 20 \AA$. 
2.2.1 Frank elastic constants

The constants $K_{ii}$ (i=1,2,3), introduced in eq. 2.7, are associated with the three basic types of deformations present in liquid crystals, displayed in fig. 2.2

$K_{11}$ describes splay ($\text{div } \mathbf{n} \neq 0$)

$K_{22}$ describes twist ($\mathbf{n} \cdot \text{curl } \mathbf{n} \neq 0$)

$K_{33}$ describes bend ($\mathbf{n} \times \text{curl } \mathbf{n} \neq 0$).

The typical value for $K_{ii}$ are $10^{-11}$ N. Eq. 2.7 required about 30 years to be defined.

2.2.2 One constant approximation

Sometimes eq. 2.7 is difficult to manipulate and one can decide to set the three elastic constants at the same value (usually they do not differ by orders of magnitude). So we have the expression for the free energy density in the
one constant approximation, that is

\[ F_e = \frac{1}{2} K [ (\text{div } \mathbf{n})^2 + (\text{curl } \mathbf{n})^2 ] . \]  

(2.8)

This equation is identical in the form to the Landau-Lifshitz free energy for distortions in the direction of magnetization \( \mathbf{M}(\mathbf{r}) \) in a cubic ferromagnet:

\[ F_m = \frac{1}{2} A [ (\text{div } \mathbf{M})^2 + (\text{curl } \mathbf{M})^2 ] . \]  

(2.9)

The main difference is that eq. 2.9 is rigorous, while eq. 2.8 is an approximation. In a ferromagnet the rotation of the spin does not change the energy, while in nematic liquid crystals a rotation of the molecules (keeping the center of gravity fixed) changes the energy.

### 2.3 Surface anchoring

Real nematic liquid crystal samples are limited by a closed surface \( \Sigma \). This implies that one has to consider a surplus of free energy density \( \Delta F_s \) due to the presence of the surface, which depends on \( Q_{i,j} \) in the harmonic approximation:

\[ \Delta F_s = \Delta F_s(Q_{i,j}) . \]  

(2.10)

\( \Delta F_s \) is partially due to the reduced symmetry of nematic liquid crystal near the surface and to the direct interaction between liquid crystal and the surface. Let \( \rho \) be the range of intermolecular forces that in the nematic phase is of the order of the size of molecules. A molecule, at a distance \( z > \rho \) from the wall (see fig. 2.3), is submitted to a complete interaction with other nematic molecules. On the contrary, if the distance is \( z \leq \rho \), the molecule experiences an incomplete interaction with the other molecules because of the wall. In this way it is possible to define the surface energy density as

\[ f_s = \int_0^\rho \Delta F_s \, dz . \]  

(2.11)
2.3. SURFACE ANCHORING

Figure 2.3: A nematic liquid crystal limited by the surface. The molecules for which \( z < \rho \) are submitted to the interaction with the surface.

If we suppose a complete absence of bulk distortion \( (Q_{i,j,k} = 0) \), using eq. 2.11, we can find the easy nematic director \( n^e \) that minimize \( f_s \)

\[
f_s(n^s_i) = f_s(n^e_i) - \frac{1}{2}W(n^s \cdot n^e)^2 ,
\]

(2.12)

where \( W \) is called the surface anchoring strength and \( n^s \) is the easy axis induced by the surface. This formula was proposed for the first time by Rapini and Papoular in 1969.

As an example, consider a surface imposing an uniaxial order \( S_0 \) along the direction \( n_0 \). The surface energy can be written as

\[
f_s = \frac{1}{2}W(Q - Q_0)^2 ,
\]

(2.13)

where \( Q = \frac{1}{2}S(nn - I/3) \) and \( Q_0 = \frac{1}{2}S(n_0n_0 - I/3) \). This implies for the free energy

\[
f_s = \frac{9}{8}W[\frac{2}{3}S^2 + \frac{2}{3}S_0^2 - 2SS_0(\cos^2 \theta - 1/3)] ,
\]

(2.14)

where \( \cos \theta = nn_0 \). If \( n = n_0 \), we simply obtain \( f_s \propto (S - S_0) \), which means that the equilibrium configuration (for which \( df_s/dS = 0 \) is reached when

\[\text{This formula derives from the most general}
\]

\[
f_s(Q^s_{i,j}) = f_s(Q^e_{i,j}) + \frac{1}{2}W(Q^s_{i,j} - Q^e_{i,j})^2 ,
\]

which is a generalization of eq. 2.12.
In the case of \( n \neq n_0 \), minimizing \( f_s \) one obtain

\[
S = \frac{3}{2} S_0 (\cos^2 \theta - 1/3) .
\]  

(2.15)

For the \textit{magic} angle \( \theta = \arccos(1/3) \), \( S = 0 \) and the surface does not tend to induce any order.

The Rapini-Papoular formula is an approximation for the surface energy, and it works better if we are in the \textit{weak} anchoring condition. \textit{Strong} and \textit{weak} anchoring are usually defined by comparing \( W \) with \( K/\eta \), where \( \eta \) is the coherence length for the nematic-isotropic transition. \( W \sim K/\eta \) is the strong anchoring condition, while for \( W \ll K/\eta \) we are in the weak anchoring regime.

### 2.3.1 High orders in surface anchoring

Experimentally deviations from the Rapini-Papoular formula in nematics have been observed in the past [5, 6]. Corrections to eq. 2.12 are of the order of \((n^s \cdot n^e)^4\) and are due to three distinct phenomena. The first one is \textit{flexoelectricity} (the analogous of piezoelectricity in solids), which means that nematics exhibit an electric polarization proportional to the distortion of the director. The second contribution named \textit{order electric}, comes from an electric polarization term due to the spatial variation of the scalar uniaxial parameter. The latest is originated from the roughness of the surface. In summary we can write \( f_s \)

\[
f_s = f_{\text{rp}} + f_{\text{fl}} + f_{\text{oe}} + f_{\text{sur}}
\]  

(2.16)

where \( f_{\text{rp}} \) is the Rapini-Papoular term, and the others are high order corrections [7].

### 2.4 Magnetic and electric field effect

#### 2.4.1 Diamagnetism

A benzene ring, when experiences a magnetic field \( \mathbf{H} \) normal to its plane, tends to rotate and to align itself to the field. Liquid crystals are formed by
2.4. MAGNETIC AND ELECTRIC FIELD EFFECT

benzene rings. One of the most common is 5CB (p-pentyl-p’-chanobiphenyl) that has two benzene rings, as shown in fig. 2.4, such as many others liquid crystals, which are diamagnetic. The coupling between $\mathbf{H}$ and a diamagnetic molecule is $(\mu_b H)^2 / U$, where $\mu_b$ is the Bohr magneton and $U$ is the electronic excitation energy. For one molecule $(\mu_b H)^2 / U \sim 10^{-18}$ eV (if $F \sim 10$ eV and $H \sim 1$ gauss) $\ll kT$, which means that the thermal agitation is stronger with respect to field alignment. If we consider that the main property of nematics is that in a real sample ($\sim 10^{23}$ molecules) all molecules rotate in unison, we obtain a coupling energy of $N(\mu_b H)^2 / E \gg kT$, and the sample aligns its optical axis $\mathbf{n}$ parallel to $\mathbf{H}$.

\[ \text{Figure 2.4: In the upper part the molecular structure of 5CB is depicted, while in the lower part the chemical formula with two benzene rings.} \]

To investigate about the effects of an external magnetic field on nematics, we have to write down the free energy density. Let’s start with the magnetization $\mathbf{M}$ induced by $\mathbf{H}$. If we suppose an arbitrary angle between $\mathbf{n}$ and $\mathbf{H}$, the magnetization will be:

\[ \mathbf{M} = \chi_\perp \mathbf{H} + (\chi_\parallel - \chi_\perp)(\mathbf{H} \cdot \mathbf{n})\mathbf{n} , \]  

where, for the diamagnetism, the magnetic susceptibilities $\chi_\parallel$ and $\chi_\perp$ are negative ($\sim 10^{-6}$), but the difference $\chi_\parallel - \chi_\perp = \chi_a$ is positive in nematics.
Figure 2.5: Interplay between the surface and magnetic forces. In this case the nematic liquid crystal is subject to pure twist. If the molecule is distant $\rho$ from the wall, when $\rho < \zeta$ the molecule feels the surface strength; when $\rho > \zeta$ it feels the field strength.

The free energy density becomes

$$F = F_e + f_s - \int_0^H \mathbf{M} \cdot d\mathbf{H} = F_e + f_s - \frac{1}{2} \chi_\perp H^2 - \frac{1}{2} \chi_a (\mathbf{n} \cdot \mathbf{H})^2$$

that is minimized when $\mathbf{H}$ is parallel to $\mathbf{n}$ ($\chi_a > 0$), as said before.

In eq. 2.18 the competition between surface anchoring and magnetic field effect is considered. From one side the anchoring establishes an easy axis for the nematic director; from the other side $\mathbf{H}$ tends to align the director parallel to itself. This competition from these two forces allows us to define a new length that depends on the interplay between the surface and $\mathbf{H}$, and also from the elastic properties of the liquid crystal. In fig. 2.5 an example is shown. The nematic liquid is forced to have, let us say, two easy axis: one induced by the wall, the other by the magnetic field. The resulting length is $\zeta$, called coherence length. It is defined as the distance over which the disturbance of the alignment propagates through the sample. If we suppose to be in the one constant approximation ($K_{ii} = K$), we have

$$\zeta(H) = \frac{1}{H} \sqrt{\frac{K}{\chi_a}}. \quad (2.19)$$
2.4. MAGNETIC AND ELECTRIC FIELD EFFECT

For $K = 10^{-6}$ dye, $\chi_a = 10^{-6}$ and $H = 10^4$ gauss, the coherence length is of the order of $1 \mu$m. This expression is derived starting from eq. 2.18 (for details see ref. [1]).

When a liquid crystal sample is studied, we have always a cell of a certain thickness, in which the two walls induce an easy axis for the nematic director. If no external field is applied the director follows the easy axis for the orientation. When $H$ is applied normally to such easy axis a magnetic torque is established

$$\Gamma_M = \chi_a (n \cdot H)n \times H.$$  \hfill (2.20)

Increasing $H$ there will be a phase transition, studied by Frederiks in 1927, from the unperturbed configuration ($H \ll H_c$) to the distorted one ($H \geq H_c$), where $H_c$ is the critical magnetic field at which the transition takes place. Obviously $H_c$ has to depend on elastic constants and on the distance $d$ between the two walls. If one suppose to be in the strong anchoring approximation, one obtains

$$H_c = \frac{\pi}{d} \sqrt{\frac{K}{\chi_a}}$$  \hfill (2.21)

in the one constant approximation. Eq. 2.21 can be applied to determine the three elastic constants and also to measure the coherence length. Obviously $\zeta$ and $H_c$ are strictly connected; for $H = H_c \rightarrow \zeta(H_c) = d/\pi$.

2.4.2 Dielectric anisotropy

A nematic liquid crystal can be considered in first approximation an insulator. In this hypothesis the coupling between a nematic and an external electric field $E$ involves only the anisotropy of the dielectric constant. What happens is somehow similar to the case of coupling between $H$ and nematics caused by diamagnetism.

Suppose we apply an electric field to a nematic cell in which the angle between $E$ and $n$ is generic. We obtain for the electric displacement $D$

$$D = \epsilon_\perp E + (\epsilon_\parallel - \epsilon_\perp)(n \cdot E)n$$ \hfill (2.22)
where, different from the magnetic case, \( \epsilon_a = \epsilon_{\parallel} - \epsilon_{\perp} \) (dielectric anisotropy) can be positive or negative. In particular, from a chemical point of view, \( \epsilon_a > 0 \) if the liquid crystal has a dominant dipole associated with the \( C \equiv N \) group. This means a permanent dipole parallel to the long axis of the molecule (this is the case of 5CB shown in fig. 2.4). In nematics we can have also a reversed situation, where the permanent electric dipole is orthogonal to the long axis. This happens when the dipole associated to the N–O groups is dominant, which means \( \epsilon_a < 0 \).

The electric contribution to the free energy density will be

\[
-\frac{1}{4\pi} \int_0^E \mathbf{D} \cdot d\mathbf{E} = \frac{\epsilon_{\perp}}{8\pi} E^2 - \frac{\epsilon_a}{8\pi} (\mathbf{n} \cdot \mathbf{E})^2 .
\]  

(2.23)

In this case if \( \epsilon_a > 0 \) the free energy density will be minimized for a parallel alignment, otherwise for \( \epsilon_a < 0 \) we observe a perpendicular alignment. Regarding the critical electric field \( E_c \) for Frederiks transition and the electric coherence length \( \zeta(E) \) we have:

\[
E_c = \frac{\pi}{d} \sqrt{\frac{4\pi K}{\epsilon_a}} \quad \zeta(E) = \frac{1}{E} \sqrt{\frac{4\pi K}{\epsilon_a}} .
\]  

(2.24)

From eq. 2.24 we can compare the magnitudes of electric and magnetic field applied to nematics to obtain the same effect for Frederiks transition. Usually the dielectric anisotropy \( \epsilon_a \sim 0.5 \) and the equivalent critical electric field for \( H_c = 1 \) gauss is \( E_c = 1 \) V/cm.

Suppose to have a nematic liquid crystal with \( \epsilon_a > 0 \). When an external electric field is applied, the nematic director follows the field. An incident light wave on an aligned cell of liquid crystals will experience different refractive indices, depending on the polarization of light. If the polarization is parallel to \( \mathbf{n} \), the refractive index felt is the extraordinary one \( n_e \); if the polarization is orthogonal to the director, the light sees the ordinary index \( n_o \). This property is called birefringency, the system possesses two refractive indices.

\[\footnote{If we use the substitution \( \frac{1}{2} \chi_a H^2 \to \frac{\epsilon_a E^2}{8\pi} \) in eq. 2.18.}\]
Bibliography


Chapter 3

3D Photonic Crystals

In this chapter experimental results on 3D photonic crystals, in the form of direct and inverse opals, are presented. Reflection measurements, in which the angle of incidence is varied, were performed for direct opals made of SiO$_2$ and for inverse opals made of TiO$_2$ and Si. We measured a stop band behavior for silica and titania photonic crystals, while for silicon inverse opals the angle resolved reflection measurements gave an indication of a possible full photonic band gap. Beyond that, the tunability of opals infiltrated with liquid crystals was explored. For the case of temperature tuning a modest shift of the stop band was measured, while for electric field tuning no sensible variations on the reflection spectra were observed. For nematic liquid crystals, confined in pores of hundreds of nanometers, the surface anchoring plays a fundamental rule on the alignment of the nematic molecules.

3.1 The formation of a photonic band gap

As introduced in chapter 1, photonic crystals possess a forbidden gap for photons, analogous to the band gap for electrons in a semiconductor. The origin of this gap is very similar to that of the electronic one. The periodic
quantities that make equal electronic and photonic crystals are: the atomic potential in first case and the dielectric constant in the latter. Let’s write down some formulas to quantify this analogy.

For simplicity we will examine in detail the 1D case, schematically presented in fig. 3.1. Considering a non magnetic ($\mu_r = 1$) dielectric system, in which free charges and polarization charges are absent ($\rho_{tot} = 0$), Maxwell’s equations become:

$$
\text{div} \, \mathbf{E} = 0 \quad \text{div} \, \mathbf{B} = 0
$$
$$
\text{curl} \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad \text{curl} \times \mathbf{B} = \epsilon \mu \frac{\partial \mathbf{E}}{\partial t},
$$

where $\epsilon = \epsilon_0 \epsilon_r$ and $\mu = \mu_0$. Combining the equations and focusing the attention to the 1D case, where light propagates in the x direction in our sample, we obtain

$$
\frac{c^2}{\epsilon_r(x)} \frac{\partial^2 \mathbf{E}}{\partial x^2} = \frac{\partial^2 \mathbf{E}}{\partial t^2}.
$$

(3.2)

To simplify the treatment we can consider eq. 3.2 in its scalar form. The dielectric function $\epsilon_r(x)$ is a periodic function of $x$, $\epsilon_r(x) = \epsilon_r(x+a)$, where $a$ is the lattice constant of the photonic crystal. $\epsilon_r^{-1}(x)$ is also periodic and can
3.1. THE FORMATION OF A PHOTONIC BAND GAP

be expanded in a Fourier series as follows:

\[ \epsilon^{-1}_r(x) = \sum_{m=-\infty}^{\infty} k_m \exp \left( i \frac{2\pi m}{a} x \right), \quad (3.3) \]

where \( m \) is an integer and \( k_m \) are the Fourier coefficients. Here we suppose that the system does not absorb light, which means that \( \epsilon_r(x) \) is real, and hence that \( k_{-m} = k_m^* \). Since \( \epsilon_r(x) \) is periodic, we can use Bloch’s theorem, which gives us the eigenmodes of a 1D photonic crystal

\[ E(x, t) = E_k(x, t) = u_k(x) \exp \left[ i(kx - \omega_k t) \right]. \quad (3.4) \]

Eq. 3.4 tells us that each eigenmode is characterized by a wave vector \( k \). \( \omega_k \) denotes the eigen-frequency and \( u_k(x) = u_k(x + a) \) is the periodic Bloch function. Hence \( E_k(x, t) \) is periodic and expanding in a Fourier series results in

\[ E_k(x, t) = \sum_{m=-\infty}^{\infty} E_m \exp \left[ i(k + \frac{2\pi m}{a})x - i\omega_k t \right]. \quad (3.5) \]

We can assume for simplicity that only components with \( m = 0, \pm 1 \) are dominant in the expansion of \( \epsilon^{-1}_r(x) \):

\[ \epsilon^{-1}_r(x) \approx k_0 + k_1 \exp \left( i \frac{2\pi}{a} x \right) + k_{-1} \exp \left( -i \frac{2\pi}{a} x \right). \quad (3.6) \]

The problem is solved if we substitute eq. 3.5 and 3.6 into the waves equation 3.2. Here we skip the details of calculation (see for a complete treatment e.g. ref. [1]) and we will discuss the results. The eigen-frequencies are:

\[ \omega_{\pm} \approx \frac{\pi c}{a} \sqrt{k_0 \pm |k_1|} \pm \frac{ac}{\pi |k_1|} (k_0^2 - \frac{|k_1|^2}{2})(k - \frac{\pi}{a})^2 \quad (3.7) \]

as far as \((k - \pi/a)^2 \ll \pi/a\), there is no mode in the interval

\[ \frac{\pi c}{a} \sqrt{k_0 - |k_1|} < \omega < \frac{\pi c}{a} \sqrt{k_0 + |k_1|}. \quad (3.8) \]
CHAPTER 3. 3D PHOTONIC CRYSTALS

Figure 3.2: Dispersion relation for a 1D photonic crystal in the first Brillouin zone (solid curve), compared with the dispersion relation for a homogeneous material $\omega = \nu k$ (dashed lines). When the two dispersion lines cross, they repel each other and a photonic gap appears.

This photonic gap disappears only if $k_1 = 0$. This result can be interpreted as due to the coupling of the modes with $k \approx \pi/a$ and $k \approx -\pi/a$ in the presence of the periodic modulation of the dielectric constant and this mixing leads to a frequency splitting. The resulting band diagram is depicted in fig. 3.2, where the dispersion relation for the 1D photonic crystal is compared with the dispersion for a homogeneous material.

For a semiconductor the treatment is very similar. Starting from the Shrödinger equation for an electron in a periodic potential $V(x) = V(x + a)$,

$$\left[ \frac{p^2}{2m} + V(x) \right] \psi(x) = E_0 \psi(x), \quad (3.9)$$

where $\psi(x)$ is the wave function of the electron and $E_0$ is the energy eigenvalue, we obtain a similar solution for the dispersion relation as in the photonic case (see for details e.g. ref. [2]).

If now we consider the waves equation 3.2 in its scalar form and we assume
3.1. THE FORMATION OF A PHOTONIC BAND GAP

that it has solutions of the type $E(x, t) = E(x) \exp (i\omega t)$, we have:

$$\frac{\partial^2 E(x)}{\partial x^2} + \epsilon_r(x) \left(\frac{\omega}{c}\right)^2 E(x) = 0 . \quad (3.10)$$

Rewriting eq. 3.10, we obtain

$$-\frac{\partial^2 E(x)}{\partial x^2} + \left(\frac{\omega}{c}\right)^2(1 - \epsilon_r(x))E(x) = \left(\frac{\omega}{c}\right)^2 E(x) . \quad (3.11)$$

We can now define a light potential $V_{\text{light}}(x, \omega) = \left(\frac{\omega}{c}\right)^2(1 - \epsilon_r(x))$, so that for photons we have

$$-\frac{\partial^2 E(x)}{\partial x^2} + V_{\text{light}}(x, \omega)E(x) = \left(\frac{\omega}{c}\right)^2 E(x) , \quad (3.12)$$

which is very similar to the Shr¨odinger equation:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x)\psi(x) = E_0\psi(x) . \quad (3.13)$$

We can now make a comparison between the waves equation 3.12 and the Shr¨odinger equation 3.13. The differences are only due to the potentials.

- When $\epsilon_r(x) = 1$ (vacuum), $V_{\text{light}} = 0$. This is valid immediately outside the sample. In contrast the Coulomb potential $V$ has a finite range for a finite piece of material, also outside the sample.

- For propagating waves $\epsilon_r(x) \geq 1$ (excluding for the moment left handed materials), which means that the difference $(\omega/c)^2 - V_{\text{light}}$ is always positive. This means that bound states for light do not exist, while for electrons the difference can be both positive or negative: one can have valence and conduction electrons.

- $V_{\text{light}}(x, \omega)$ depends on the energy and it vanishes for low values of $\omega$; in other words for small frequencies the material becomes more and more transparent.

The band diagram and the comparison between waves and Shr¨odinger’s
equations was made in one dimension, but similar considerations hold in two and three dimensions. The photonic band gap forms because of the periodicity of the refractive index, similar to the formation of the electronic bandgap in a semiconductor. In the following pages of this chapter we will focus our attention to 3D photonic crystals, in the form of inverse opals.

### 3.2 Synthesis of opal photonic crystals

The growth of photonic systems in the near-infrared or in the visible is not so easy, as pointed out in chapter 1, in particular for three-dimensional structures. Direct opal structures are formed by packing spheres (usually dielectric, but sometimes also conducting [3]), following the face centered cubic geometry. In a typical sample the volume fraction for the spheres is $\sim 75\%$, while the rest is air. Calculations by Li and Zhang show that a complete photonic band gap can be opened in direct opals only if the polydispersity ($\Delta R/R$, introduced in chapter 1) of the spheres is less than 5% [4]. The other important parameter is the refractive index contrast; for a closed packed FCC crystal the contrast should be at least 2.8 to open a complete photonic band gap [5]. If we use a different packing, like a diamond structure, a contrast of 2.0 is enough to open the gap [6]. However opal photonic crystals with a diamond structure would be very hard to grow, due to natural sedimentation according to the FCC packing. Finally another important condition is that the constituent material should have negligible absorption in the wavelength range of interest.

In opal photonic crystals the spheres are usually made of silica ($SiO_2$) or polystyrene, with a typical refractive index of $\sim 1.5$. These spheres are nowadays commercially available, or can be synthesized using chemical nucleation [7]. For photonic crystals in the visible range the spheres have to have a radius of hundreds of nanometers. Problems on polydispersity arise when we go below 100 nm. To build up a direct opal, the dielectric spheres are usually suspended in water, with a typical concentration of $\sim 3 - 4\%$. The growth process is done in thin flat capillaries. For “large” spheres with radius of $\sim 500$ nm two months are required using natural sedimentation. If one
3.2. SYNTHESIS OF OPAL PHOTONIC CRYSTALS

Figure 3.3: Self-assembled silica direct opal with FCC packing (Polytechnic of Turin, project MIUR-COFIN 2002).

uses “smaller” spheres of \( \sim 200 \text{ nm} \) of radius, it will take almost six months to obtain a crystal structure with \( \sim 1000 \) layers. Centrifugation can reduce drastically this time by accelerating the sedimentation process [8]. When the opal is completely formed, the top of the capillary is opened and the water is left to evaporate very slowly for 1 month. The result is a direct opal displayed in fig. 3.3.

These direct opals are typically formed of materials with low refractive index (\( \sim 1.5 \)) and therefore cannot possess a complete gap. They are used as a template for the inverse structure, where air spheres and interstitial dielectric material form an inverse opal. When the direct structure is ready, the voids are filled with a precursor liquid of the new constituent for the inverse structure. The precursor technique is usually applied for inverse opals of titania (\( \text{TiO}_2 \)), zirconia (\( \text{ZrO}_2 \)), alluminia (\( \text{Al}_2\text{O}_3 \)) and niobia (\( \text{Nb}_2\text{O}_5 \)). If one wants to grow a semiconductor (silicon, galliumarsenide, germanium) opal, typically the chemical vapor deposition (CVD) technique is used to fill the voids of the direct structure. The inverse samples studied in this thesis\(^1\) are formed by silicon and by titania, but here, for brevity, only the precursor method will be described.

\(^1\)The opal samples were grown at: Polytechnic of Turin, Italy (titania inverse opal and silica direct opal); University of Twente, The Netherlands (titania inverse opal and silica direct opal); and University of Toronto, Canada (silicon inverse opal).
Figure 3.4: SEM images of an inverse opal made of titania with FCC packing (Polytechnic of Turin, project MIUR-COFIN 2002).

In order to grow an inverse opal of titania \((n = 2.7)\), one starts from titanium (IV) propoxide \(TPT\) as a precursor. The voids of the direct structure are filled via capillary forces. Since, usually, the precursor is quite viscous, it is convenient to dilute it with alcohol. After the infiltration, the precursor is hydrolyzed with water to yield a solid pre-stage of metal oxide. Then the template is removed by heating at high temperature (from 350 to 600 °C, depending on the template). The heating removes also the remaining hydroxyl groups from the metal oxide, resulting in an inverse opal, as shown in fig. 3.4.

This technique is called calcination. The resulting structure consists of \(\sim 80 - 90\%\) of air and is very fragile. The quality of the sample can be tested using a scanning electron microscope (SEM), or via X-ray scattering \([9]\), that is an excellent probe for the surface roughness and the polydispersity.

### 3.3 The Bragg law

The main property that determines the opening of a complete photonic gap for a photonic crystal, as seen in section 3.1, is the modulation of the refractive index. The opening of the gap can be observed also if we study interference phenomena. Scattering studies from solids with X-ray radiation shows a set of reflection peaks that characterize a crystalline material. A crystal is formed
3.3. THE BRAGG LAW

by crystalline planes, at a distance \( d \) from each other, and the reflected X-rays from successive planes interfere constructively under a specific angle \( \theta \). This gives the well-known Bragg formula

\[
m\lambda = 2d \cos \theta ,
\]

where \( m \) is the order of the refraction and \( \theta \) is the angle of incidence of the radiation with respect to normal to the atomic planes.

Fig. 3.5 explains the concept of Bragg’s diffraction. Reflection occurs, due to constructive interference, whenever the angle \( \theta \) is such that the path length difference \( 2d \cos \theta \) between reflections of successive layers equals an integer \( m \) times the wavelength \( \lambda \).

The same Bragg law of diffraction holds for photonic crystals in the visible and near-infrared wavelength regime. In this case the interplane distance \( d \) is of the order of hundreds of nanometers, instead of the order of Å as for atomic crystals. The Bragg diffraction causes the well-known iridescence of 3D photonic crystals. Changing the angle of incidence we simply change the wavelength of the reflected radiation.
3.4 Reflection measurements

If we consider a homogenous medium, where no absorption and no light scattering take place, we have that $R + T = 1$ ($R$ is the total reflectivity and $T$ the total transmission); so once we have measured $R$ (or $T$) we know $T$ (or $R$). This means that from transmission or reflection measurements we can extract the same information. If light scattering from defects of the system is present, $R + T \neq 1$. For opal photonic crystals we can neglect absorption but we cannot for scattering form crystal imperfections. The state of art for opals today offers a structure without defects only in limited regions (domains) of $\sim 100 \times 100 \ \mu m$ of surface and some layers ($\sim 15$) in depth [10]. So the incoming light undergoes either constructive interference for Bragg’s diffraction or multiple light scattering caused by imperfections of the crystal.

If one looks at a 3D opal, the Bragg reflection is connected to the iridescence of the sample, but away from the photonic band gap, the system does not look transparent as one might expect. This is because of the presence of imperfections and defects that multiply scatter the light. This is why opals are usually white. In this case transmission measurements give no appreciable results, the light does not pass through the sample, but it is scattered over the whole solid angle. A picture of an inverse opal of titania is shown in fig. 3.6 and we can identify two regions. The first is the Bragg region where light is reflected back, meaning that for these wavelengths a stop band is present; the second is the multiple scattering region, where white light is scattered. The multiple scattering, due to defects, affects reflection measurements only partially, because we observe the Bragg reflection only from the first planes of the photonic crystal, not from all. While, when transmission measurements are performed, the light has to cross the sample and so it is subject to the multiple scattering caused by defects. In summary we can say that, when we measure reflectivity from an opal sample of thickness 1000 layers, we are measuring effectively the reflectivity of the first layers (let say 10-20 layers), not from 1000. The contribution from the others is washed away by the multiple scattering from defects.
3.4. REFLECTION MEASUREMENTS

Figure 3.6: Photograph of an inverse opal of TiO$_2$. The Bragg diffraction is visible on the top of the sample, while the white scattering of light is caused by the imperfections and defects of the periodic structure (In collaboration with the University of Twente).

Figure 3.7: Reflection measurements from an inverse opal of TiO$_2$. A reflection maximum of more than 90% is reached (black curve). The diffuse light scattered by defects in the inverse opal is visible out of the plane where we measure Bragg reflection (light gray curve) and it represents the 2% of the incoming light.
This is not so dramatic, because band diagram calculations show the possibility to open a band gap also for a 10 layer sample [11].

Reflection measurements show, for inverse opals, high reflection close to 100% for the stop band, as depicted in fig. 3.7. In this case we excite 2 or 3 sample domains (the details will be given in the section 3.5). The gray spectrum of fig. 3.7 shows the diffuse white light scattered by imperfections of the system. This diffuse light is visible out of the plane where we measure Bragg reflection, so it does not affect the reflectivity caused by the stop band of the photonic crystal. So for inverse and direct opal structures reflectivity measurements are an important tool to understand their main properties.

3.4.1 Setup for reflection

To test if a 1D photonic crystal has a complete photonic gap is very simple. If we measure a deep valley having zero transmission, this means that the sample has a complete photonic band gap in that frequency range.

When we characterize 3D photonic crystals in the form of opals, with reflection measurements, we cannot say for sure that such samples have a complete photonic gap, because we can scan for 3D systems only a restricted region of the Brillouin zone. But a band gap can be inferred for angular resolved reflection data.

Fig. 3.8 shows our variable angle reflection setup. It is formed by a tower in which two arms, controlled by stepper motors, allow to scan the incidence angle from 5° to 90°. Two multimode optical fibers are mounted on the two arms. They are used to illuminate the sample and to collect the reflected light. A collimator and a cylindrical lens (giving a magnification of a factor of 4 with respect to the fiber diameter) are used to focalize the light, that exits from the fiber, on the sample and to collect the reflected light for the other fiber. One fiber is coupled to a tungsten lamp (350-2000 nm of spectral range), the other one is coupled to a spectrometer that can have a silicon (spectral range: 350-1000 nm) or an PbS (1000-2200 nm) detector. In this way the setup allows us to cover a broad spectral range from ultraviolet to near-infrared. The spectral
3.4. REFLECTION MEASUREMENTS

Figure 3.8: Schematization of the variable angle reflection setup. The source and the detector can rotate around the main axis of the tower and so around the sample. The angular precision is very accurate $\sim 0.1^\circ$. The reflection spectra can be measured from 350 to 2000 nm, with a resolution that can reach 0.3 nm.

precision can range from 1 nm to 0.3 nm, depending on the detector and on the grating used in the spectrometer. The angular precision of the setup is very accurate reaching $0.1^\circ$. The sample is fixed at the top of the tower on a tilting mounting, in such a way that the arms can rotate around the sample itself. Moreover the setup allows one a very accurate positioning of the sample normal with respect to the incidence light. In principle our setup allows one also variable angle transmission, because the two arms are free to move over $360^\circ$.

Once that everything is aligned, that is the sample lays on the axis of rotation of the arms, and the incoming and the reflected beams lie in a plane orthogonal to the sample surface, a complete scan, usually at steps of $5^\circ$, is very fast, taking $\sim 10$ minutes.

This setup was built up for reflection on opal photonic crystals, because changing the angle of incidence gives some additional information regarding the chance to have a full photonic band gap material.
3.5 Direct opals

With the reflection setup presented in fig. 3.8 we can access angles from 5° to 85°. A measurement at 90° has, in practice, no sense because it means that the light beam has to be parallel to the surface of the sample. Fig. 3.9 depicts schematically the effect of the increasing of the spot diameter as the angle of incidence \( \theta \) increases. The spot becomes gradually elliptic when \( \theta \) is increased. Until \( \sim 85^\circ \) the effect is not so dramatic, but above this value the shape of the spot becomes heavily elliptic, illuminating a large number of photonic crystal domains. This effect has to be avoided in our measurements, because a drastic reduction of the reflection from the sample is expected.

![Figure 3.9](image)

Figure 3.9: The effect of the increase of the incidence angle on the spot diameter that illuminates the photonic crystal. This spot gradually increases with the angle of incidence, thereby illuminating an increasing number of domains of the photonic crystal.

The most common material used for the fabrication of a direct opal structure is \( SiO_2 \), that has a refractive index \( n_{SiO_2} = 1.46 \). An opal of silica cannot have a complete photonic gap due to this low refractive index value, far below the required contrast of 2.8. But it is a good candidate for preliminary studies.

For an opal, the FCC packing gives a relation between the radius of the dielectric spheres \( R \) and the lattice constant, that is

\[
a = 2\sqrt{2}R
\]

(3.15)
3.5. DIRECT OPALS

and for the interplane distance $d_{ijk}$ we have

$$d_{ijk} = \frac{a}{\sqrt{i^2 + j^2 + k^2}},$$  \hspace{1cm} (3.16)

where $i, j, k$ are the Miller indices that identify the plane. In our case the opals are grown with the [111] plane parallel to the main surface of the sample. So when we measure the reflection, we measure the reflection from the [111] plane. The distance between [111] planes is $d_{111} = a/\sqrt{3}$.

The reflection peaks of opals will have a central wavelength

$$\lambda_{111} = 2 < n > d_{111} \cos \theta,$$  \hspace{1cm} (3.17)

where $< n >$ is the mean refractive index of the opal. For a typical direct opal the volume fraction $\phi_{SiO_2}$ of dielectric spheres is $\sim 75\%$ and hence the volume occupied by the air is $\sim 25\%$. So for $< n >$ we can suppose in first approximation that a geometrical average holds:

$$< n > = \phi_{SiO_2} n_{SiO_2} + \phi_{air} n_{air} = 1.34.$$  \hspace{1cm} (3.18)

Fig. 3.10 shows the reflectivity for a silica direct opal in function of wavelength and in function of the internal refraction angle $\theta_{ref}$, defined by Snell’s law as

$$\theta_{ref} = \arcsin(\frac{n_{air}}{< n >} \sin \theta),$$  \hspace{1cm} (3.19)

that ranges from $7.5^\circ$ to $37.7^\circ$ ($10^\circ$ to $55^\circ$ for $\theta$). Upon increasing $\theta_{ref}$ the peaks shift towards shorter wavelengths as predicted by the Bragg law. For this particular sample the reflectivity is very low. The measurement was performed using a spot size of $\sim 200 \mu m$. This low value for the reflectivity means that for this sample the domains are very small. Using a 200 $\mu m$ spot size means that we are illuminating a large number of defects, which drastically reduce the reflectivity.

Analyzing a higher quality sample, the reflectivity value increases, as shown in fig. 3.11 (a). This opal is formed by spheres with radius 160 nm. The central
Figure 3.10: Reflection spectra in function of the angle of refraction. The spot size is 200 µm. The opal is formed by silica spheres of radius R=170 nm and so the central wavelength of the peak at an angle of 10° of incidence is \( \lambda_{111}(\theta = 10) = 732 \text{ nm} \), extracted from the Bragg formula 3.17. It agrees with the measured spectra. The blue shift of the peaks is also predicted by the Bragg law.

Peak wavelength at an angle of incidence of 5° is \( \lambda_{111}(\theta = 5) = 702 \text{ nm}, \) that agrees with the measured one. In fig. 3.11 (a) the reflectivity is plotted in function of \( \theta_{ref} \), in the range from 3.8° to 37.7° (5° to 55° for the angle of incidence \( \theta \)). With respect to the other opal structure, this sample has a reflectivity coefficient that is an order of magnitude higher. The measurements were performed with a beam diameter of 200 µm. This indicates a higher quality sample with a reduced number of defects and so larger crystal domains.

We can compare the measurements with 200 µm spot diameter to those with 40 µm spot diameter. The latter require an input fiber of 8 µm core diameter. Fig. 3.11 (b) shows the opal of fig. 3.11 (a) excited with a beam of 40 µm diameter. The angular behavior is the same as in the previous case, but the spectra are more noisy because decreasing the spot size means decreasing the intensity of the incoming light. In fact, because of the high noise level,
3.5. DIRECT OPALS

Figure 3.11: (a): Reflection spectra in function of the angle of refraction for a SiO$_2$ direct opal. The spot size is 200 µm. The radius of the spheres is 160 nm. If we compare this sample with the previous analyzed, we extract a reflectivity an order of magnitude higher. This is an indication of larger domain size. (b): Reflection spectra in function of the angle of refraction for the same sample, but with 40 µm spot size. The measurements are more noisy because of the smaller optical fiber used. The increase of the reflectivity is due to the smaller region investigated.
CHAPTER 3. 3D PHOTONIC CRYSTALS

Figure 3.12: Central wavelength (dots) and FWHM (triangles) for the Bragg reflection peaks of the direct opal with \( R = 160 \text{ nm} \) (the one presented in fig. 3.11 (b)), in function of the refractive angle. Just after 20° the superposition of the reflected peaks disappears, indicating no complete photonic band gap. The gray straight lines indicates the wavelength region in which the peaks would stay if the photonic crystal has a complete photonic gap.

we stopped the measurements at \( \theta_{\text{ref}} = 35^\circ \). It is clear that the absolute reflectivity is increased with respect to the measurement with 200 \( \mu \text{m} \) spot, and the reason is that in this case we illuminate a reduced number of crystal defects. The reflectivity increases from 0.28 (for the 200 \( \mu \text{m} \) case) to 0.42 (for the 50 \( \mu \text{m} \) case). So we obtain an increase of 33% in reflection if we reduce the spot by a factor of 5. Reducing more and more the spot diameter does not mean that we can reach the 100% reflectivity, because other types of imperfections are present in the opal structure besides the defects, like deviations from the periodicity and surface roughness of the spheres. Both effects can reduce the reflectivity [12].

To test if a photonic crystal is a candidate to have a complete photonic gap, we can plot the full width half maximum (FWHM) of the Bragg reflection in function of the angle of refraction. This is plotted in fig. 3.12 for the direct
opals with radius 160 nm. The dots represent the peaks wavelength, while the triangles represent the FWHM. From 3.7° to 20° there is a superposition of the peaks. But beyond 20° the peaks move away. A complete gap means that almost for one wavelength the photons are forbidden to cross the sample in any direction and are reflected back. From the fig. 3.12 it is clear that for this sample this wavelength does not exist. This is the expected behavior for opals with low refractive index contrast.

### 3.6 Silicon inverse opals

Inverse opals made of silicon have the right refractive index contrast $\sim 3.5$ to open the photonic band gap. Fig. 3.13 (a) shows the density of states for a silicon inverse opal and the region where $DOS = 0$ is the photonic gap.

![Figure 3.13](image)

**Figure 3.13:** (a): The density of states in function of the normalized frequency shows the complete photonic band gap for this type of structure around $\omega/a/2\pi c = 0.8$. (b): SEM image of a silicon inverse opal with air spheres of 425 nm of radius (In collaboration with the University of Toronto).

To produce a silicon inverse opal, the starting point is the $SiO_2$ direct opal template. The silicon is infiltrated in the structure via chemical vapor deposition and the template is removed by heating [14]. The resulting sample is shown in fig. 3.13 (b). The SEM picture show a good quality sample with
100 × 100 µm domain size and a radius of 425 nm.

The sample depicted in fig. 3.13 (b) had 15 layers and was grown on a PMMA substrate (transparent in the interesting wavelength region). We performed reflection measurements on it changing the angle of incidence $\theta$ from 10° to 80°, using a 200 µm spot size for the white light beam. Due to the “large” radius of the spheres ($R = 425$ nm), we expected that the band gap was in the near-infrared and so a spectrometer equipped with a PbS detector was used, as described in section 3.4.1, which allowed us to scan a wavelength region from 1000 to 2000 nm.

The volume fraction of Si in our samples is $\sim 10\%$ and the rest is air. From eq. 3.18 we obtain for the mean refractive index $\langle n \rangle \approx 1.24$. This means that the angle of refraction $\theta_{ref}$ in our measurements can range from $8^\circ$ to $52.3^\circ$. To test the homogeneity of the sample we performed measurements changing the position of the spot of the lamp on the sample surface. Moving from point to point some shifts of the peaks were observed, but the effect was small within 5% of the wavelength. The results are plotted in fig. 3.14. The three main peaks are numbered and we can observe from the graph that the structure is shifted, but not modified. The maximum shift is observed for the third peak and is 80 nm. For the other two roughly 40 nm shifts are observed. The origin of each peak is different, while for the first and the third we can speak of stop bands, for the second we can say that it is the candidate for the complete photonic gap. From the density of states of our sample (fig. 3.13 (a)), the wavelength position of the second peak around 1500 nm coincides with the photonic gap ($\omega a/2\pi c = a/\lambda = 0.8$ if $\lambda = 1500$ nm in our sample).

The angular resolved measurements show something very interesting with respect to direct structures. In fig. 3.15 the evolution of the second reflection peak in function of $\theta_{ref}$ is shown. From $8^\circ$ to $52.3^\circ$ the reflection spectra change a lot, but around 1500 nm the reflection peak remains roughly unchanged. This behavior is very different if compared to that of fig. 3.11 (a), where the direct opal shows a pure stop band that follows the Bragg law. This is a clear indication that maybe for this sample we have at least 1 wavelength reflected back from all directions, which means a complete photonic band gap. Another
3.6. SILICON INVERSE OPALS

Figure 3.14: Reflectivity for a silicon inverse opal taken at different points on the sample. These spectra give an idea on the homogeneity of the sample. The three reflection peaks, numbered for simplicity, move not more than 80 nm.

An interesting feature of the angular resolved spectra is that the second and the third peaks join together to give a single peak when $\theta_{ref} > 47^\circ$.

We can plot the central wavelength evolution for the three peaks. In fig. 3.16 (a) the gap position is plotted with error bars that indicate the FWHM for each reflection peaks in function of $\theta_{ref}$. In fig. 3.16 (b) the evolutions for the other two peaks are also plotted, without FWHM indication. To extract the position of each peak we have fitted them with a gaussian function. In particular for the second and the third peaks, that melt in one single peak above $47^\circ$, a double gaussian function was required.

For the position of the gap we can observe a wavelength range of 66 nm (the gray straight lines in fig. 3.16 (a)) in which the photons are always reflected back. Obviously this is only an indication for having a complete gap, because we do not scan the whole Brillouin zone. The peak evolution is quite different with respect to the direct opal case shown in fig. 3.12, where the reflection
peaks were due to a pure stop band. Also the other two peaks exhibit a non Bragg behavior: they move both towards the second peak when the angle is increased. In particular the first one disappears at large angles.

The data analysis for this sample is not so trivial due to the presence of three peaks. At a normal angle of incidence we can compare the reflection spectrum with the band diagram for this photonic crystal, but when the angle is larger than zero the comparison is not still valid. For the moment we can conclude only that this inverse opal gives promising results, due to the presence of a wavelength range of 66 nm that reflects the photons back. To demonstrate that a 3D direct and inverse opals have a full photonic band gap a step further has to be made, as discussed in the next section.

Figure 3.15: Reflectivity for an inverse silicon for four angle of refraction $\theta_{\text{ref}}$. The first and the third peaks move towards the second one when $\theta_{\text{ref}}$ increases. For angles larger than 47° the second and the third melt in one broad peak. Note that around 1500 nm there is a range of wavelengths that are always reflected back. This is an indication of a possible full photonic gap.
Figure 3.16: (a): The position for the supposed photonic gap is plotted with the error bars that indicate the FWHM. The two gray lines indicate the wavelength range for which the photons are reflected back by the sample for the studied angular range. (b): The evolution for the first and the third peaks is plotted. They move towards the central one indicating a non Bragg behavior. The behavior for these three peaks is very different compared to what happens for the direct opal plotted in fig. 3.12, where the stop band follows the Bragg law.
3.6.1 The Brillouin zone of an opal

To have experimental evidence of the presence of a complete photonic gap in a 3D photonic crystal, one can think of an experiment where a light source, like for example a quantum dot, is introduced into a photonic crystal, without altering the photonic structure. If one measures that the emitted light from the source is inhibited to exit from the photonic crystal, the existence of a full gap is demonstrated for that particular sample. This experiment is not so simple, because first a source has to be placed into the crystal, without compromising the dielectric contrast, and then a detector that collects the light from all angles is required. For opals there is an easier way that can give the same response.

Because the spheres that form direct and inverse opals are grown by natural sedimentation, the main surface of the sample, the one used for reflection measurements, is parallel to the [111] plane. The Brillouin zone for a face center cubic lattice is the Wigner-Seitz cell for a body center cubic. The solid that represents the Brillouin zone is depicted in fig. 3.17. The Γ point stays in the center of the solid, while the other symmetry points \(L, W, U, K\) and \(X\) stays on its surface. Also the indication for the planes [111] and [200] are given. What is important for us is the [111] plane, so we will focus our attention on that.

Because of defects, dislocations, surface roughness and so on, in a real photonic crystal sample, the crystal domains where the sample can be considered quasi-perfect are not too large. In practice in a “good” sample, when we measure the reflectivity, we excite at least 3-4 of these domains, using a spot of 200 \(\mu\)m. Also reducing the spot to 40 \(\mu\)m it is not enough to excite a single crystal domain, because we do not know exactly where our spot is on the sample surface. In general a photonic crystal is formed by a large numbers of domains; each domain presents a Brillouin zone rotated by an arbitrary angle with respect to the others.

We can say, independently from the orientation of the Brillouin zone, that reflection measurements at normal incidence (\(\theta = \theta_{\text{ref}} = 0\)) gives us the
reflection in the $\Gamma \rightarrow L$ direction, because the $\Gamma \rightarrow L$ is orthogonal to the [111] plane. So we can compare the reflection results with the theoretical predictions derived from the band diagram in the $\Gamma \rightarrow L$ region. Fig. 3.18 shows this comparison for the normal reflectivity for the silicon inverse opal. The central reflectivity peak at $\omega a/2\pi c = 0.8$ agrees with the position of the calculated band gap for this sample\(^2\). The other gray region in the band diagram can be associated to the main stop band of the photonic crystal around $\omega a/2\pi c = 0.5$, as discussed also in ref. [13].

From the band diagram of fig. 3.18 the most critical point is the W point. To demonstrate that an inverse opal has a full photonic gap we need a reflection measurements from the $L \rightarrow W$ direction. If we find that almost for one wavelength the reflection spectra from $L \rightarrow W$ and $\Gamma \rightarrow L$ are overlapping between the FWHM, we would demonstrate it. Since from reflection measurements we access the [111] plane, increasing the angle of incidence of the incoming beam we can arrive at two critical refraction angles. The first is the angle formed by $L - \hat{\Gamma} - U$ that we call $\theta_{\text{ref}}^{U}$, the second is $L - \hat{\Gamma} - W$ that

\(^2\)The band diagram was calculated by Alongkarn Chutinan, University of Toronto
we call $\theta_{\text{ref}}^W$ (see fig. 3.17). In this way we can access the $L \rightarrow W$ and $L \rightarrow U$ regions of the Brillouin zone. The $X$ point is not accessible from this plane because it lays in the [200] plane. So to map all the Brillouin zone we would need, at least, two crystal planes from which we have to measure reflectivity. But measurements from the [111] plane would be enough for opal photonic crystals.

Our samples in general present a lot of domains and the difference between them is the orientation of the Brillouin zone. Suppose to excite a single crystal domain and to know exactly the position of the $W$ point. We could rotate the sample around the axis orthogonal to the [111] plane of a certain angle. In this way we can access to $L \rightarrow W$ direction, if the incoming light enters the sample with an angle $\theta_{\text{ref}}^W$, and measure the reflectivity. After that we can compare it with the reflectivity at normal incidence.

In order to demonstrate the existence of a full gap two condition has to be fulfilled:

Figure 3.18: Reflection measurement, at normal incidence, for the inverse silicon opal presented in section 3.6 compared to the calculated band diagram. The agreement between the central measured peak and the gap position in the diagram is good. The peak around $\omega a/2\pi c = 0.5$ exhibits a stop band behavior, because it does not extend over all the Brillouin zone.
3.7 LIQUID CRYSTALS INFILTRATION

- The reflectivity from a single domain has to be recorded.
- For the excited domain we must know the position of the $W$ point and rotate the crystal to access this point.

The first point is not a great problem, because our $Si$ opals have domains of $100 \times 100 \, \mu m$. The second point requires a coupling of the angular resolved setup with a powerful optical microscope or a SEM.

### 3.7 Liquid crystals infiltration

As introduced in chapter 1, we can change the scattering strength of opals by infiltrating them with nematic liquid crystals. Nematic liquid crystals are birefringent and have an average refractive index $n_{ave}$ that is temperature dependent. Birefringent means that they have two distinct refractive indices $n_o$ (ordinary) and $n_e$ (extraordinary). From section 2.4.2 we know that if the dielectric anisotropy is positive ($\epsilon_a > 0$), the nematic molecules align parallel to an external field. This means that the light that crosses the nematic liquid crystal feels the ordinary refractive index $n_o$, if its polarization vector $P$ is orthogonal to the field and hence to the molecular axis. If $P$ is parallel to the field, light experiences the extraordinary refractive index $n_e$.

We can infiltrate both inverse and direct opals with nematics, and measure the effects of temperature variations and of an external electric field. For opal photonic crystals, a night is required for the infiltration and the liquid crystals have to stay in the isotropic phase to reduce the viscosity. The infiltration takes place due to the capillary forces that attract the liquid crystal molecules into the voids for direct opals, or into the air spheres for inverse opals. One of the nematic liquid crystals used for opals infiltration is E7, that has $n_o = 1.53$ and $n_e = 1.75$ and a nematic temperature range from $-10 \, ^\circ C$ to $60 \, ^\circ C$. Above $60 \, ^\circ C$ this liquid crystal becomes a standard liquid with an index of refraction $n_{iso} = 1.57$. Nematic liquid crystals present typically nematic domains; each domain is oriented with a different angle with respect to the others, as happens for opals domains. We can define an average refractive index for the nematic
Figure 3.19: Reflection measurements at a normal incidence for a silica direct opal. The spot size used is 40 µm. The reflection from the non filled structure (dotted curve) is compared to the infiltrated system when the liquid crystal stays in the nematic phase (light gray curve) and in the isotropic phase (black curve). The shifts between the peaks are simply due to the different refractive indices involved. The reflectivity from infiltrated sample is amplified by a factor 5 to visualize better the shifts.

\[
 n_{\text{ave}} = \sqrt{\frac{n_e^2}{3} + \frac{2n_o^2}{3}},
\]  

that for liquid crystal E7 is \( n_{\text{ave}} = 1.60 \).

To study the effects of temperature tuning on 3D photonic crystals infiltrated with nematics, we chose a direct opal structure made of \( \text{SiO}_2 \). The sample had spheres with radius of 165 nm, which means form eq. 3.16 an interplane distance \( d_{111} = 270 \text{ nm} \) and so \( \lambda_{111} = 722 \). Reflection at normal incidence gave a peak wavelength \( \lambda_{111} = 714 \text{ nm} \) as shown in fig. 3.19 by the dotted curve.

The reflection was taken at normal incidence with a spot size of 40 µm, that allow us to obtain 25% of reflectivity. A SEM picture of this sample is
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Figure 3.20: SEM picture for the sample used for the liquid crystal infiltration (Polytechnic of Turin, project MIUR-COFIN). In this case the crystal domains are smaller with respect to silicon inverse opals, but we reach 25% in reflectivity because of the small spot size used (40 µm).

depicted in fig. 3.20. The other two peaks plotted in fig. 3.19 are relative to the same sample infiltrated with liquid crystal E7. The light gray curve corresponds to the direct opal plus liquid crystals in the nematic phase (25 °C), while the black curve is referred to the infiltrated structure with liquid crystals in the isotropic phase (62 °C). These two peaks are shifted from each other by 8 nm. The shifts are due simply by the different mean refractive indices of the opal. Without liquid crystal, the photonic crystal has $<n>$ = 1.34 (with 75% of silica and 25% of air). When the liquid crystal is infiltrated in the nematic phase $<n>_{nem}$ = 1.495, while for the isotropic phase $<n>_{iso}$ = 1.487. Calculating the central peak wavelength $\lambda_{111}$ for each case we find a good agreement between measures and the Bragg law. In particular for the shift between nematic and isotropic phase, the Bragg law gives us 5 nm of shift with respect to 8 nm measured.

In order to obtain a global anisotropy in the system, an external magnetic or electric field can be used to align the nematic director. The surface anchoring of the liquid crystal is, however, hardly ever negligible, see also chapter 2. Close to the pores surface the liquid crystal alignment will be dominated by the surface anchoring, even at high field strengths. This fixed surface alignment will persist over a distance that is about equal to the magnetic (or electric)
coherence length $\zeta$ at the given field strength. Therefore, ideally, the voids should be larger than the coherence length to enable external field switching of the photonic crystal.

Liquid crystal infiltration in direct silica opals was studied by Kang et al. [15], who found a modest shift ($\sim 3$ nm) of the stopband upon applying an external electric field over the sample. The limited effect of the external field was attributed to confinement effects inside the voids of a direct opal. One might expect that inverse opal structures, having spherical voids, are favorable for external field switching since a spherical void does not impose a preferred alignment direction. In addition, at fixed lattice constant, the inverse opal voids are bigger than those of the direct opal. To further exploit the possibilities of electric field tuning of photonic crystals we characterized the stopband of infiltrated titania inverse opals.

The titania inverse opal ($R = 160$ nm) was infiltrated overnight with the liquid crystals 5CB. The infiltrated samples were mounted between two glass slides coated with a thin transparent layer of indium doped tin oxide (ITO) on the glass surface facing the sample. Before mounting the glass slides, part of the ITO coating was removed in order to avoid regions of facing ITO layers without sample in between. The sample thickness equals the distance between glass plates and ranges from 0.2 to 0.5 mm in our case. The two refractive indices for 5CB are $n_o = 1.48$ and $n_e = 1.67$ and the nematic temperature range goes from 24 °C to 32.5 °C.

The electric conductance of the ITO layer allows one to apply an electric field over the sample perpendicular to the sample plane. Without the electric field the optical properties of the sample are expected to be isotropic, whereas at high enough field the nematic director should obtain some global alignment and hence the stopband of the infiltrated photonic crystal is expected to shift towards higher wavelengths. Since the sample is a very good insulator (much better than air), and facing ITO layers always have sample material in between, we can apply an electric field as high as 120 kV/cm to the sample (ac at 500 Hz).

In fig. 3.21 we plot angular resolved reflection spectra for a titania inverse
3.7. LIQUID CRYSTALS INFILTRATION

Figure 3.21: Reflection spectra of titania inverse opal, with $R = 160$ nm, infiltrated with the liquid crystal 5CB. The scanned range for $\theta_{ref}$ is given in figure. The Bragg law behavior is confirmed for the reflection peaks. The inset shows the tiny red-shift and the increase of the reflection peak at $\theta_{ref} = 5.5^\circ$ upon switching on the electric field. (Field strength 120 kV/cm). This is not an effect due to the electric field alignment, but it is a heating effect. The liquid crystals, due to high applied voltage ($V = 6$ kV), are heated so that the refractive index changes.

opal infiltrated with liquid crystals [16]. As expected there is no superposition for all peaks as happens for the silicon inverse opal, due to the low contrast in the structure $n_{TiO_2}/n_{ave} = 2.7/1.57 = 1.71$ compared with the predicted 2.8 for FCC crystals. When we apply the electric field, the position of the stopband is not changed considerably within the accuracy of our experiment (resolution about 1 nm). At the maximum electric field of 120 kV/cm, we observe only a minor increase of the reflected intensity (see inset of fig. 3.21). These data might indicate also a tiny red shift of the reflection peak which however can not be considered significant. This increase and the red shift could be mistakenly interpreted as a switching effect of the stopband of the sample by the electric field. We observe that it sets in slowly after applying the electric field, which suggests an interpretation in terms of a heating effect of the sample and not a field effect. Apparently, the alignment of the liquid
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crystal due to the electric field is too small to induce any appreciable global anisotropy in our system.

For our system we can calculate the coherence length \([17]\)

\[
\zeta(E) = \frac{1}{E} \sqrt{\frac{K}{\epsilon_0 \epsilon_a}}. \tag{3.21}
\]

Using \(K = 1.2 \cdot 10^{-11} \) N, \(\epsilon_a = 0.7\) and \(E = 120 \) kV/cm for our sample, we obtain \(\zeta(E) = 120 \) nm. The coherence length in this case is of the order of the radius of the spheres (160 nm). So no alignment is possible. To align them in this case a larger field (almost a factor of 5) is required with respect to our maximum field applicable. A possible improvement for the coupling with the external electric (or even magnetic) field could be obtained by the addition of a low-concentration highly dielectric (or magnetic) nano rods, suspended in the liquid crystal. This would reduce the strength required to obtain \(\zeta \ll R\) in such a way that the field effect dominates over the surface anchoring.

We are able to apply a huge electric field to silica direct opal 10 µm thick. The advantage in using direct opals instead of inverse one resides on the fact that we can sandwich the sample in a better way between the two ITO glasses. In fact for inverse structure we must pay attention in cracking the system, since it results more fragile with respect to the direct structure. The shift of the stopband in function of the applied field is plotted in fig. 3.22. The stop band moves of 5 nm and we obtain a critical electric field of 0.5 MV/cm. Note that above 3 MV/cm the shift is stopped, indicating a complete alignment of the liquid crystal molecules. From eq. 2.24 we can calculate the distance \(d = (\pi/E_c)\sqrt{\frac{K}{\epsilon_0 \epsilon_a}}\) of the walls, where the liquid crystal is confined in the direct opal. Imposing a critical field \(E_c = 0.5\) MV/cm we obtain \(d \approx 90\) nm, which is consistent for our system since the spheres radius is 150 nm.

In liquid crystal infiltrated photonic crystals a complex interplay takes place between liquid crystal molecules and surfaces of the spheres that contain the liquid crystal. The surfaces dominate the alignment when distances of the order of 100 nm are considered, as for opals in the visible or near-infrared wavelength region. To overcome the surface anchoring, huge magnetic or elec-
3.7. LIQUID CRYSTALS INFILTRATION

Figure 3.22: Stopband shift upon the application of an electric field for a direct opal made of silica infiltrated with liquid crystal E7. The radius of the spheres is 150 nm and the thickness 10 µm. The movement of the reflection peak is 5 nm and we obtain 0.5 MV/cm as value for the critical field.

Electric fields are needed ($H > 10$ T and $E > 0.5$ MV/cm). These values are too high for applications like fast switching of the photonic band gap. Magnetic or dielectric nanotubes dispersed in the liquid crystal can help the alignment reducing the critical field, or, alternatively, one can use a surfactant for the walls to reduce the nematics-surface coupling and hence the surface anchoring.


In this chapter the properties of a polymer dispersed liquid crystal (PDLC) random laser are investigated. The system possesses interesting properties, because liquid crystals allow to change the scattering strength of the system by the nematic-isotropic phase transition. In the nematic phase the PDLC random laser amplifies the light and the system is above threshold. For the isotropic phase the system results nearly transparent and the random laser is below threshold. When an external electric field is applied the PDLC random laser becomes transparent in the direction parallel to the field. For large field values (120 kV/cm) the systems scatters more efficiently the light even if it looks transparent. The light in this case follows a quasi-two-dimensional type of transport, in particular in the planes orthogonal to the applied field. The application of the field makes the system switch from a 3D isotropic transport of light to a 2D anisotropic transport. The emitted light is extraordinary polarized and spatially anisotropic.
4.1 Random laser properties

4.1.1 Laser dyes

Multiple scattering and amplification of the light are the mechanisms that govern the random laser action. As seen in chapter 1, there are at least two ways to obtain a random laser: the first one is to have a powder that scatters and amplifies the light (ZnO, Ti:Sa and Nd:YAG powder), while the second way is to dissolve a gain medium (laser dye) into a scattering system. Here we are interested in the second type of systems to build up a random laser.

Dye lasers use an active medium consisting of a solution of an organic dye in a liquid solvent, such as ethyl or methyl alcohol, liquid crystals, water and many others. The concentration of dye in the solvent is typically of the order of $10^{-3}$ mol/l. Dyes usually show wide absorption and fluorescence bands without sharp features. At room temperature the rotational-vibrational structure is unresolved as depicted in fig. 4.1, where the energy levels of a dye molecule dissolved in a solvent are shown. The fundamental level is the singlet state $S_0$. The two roto-vibrational bands $S_0$ and $S_1$, because of their energy width, can be used as a four level system. An external laser is usually required to pump a laser dye, that absorbing the pump light excites the molecule in a high roto-vibrational level $S_1$. This quickly relaxes (with a time constant of order of 0.1 ps) to a vibrational level at the bottom of $S_1$. The level 2 has a lifetime of a few ns, after which the molecule decays to a high level of $S_0$, followed by again a quick vibrational relaxation. The transition between the levels 2 and 1 is the laser transition.

Other levels are present for dyes, as for example triplet states $T_1$ and $T_2$. The transition between $S$ and $T$ is, in first approximation, forbidden by the selection rule $\Delta S = 0$, but evidences of bichromatic emission (from both the singlet and the triplet states) were reported in literature for high dye concentration in the solvent, usually larger than $10^{-2}$ mol/l [1, 2]. A typical emission spectrum of laser dye is shown in the right side in fig. 4.1. In this particular case the organic dye is DCM special and the solvent is methanol. One can observe that the width of the emission is very broad ($\sim 70$ nm),
4.1. RANDOM LASER PROPERTIES

Figure 4.1: On the left side, the levels of a laser dye are shown. The laser transition is usually between the singlet states $S_0$ and $S_1$, from level 2 to level 1. If the concentration of the dye in the solvent is larger than $10^{-2}$ mol/l we can observe the emission from the triplet states. On the right side, the fluorescence of DCM special dissolved in methanol is shown. The spectrum is broad because the emission is caused by a transition between two roto-vibrational bands.

because the fluorescence comes from the electronic transition between two broad roto-vibrational levels.

4.1.2 The transport equations

As discussed in chapter 1, the crucial parameter that describes the disorder in a random amplifying medium is the transport mean free path $\ell_t$. If we assume that $\lambda \ll \ell_t \ll L$, we are in the diffusion approximation. This means that we are far away from the Anderson localization regime and also that the sample dimensions $L$ are longer with respect to the transport mean free path, so the light is subject to multiple scattering. The equation that governs light diffusion in that case is:

$$\frac{\partial W}{\partial t} = D\nabla^2 W + S ,$$  \hspace{1cm} (4.1)
where $W$ is the energy density, $S$ is the source, and $D$ is the diffusion constant. Eq. 4.1 holds for conservative systems and in absence of absorption. When we add gain to a diffusive system, we take into account in the diffusion equation by the additional term $k_g v W$, where $k_g$ is the gain coefficient and $v$ is the phase velocity. Eq. 4.1 becomes

$$\frac{\partial W}{\partial t} = D \nabla^2 W + k_g v W + S .$$  (4.2)

In a typical experiment, a random laser is pumped externally by a laser source and we usually measure the emitted spectrum from the sample. Since our systems are in the diffusive regime, we have to take into account the diffusion of the energy density of the pump beam $W_p$ and the energy density of the “laser” beam $W_\ell$, and the rate equation for the concentration of molecules in the excited state $n_1$:

$$\frac{\partial W_p}{\partial t} = D \nabla^2 W_p - \sigma_{abs} v (n_{tot} - n_1) W_p + \frac{1}{\ell_t} I_{in}$$  (4.3) 

$$\frac{\partial W_\ell}{\partial t} = D \nabla^2 W_\ell + \sigma_{em} v n_1 W_\ell + \frac{1}{\tau} n_1$$  (4.4) 

$$\frac{\partial n_1}{\partial t} = \sigma_{abs} v (n_{tot} - n_1) W_p - \sigma_{em} v n_1 W_\ell - \frac{1}{\tau} n_1 .$$  (4.5)

$\sigma_{em}$ and $\sigma_{abs}$ ($\sim 10^{-20} \text{ m}^2$) are respectively the emission and the absorption cross sections of the gain medium; $n_{tot}$ is the total concentration of excited dye molecules ($\sim 10^{15}$ molecules, assuming a dye concentration of 1 mmol/l); $I_{in}$ is the intensity of the pump beam and $\tau$ is the natural lifetime of the excited state ($\sim 1 \text{ ns}$). In the first equation describing the diffusion of the pump light we first have a diffusion term, then an absorption term, and finally a scattering term. Note that the scattering term depends on $1/\ell_t$, which means that in strongly scattering media, where the transport mean free path is small, the pump light is mostly reflected back by the sample without being absorbed. The second equation describes the emitted light. We have a diffusion term and both stimulated ($\sigma_{em} v n_1 W_\ell$) and spontaneous emission ($n_1 / \tau$) terms. The third equation describes the population evolution of the excited state. If
we make a comparison between $\frac{\partial n_1}{\partial t}$ for a diffusive random laser and for a standard one [3], we find no difference, except for the fact that in a diffusive random laser $n_1$ depends on the position. This happens because the gain region is not homogeneously excited in a random laser. Eq. 4.3 - 4.5 are a set of partial differential equations that need to be solved simultaneously by numerical integration. They provide all the information on the spatial and temporal behavior of the energy densities and population dynamics. For a detailed analysis see ref. [4].

4.1.3 A schematic view

A schematic view of the random laser action is shown in fig. 4.2. The absorption of the pump beam follows the Beer law

$$I(z) = I(z = 0) \exp(-k_{abs}z),$$

(4.6)

where $k_{abs} = 1/\ell_{abs}$ is the absorption coefficient. This means that after a distance equivalent to $\ell_{abs}$ the light intensity that enters the sample is reduced by a factor $e^{-1}$. Pump light is absorbed and part of the system becomes amplifying. Emitted photons are amplified while they travel into the gain region (gray box in the figure). Outside the gain region only scattering takes place, but photons have also the chance to enter again into the gain region and to be amplified again.

Gain in a diffusive medium mainly amplifies long light path, just like absorption attenuates them. In a diffusive random laser the spatial selectively of a cavity, which is essential in concentrating the stored energy in few modes, does not exist. The only selection mechanism is the wavelength dependence of the gain. Said otherwise, the electromagnetic modes of the system are broad (because of large losses) and strongly overlapped. A system that provides very strong scattering could decouple the modes of the system. This is called “random laser with resonant feedback” due to the supposed formation of random cavities in the Anderson localization regime [5]. The latter is still an argument of debate for three-dimensional systems and will not be treated in this thesis.
4.1.4 Relevant quantities for a random laser

Apart from the transport mean free path, two other lengths are important in a random laser system: the gain length $\ell_g$ and the amplification length $\ell_{\text{amp}}$. The gain length is defined as the path length over which the intensity is amplified by a factor $e^{+1}$. The amplification length is defined as the root mean square value of the average distance between the beginning and ending points for path of length $\ell_g$:

$$\ell_{\text{amp}} = \sqrt{\frac{\ell_t \ell_g}{3}}. \quad (4.7)$$

The threshold for the random laser action is given by the condition that the gain is larger than losses (see chapter 1). The threshold criterion can be expressed in terms of a critical volume $V_{cr}$ above which the system lases, since the losses are proportional to the total sample surface and the gain is proportional to its volume. For a slab geometry, in which the dimensions of the surface are larger than the thickness, this translates into a critical thickness $L_{cr}$ defined as

Figure 4.2: Schematic representation of a random walk in an amplifying random medium. The pump light is diffusively scattered in the system and creates the gain region (gray box). When a photon travels inside the gain region it is amplified, while outside it is only scattered. There is a chance for photons to enter again into the gain region and to be re-amplified.
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\[ L_{cr} = \pi \ell_{amp} = \pi \sqrt{\frac{\ell_t \ell_g}{3}}. \]  (4.8)

We can now give an estimate for the critical thickness. For the studied random laser systems, the diffusion constant has a typical value of \( D = 5000 \) \( m^2/s \). If we assume that \( \ell_t = 3D/v \), where \( v \) is the phase velocity, we obtain a transport mean free path value of \( \ell_t = 75 \) \( \mu m \) (considering a medium with a mean refractive index of 1.5). The organic dye used in our samples is DCM special, with a typical concentration of 1 mmol/l. For this particular dye we have an overall concentration of dye molecules of \( n = 6 \cdot 10^{23} \) \( m^{-3} \). The gain length is related to the emission cross section of the dye by \( \ell_g = 1/n \sigma_{em} \); for DCM \( \sigma_{em} = 1.0 \cdot 10^{-20} \) \( m^2 \) and so the minimum gain length is \( \ell_g = 160 \) \( \mu m \). The critical thickness for the slab for going above threshold is \( L_{cr} = 200 \) \( \mu m \). This means that if our sample has a thickness \( L > 200 \) \( \mu m \) we expect that, for a certain pump power, it can go above threshold.

4.1.5 Threshold for a random laser

In a random laser the threshold is reached when the gain is equal to the losses. For a standard laser, the rate equations determine the threshold at a certain pump rate \( P_r \) [3]. Fig. 4.3 shows how the number of excited molecules \( n_1 \) and output power \( P_{out} \) for a single cavity mode are related to the external pump rate. The population \( n_1 \) grows linearly until the threshold value \( n_{th} \), then it remains constant, indicating that \( n_{th} \) represents the maximum value for the population inversion. For the output power \( P_{out} \), fig. 4.3 shows a linear behavior below threshold. Then at \( P_r = P_{th} \) a kink, that identifies the threshold. Above threshold the output is again linear, with a different slope. The threshold in a standard laser discrimines also between spontaneous and stimulated emission. Below threshold, at very low pump rate, the spontaneous emission starts to build up and grows as the pump rate increases. Once the threshold is reached, stimulated emission compensates the losses. Above threshold stimulated emission dominates and the system lases.

For random lasers the considerations made for standard lasers regarding
Figure 4.3: Population evolution ($n_1$) and output power behavior ($P_{out}$) in function of the pump rate $P_r$ for a standard laser. Above the threshold pump rate $P_{th}$, $n_1$ stays constant and the output power increase linearly. For a random laser we observe a similar behavior.

the threshold hold, even if we cannot select a single cavity mode. In this case the laser action is characterized by a multimode emission. Fig. 4.4 (a) shows the intensity of the emission peak as a function of the pump energy. The transport mean free path of the sample was 100 µm and the dye was DCM special. The pump laser was a doubled frequency Nd:YAG, with a pulse duration of 5 ns. The threshold is visible at 800 µJ where the two regimes, below and above threshold, are well distinguishable. If we compare fig. 4.4 (a) with fig. 4.3, we can recognize the same threshold behavior for both laser systems. From the measurements we can extract also the FWHM for each peak, which is plotted in fig. 4.4 (b). The plot is in logarithmic scale to visualize better the threshold effect. The width ranges from 65 nm (dye fluorescence) to 15 nm (random laser emission).

Just above threshold the emission contains a large fraction of stimulated emission, that it is stronger in the spectral region where the net gain is higher. Measurements on the lifetime of the emitted light from a random laser show a temporal narrowing from some nanoseconds below threshold, to some picoseconds above [1]. This confirms that below threshold we measure the florescence spectra of the system (spontaneous emission), while above the stimulated emission is dominant.

The threshold behavior occurs only for the peak intensity and it is not
Figure 4.4: (a): Peak intensity for the emitted light from a random laser in function of the pump energy. The wavelength of the excitation light was 532 nm and its pulse duration 5 ns (2nd harmonic of a Q-switched Nd:YAG laser). The kink between the two different linear profiles (at $P_{th} \approx 800 \mu J$) identifies the threshold value for the pump energy. (b): The FWHM of the spectra versus the pump energy. The bandwidth ranges from 65 nm (spontaneous emission) to 15 nm (stimulated emission). The gain narrowing is caused by the spectral dependence of the gain profile.
present for integrated spectra. The total emitted energy has a linear dependence on the pump energy without any kink. In a standard laser the threshold is observed also for the total emitted energy, where the main selection mechanism is the mode profile of the cavity. Only photons radiated in the right solid angle contribute to the emitted spectrum. If we were to collect laser light from all angles, we would observe that the threshold kink disappears also in a regular laser, because we measure the sum of both spontaneous and stimulated emission in that case.

In a random laser the total amount of amplification is related to the product between the gain coefficient $k_g$ and the traveled path length inside the gain region $\Upsilon$. Only photons in the gain region are amplified. If we now assume that the transport mean free path does not depend on wavelength, then all the spectral features of the emission originate from the wavelength dependence of the gain of the active medium. The photons at a wavelength near the maximum of the gain will be amplified more with respect to the others. This phenomenon is called gain narrowing. This gain narrowing causes an energy redistribution of photons around the maximum of the gain profile. The wavelength dependence of gain is the main selection mechanism for photons in a random laser.

### 4.2 Polymer dispersed liquid crystals

Polymer dispersed liquid crystals (PDLCs) were discovered in 1984 by Fergason [6] and optimized by Doane et al. [7] in 1987. In a PDLC system, droplets of nematic liquid crystals with positive dielectric anisotropy ($\epsilon_a > 0$) are dispersed in a polymer matrix. The PDLC can be switched from a scattering opaque state, to a non scattering transparent state, by applying an external electric field. This electro-optical effect is due to the refractive index matching between the liquid crystal and the polymer in the field-on state, and due to the mismatch of the refractive indices in the field-off state. PDLC systems are suitable for applications in large-area light shutters (smart windows), flexible displays (e.g. for touch switches), projection displays with high brightness,
and so on.

PDLC films can be prepared by encapsulation, starting from an emulsion of liquid crystal droplets in a polymer solution or by phase separation. The latter may be induced by thermally initiated polymerization, by photopolymerization of a polymer precursor mixed with the liquid crystal, or by evaporation of the solvent from a liquid crystal/polymer solution. For a complete review on preparation methods of PDLCs see ref. [8].

The interest on random lasers based on PDLC systems regards the possibility to change the scattering strength of the system applying an external field or changing the system temperature, in such a way that the liquid crystals are in the isotropic phase.

### 4.2.1 Scattering states of a PDLC

Fig. 4.5 shows a schematic view for a PDLC film. Three refractive indices are involved in a PDLC, the two of the nematic phase ($n_o$ and $n_e$) and the one of the polymer ($n_p$). A typical choice of the polymer and the liquid crystal is the one for which $n_o \approx n_p$. Liquid crystal droplets are drawn spherical for simplicity. The off-state (opaque state) is depicted in fig. 4.5 (a). The alignment depicted for nematic molecules inside the spherical droplets is in this case planar (nematic director parallel to droplet surface). It could be also homeotropic (nematic director perpendicular to droplet surface). The alignment is caused by the surface anchoring and depends strongly on the geometry in which nematics are confined. Minimizing the free energy density for nematics in a spherical geometry, once that the radius of the sphere is fixed, one obtains the resulting alignment. A lot of variants exist to the homeotropic and planar configurations. In fact the correct name of the planar configuration of fig. 4.5 (a) is “circular planar polar” [9]. One way to distinguish them is to perform nuclear magnetic resonance (NMR) on nematics embedded in such confined geometries [10].

In fig. 4.5 (a) no external field is applied, so the orientation of each droplet is independent from the others. In this case, the system scatters the light and
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Figure 4.5: (a): PDLC in the off-state, where no external field is applied. The nematic liquid crystals align, for example, in the circular planar polar configuration. Each droplet is tilted with respect to the others; this gives a system in which the light is multiply scattered. (b): PDLC in the on-state. The external field aligns the nematic director parallel to field direction. The PDLC is transparent for an incoming light beam parallel to the field direction, independently from its polarization. (c): Transmission through a PDLC sample with thickness $\sim 100 \, \mu m$. The measurements were performed with a diode laser ($\lambda = 670 \, \text{nm}$) beam, parallel to the field direction. The system goes from an opaque state to a transparent one.

is opaque. When an external electric (or magnetic) field is applied to the film, the nematic director follows the field direction, because of its positive dielectric anisotropy. This is shown in fig. 4.5 (b). An incoming light beam, with $\mathbf{k}$ vector parallel to the field direction, experiences a transparent medium, independently from the polarization of the light. The incoming light experiences the ordinary refractive index of the nematic droplets that is matched with the one of the polymer, so no scattering takes place and the medium is transparent.

Fig. 4.5 (c) shows the transmission for a PDLC film with thickness $\sim 100 \, \mu m$. In this case the incoming laser beam (diode laser $\lambda = 670 \, \text{nm}$, with a
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circular polarization) was parallel to the external electric field. At high field values (the maximum applicable is 120 kV/cm) the system is transparent, independently of the polarization.

If the incoming light is polarized along the direction parallel to the nematic molecules, the light experiences the extraordinary refractive index of the nematic droplets $n_e$. Usually $n_e \approx 1.15 \cdot n_o \approx 1.15 \cdot n_p$ and so the system is strongly scattering. In this case the PDLC behaves like a “white polarizer” [11]. It scatters the light only for one polarization channel, while for the other it results transparent and its appearance is white.

4.2.2 PDLCs preparation

As discussed in previous pages, there are many ways to grow a PDLC film. Our PDLCs were grown by phase separation induced by photopolymerization. To obtain a system in which light is amplified, also a gain medium is required. We chose to dissolve a laser dye in PDLCs.

As a first preparation step, nematic liquid crystals were mixed in the isotropic phase with the laser dye DCM special in an ultra-sonic bath for 60 minutes. This was required to dissolve properly the dye into the liquid crystal. Liquid crystals are not good solvents for laser dyes, for example like methanol, and so a long-time bath is required. As a second step, a pre-polymer composition, in which an ultraviolet photoinitiator with a typical concentration of 1% was dissolved, was added to the previous mixture and mixed again into the ultra-sonic bath for 30 minutes. The final mixture, that contained the liquid crystal, the pre-polymer and the dye, was polymerized under ultraviolet light for 1 hour. In this way, the ultraviolet photoinitiator generated the phase separation between the polymer and the liquid crystal, creating the PDLC structure. The laser dye resulted dissolved in both nematic droplets and in the polymer matrix.

The concentration of the liquid crystal was 85 wt% and that of the pre-polymer was 15 wt%. For the laser dye we chose a concentration of 1 mmol/l over the whole sample. The PDLC was prepared using two types of liquid
Figure 4.6: (a): SEM picture of a PDLC. The nematic droplets in this case have a mean radius of \(\sim 7 \, \mu m\). The sample has a polymer and liquid crystal concentration of 50 wt\%. (b): Optical microscope image of a PDLC. In this case the mean radius is \(\sim 1 \, \mu m\). The sample composition is 85 wt\% for the liquid crystal and 15 wt\% for the polymer.

Crystal, 5CB and E7, that have similar values for the ordinary \((n_0)\) and the extraordinary \((n_e)\) refractive indices (for E7: \(n_0 = 1.53\) and \(n_e = 1.75\) and for the polymer \(n_p = 1.53\)). The sample was inserted between two glasses, coated with a film of Indium Tin Oxide (ITO) to allow the application of an external electric field. The sample had a slab geometry of dimensions 3x2 cm and 1 mm thickness.

The growing difficulties lie in producing samples with a thickness of 1 mm. Typical PDLCs are grown with a thickness that can range from 10 to 100 \(\mu m\). In our case the critical thickness \(L_{cr}\) required for going above threshold for the PDLC random laser is the one calculated in section 4.1.4, so \(L_{cr}\) has to be larger than 200 \(\mu m\). Growing such thick sample was not so easy because sometimes samples with visible cracks were produced, due to a non completed polymerization.

Fig. 4.6 shows two pictures of PDLC systems. In (a) a SEM picture is shown. From this we can extrapolate a radius for the nematic droplets of \(\sim 7 \, \mu m\). In fig. 4.6 (b) an image taken with an optical microscope is shown. From this sample we extrapolate a mean radius of \(\sim 1 \, \mu m\). The first sample depicted is prepared with a polymer and a liquid crystal concentration of 50 wt\%. The second is one of the samples that we have used to study the random
laser measurements for which the composition was reported previously.

4.3 PDLC random laser: the temperature effect

4.3.1 Experimental setup

![Experimental apparatus for measuring the emission features of a random laser sample.](image)

Figure 4.7: Experimental apparatus for measuring the emission features of a random laser sample. The laser was a frequency doubled ($\lambda = 532$ nm) Nd:YAG. It operated at 10 Hz repetition rate and had a pulse width of 5 ns. The laser was operated in single shot mode to prevent cumulating heating of the sample. The emitted light was collected by a spectrometer that allowed a resolution of 0.5 nm. An energy meter allowed also to monitor the energy of each laser pulse. The pump beam on the sample was mildly focused, resulting in a spot size of 1.6 mm of diameter.

The experimental setup used for studying the emission properties of a PDLC random laser is depicted in fig. 4.7. To excite the sample we used a frequency doubled ($\lambda = 532$ nm) Q-switched Nd:YAG laser. It operated at 10 Hz repetition rate and had a pulse width of 5 ns. The emission spectrum
was recorded by imaging the diffuse emission from the front sample surface on input slits of a single grating spectrometer equipped with a silicon detector. The detection system provided a spectral resolution of 0.5 nm. During the measurements the laser operated in single shot mode to prevent cumulative heating and hence damaging of the sample. For each laser shot we could also record the pulse energy.

The pump beam was only mildly focused on the sample. There are two advantages for that:

- A large spot on the sample allows one to increase the region in which the population inversion takes place.

- At a certain pump intensity the sample will be damaged, because of dye ionization. If we use a large spot we have a better control over the critical intensity at which the sample results damaged.

For these two reasons the spot size on the random laser sample was fixed to a diameter of 1.6 mm for all measurements.

### 4.3.2 The temperature effect

To study the effect of temperature changes on a PDLC random laser, we prepared samples with the liquid crystal 5CB. As said in section 3.7, refractive indices of the nematic phase are: $n_o = 1.48$, $n_e = 1.67$. Above $32.5 \, ^\circ\text{C}$, 5CB is a classic liquid with $n_{iso} = 1.57$. We chose the liquid crystal 5CB instead of E7 because it has a lower temperature for the nematic-isotropic phase transition (32.5 ºC instead of 61 ºC). Emission measurements at a temperature greater than 40 ºC for a system in which a laser dye is dissolved suffers from the degeneracy of the dye. We measured at a fixed pump energy the emission of a pure dye dissolved in methanol. Above 40 ºC the quantum efficiency of the laser dye decreases, indicated by a decrease of the emitted signal. The gain length of the dye is temperature dependent and in particular above 40 ºC grows considerably.
4.3. PDLC RANDOM LASER: THE TEMPERATURE EFFECT

![Image showing emission spectra and peak intensity graphs.](image_url)

Figure 4.8: (a): Emission spectra in function of the pump energy. The sample is a PDLC random laser, where the liquid crystal is 5CB. The effect of the gain narrowing is visible from the spectra. The intensity of the peak increases more than the tails. (b): The peak intensity in function of the pump energy. The kink behavior for the threshold is visible at 5 mJ. The spot size of the pump laser is 1.6 mm in diameter.

Emission measurements on this PDLC sample show a behavior depicted in fig. 4.8. The spectra were taken at a temperature of 27 °C. In (a) the behavior of the emitted spectra is depicted. The pump energy $E_p$ in this case ranges from 1 mJ to 12 mJ. The gain narrowing effect is visible when the energy is increased. The FWHM goes from 74 nm to 30 nm for the highest pump energy. We cannot increase more the pump energy, because above $E_p = 12$ mJ the sample is damaged. In fig. 4.8 (b) the peak intensity of the spectra is plotted as a function of $E_p$. The threshold behavior is visible at $E_p = 5$ mJ; above this pump energy the system is above threshold. In this case the spectrum has a FWHM of 42 nm at $E_p = 5$ mJ.

Since we are sure that our system can go above threshold, we can study how the spectrum changes if our system performs the nematic-isotropic phase transition. The PDLC film in this case was inserted between two optical windows (without ITO coating) and the sample was put in a heat dissipator to scan a temperature range from 22.5 °C to 37.6 °C. A heat sensor was used to measure the sample temperature with an accuracy of 0.1 °C.

The behavior of the nematic-isotropic phase transition for a PDLC random
Figure 4.9: (a): Spectral dependency of a PDLC random laser on temperature. The system goes from the nematic to the isotropic phase (32.5 °C is the phase transition temperature). The inset shows the sample transmission in function of the temperature. The system passes from a scattering state (nematic phase) to transparent one (isotropic phase). (b) The bandwidth (white triangles) and the peak intensity (gray dots) of the emitted spectra in function of the temperature. The nematic phase is characterized by a narrow (29 nm) and high intensity emission. The isotropic phase is characterized by a broad (53 nm) and low intensity emission. The random laser passes, at the phase transition temperature, from above threshold to below threshold. In other words we can turn on or off the random laser using this phase transition.
4.3. PDLC RANDOM LASER: THE TEMPERATURE EFFECT

laser is shown in fig. 4.9. In (a) the emission spectra are shown when the sample temperature is increased from 22.5 °C to 37.6 °C. The measurements were taken at a fixed pump energy of 9 mJ. The emission peak at 32 °C is pointed out. This is in between the two scattering regimes. For $T < 32$ °C the system is opaque, while for $T > 32$ °C it is quasi-transparent. Fig. 4.9 (b) shows clearly the temperature effect. On the left y axis the bandwidth (white triangles) and on the right y axis the peak intensity (gray dots) in function of the temperature are plotted. For the bandwidth we pass from 29 nm at 22.5 °C to 53 nm at 37.6 °C. For the peak intensity in the studied temperature range we observe a reduction of a factor 3.5. The phase transition temperature is 32.5 °C [12], as also confirmed by our emission measurements.

In the nematic phase our sample scatters the light. It behaves like a standard random laser with a transport mean free path of $\sim 100$ µm (for the details on the mean free path measurements see section 4.4.1) The multiple scattering provides the feedback to observe a narrow emission. When we are approaching to the isotropic phase of the liquid crystal, the sample becomes more and more transparent, as depicted in the inset of fig. 4.9 (a). The transparency is a signature of weak scattering that is connected to the isotropic phase. In this case multiple scattering cannot take place and the feedback mechanism for the random laser is not present. The system goes from an above threshold state, for the nematic phase, to a below threshold state, for the isotropic phase. The threshold is identified in fig. 4.8 (b), and it is characterized by a FWHM of 42 nm.

The temperature gives us a total control on the random laser emission. We can choose if we want to turn on the device ($T < 32$ °C) or if we want to turn off it ($T > 32$ °C). This is an example of a totally controllable photonic device. The temperature allows us to tune the transport properties for this disordered system.

The refractive indices of the polymer ($n_p = 1.53$) and of the liquid crystal droplets in the isotropic phase ($n_{iso} = 1.57$) are not completely matched. This gives a not completely transparent medium, as pointed out in the inset of fig. 4.9 (a), where the transmission reaches only 60%. Since the medium scatters
the light somewhat the random laser is not turned off completely. If we would have a completely transparent medium we would expect that the emission is equal to the fluorescence of the laser dye. In our case the fluorescence is characterized by a bandwidth of 70 nm, while the PDLC in the isotropic phase has a bandwidth of 53 nm. Wiersma and Cavalieri [13] have shown that, if the matching between the two refractive indices is perfect, the off-state of the random laser is reached, with an emitted spectrum equal to the fluorescence of the dye.

4.4 PDLC random laser: the electric field effect

We do not have a perfect matching at high temperature because the growing technique for our PDLCs is optimized to use the liquid crystal E7 and to study the effects of an applied external electric field. The sample had a slab geometry and we can define a coordinate system in this way: the slab surface lays in the x-y plane, while the z axis is perpendicular to the slab. In all our measurements the external electric field was applied along the z axis and it had a maximum peak to peak voltage of 12 kV. Since our samples were 1 mm thick, the maximum field was $F = 120$ kV/cm. The field oscillated at 500 Hz to avoid the diffusion of charged particles in the sample. As discussed in section 4.2.1 the PDLC is transparent along the z axis upon electric field application independently of the polarization of the incoming light.

4.4.1 Diffusion constant measurements

The diffusion constant $D$ characterizes the scattering strength of our system. The two limiting values for $D$ are: small $D$ value means that the systemdiffuses strongly ($D = 0$ is the Anderson localization regime), while when $D \to \infty$ the system becomes transparent. To measure $D$ we used a time-resolved technique, in which the decay of the transmitted diffuse intensity was monitored with a streak camera. The setup is shown in fig. 4.10. The laser was a Ti:Sapphire ($\lambda = 750$ nm), with a pulse duration of 1 ps. The incoming
4.4. PDLC RANDOM LASER: THE ELECTRIC FIELD EFFECT

Figure 4.10: Time-resolved setup for diffusion constant measurements. The laser used is a Ti:Sapphire (λ = 750 nm), with a laser pulse duration of 1 ps. The diffuse transmitted light is collected by a streak camera coupled to a monochromator. The temporal resolution of the setup is 3.5 ps.

light was incident on the sample surface and the diffuse transmitted light was collected by a streak camera, with a resolution of 3.5 ps. A monochromator was used to focus the diffuse light on the streak camera, by the help of its exit slits.

In general $D$ is a second order tensor and with the above technique we measure the component $D_{zz}$. Obviously $D_{zz} = D_{yy} = D_{xx} = D$ if the system diffuses isotropically. But if the light is diffused anisotropically, the components of the tensor are different from each other. For example, for nematic liquid crystals oriented by an external field, the diffusion is anisotropic [14]. In our case the hypothesis of isotropic diffusion is valid only when the droplets of the PDLC are not aligned by an external field. This means that with the time-resolved technique we measure $D_{zz}$ if the electric field is applied.

In the diffusion equation 4.1 the energy density $W$ and the source function $S$ depend on time and on position; so in general $W = W(r, t)$ and $S = S(r, t)$. The time evolution of the diffuse transmitted intensity $I_{tr}$ follows the Fick law [15]

$$I_{tr} = -D_{zz} \nabla W(r, t). \quad (4.9)$$
Combining eq. 4.1 and 4.9 we obtain a solution for the transmitted intensity

\[
I_{tr} = I_0 \exp \left(-\frac{\pi^2 t D_{zz}}{(L + 2z_0)^2} \right) \times \frac{\pi^{3/2} \sqrt{D_{zz}^3 (4t)^5}}{\pi^{3/2} \sqrt{D_{zz}^3 (4t)^5}} \\
\sum_{j=-\infty}^{+\infty} A(j) \exp \left(-\frac{A(j)^2}{4D_{zz} t} \right) - B(j) \exp \left(-\frac{B(j)^2}{4D_{zz} t} \right),
\]

(4.10)

where \(L\) is the sample thickness, \(z_0\) is the extrapolation length and \(A\) and \(B\) are:

\[
A = (1 - 2j)(L + 2z_0) - 2(z_0 + \ell_t) \quad \text{and} \quad B = (1 + 2j)(L + 2z_0).
\]

(4.11)

For a detailed treatment see ref. [14].

The function \(I_{tr}\) is used to fit the transmitted diffuse light as measured by the streak camera and to extract the value of \(D_{zz}\). Fig. 4.11 (a) shows the measured diffuse light for the PDLC (black dots) and the profile of \(I_{tr}\) that fits the data (gray curve). The fit gives a value for the diffusion constant of \(D_{zz} = 5080 \text{ m}^2/\text{s}\). Here no electric field is applied, so the diffusion can be considered isotropic and eq. 1.8 is valid. From this equation we can extract the transport mean free path, that is \(\ell_t = 80 \mu\text{m}\), if we approximate the energy velocity by the phase velocity. Applying an electric field the diffusion is no more isotropic and eq. 1.8 cannot be used to obtain \(\ell_t\).

Fig. 4.11 (b) shows the behavior of \(D_{zz}\) as the applied electric field is increased. From 0 kV/cm to 80 kV/cm the value of the diffusion constant doubles. Above \(F = 80 \text{ kV/cm}\) we reach the setup resolution. The increase of the diffusion constant means that the sample becomes less and less scattering, as also depicted in the inset of fig. 4.11 (b). Here the transmission along the \(z\) direction is measured with a diode laser (\(\lambda = 670 \text{ nm}\)). The sample is transparent when a high field is applied along the \(z\) axis, independently of the polarization of the incoming beam, for both the transmission and time-resolved measurements. So we can expect that for the emission spectra something similar to temperature tuning effect happens, in the sense that at high electric field (120 kV/cm) the random laser is in the off-state, while for \(F = 0 \text{ kV/cm}\).
4.4. PDLC RANDOM LASER: THE ELECTRIC FIELD EFFECT

![Image of graph showing time evolution and diffusion constant](image)

Figure 4.11: (a): Time evolution of the diffuse light for a PDLC film (black dots), without any applied external field. The function $I_{tr}$ is used to fit the data (gray curve). In this case we extract the value of 5080 m$^2$/s for the diffusion constant. (b): Diffusion constant in function of the external electric field applied to the PDLC. From 0 kV/cm to 80 kV/cm the value of the diffusion constant doubles. Above $F = 80$ kV/cm we reach the setup resolution. This means that at high field the sample becomes less scattering. In the inset the transmission along the z axis is depicted in function $F$ until 120 kV/cm, where the sample has a transmission near 50%. For both time-resolved and transmission measurements the absorption of the laser light ($\lambda = 750$ nm for time-resolved and $\lambda = 670$ nm for the static measurements) can be considered negligible.

the random laser is in the on-state. The experimental results do not follow this simply behavior, as we will see in the next section.

4.4.2 The electric field effect

Fig. 4.12 shows the gain narrowing effect for three different scattering states for a PDLC random laser. The first one refers to the isotropic phase (black squares), the second to the nematic phase at $F = 0$ kV/cm (black dots), while the third to the nematic phase at $F = 120$ kV/cm (black triangles). Two samples were studied: for the isotropic phase we used a PDLC prepared with the liquid crystal 5CB, to avoid dye degeneracy; for the nematic phase the liquid crystal is E7. In the isotropic case we observe only a minor narrow-
Figure 4.12: Bandwidth of the emission spectra in function of the excitation energy. The spot size of the excitation beam was chosen to be 1.6 mm. In the isotropic case (black squares) \((T = 37 \, ^\circ\text{C}, \text{liquid crystal 5CB})\) the sample is transparent in all directions (no multiple scattering) and indeed no substantial peak narrowing occurs. The other two curves represent the PDLC in the nematic phase; black dots for \(F=0\) kV/cm and black triangles for \(F=120\) kV/cm. Although the nematic system is nearly transparent in the \(z\) direction when the field is maximum, strong peak narrowing is observed.

ing upon increasing the excitation energy, which is consistent with the near absence of multiple light scattering: the system remains below threshold, as discussed in section 4.3. For the nematic case without field we observe strong narrowing. This difference between the isotropic and nematic phase is consistent with the temperature tuning of a random laser and can be attributed to the temperature dependence of the scattering strength.

From fig. 4.11 (b) we can see that both at high temperatures and at high electric field the sample becomes transparent. Nevertheless we observe in fig. 4.12 that, upon application of the maximum electric field, the random laser effect does not disappear as in the isotropic phase, but becomes even stronger. The bandwidth at 10 mJ excitation energy decreases from 30 nm
at zero field, to 20 nm at 120 kV/cm. Although the sample appears nearly transparent at 120 kV/cm, the random laser effect increases, indicating strong multiple scattering somewhere inside the sample. The explanation lays in the strong anisotropy of the scattering in the polymer dispersed liquid crystal. The liquid crystal droplets are aligned by the electric field with the nematic director in the z direction. This means that the polarization vector $P$ of a light wave propagating in the z direction is always orthogonal to the director. Therefore, this wave experiences the ordinary refractive index of the liquid crystal, which is nearly equal to that of the polymer host ($n_o \cong n_p$), so that the sample looks transparent. On the other hand, a wave propagating in the x-y plane of the sample with polarization vector $P$ parallel to the director probes the extraordinary refractive index of the liquid crystal droplet. Hence the extraordinary wave in the x-y plane of the sample experiences the highest possible refractive index contrast of $n_e/n_p = 1.15$ and is therefore strongly scattered. In our sample, with slab geometry, this anisotropy leads to strong scattering in the plane of the slab and at the same time optical transparency in the direction perpendicular to it.

### 4.4.3 Scattering cross section for a PDLC droplet

To understand why our samples look transparent and at the same time scatter the light when $F$ is applied, we have to start from the differential scattering cross section of a nematic droplet. It has been calculated by, amongst others, Žumer et al. [16, 17]. We are interested in the cross section relative to an aligned droplet and here we consider only elastic scattering. We can take for simplicity the two extreme scattering cases. The first is when light experiences the ordinary refractive index of the droplet and the second is when light experiences the extraordinary one. In fig. 4.13 these two cases are shown. For ordinary incoming polarization $P_i$, the incoming wave vector $k_i$ is not scattered by the droplet. For extraordinary incoming polarization, $k_i$ is scattered by the droplet, and the scattered wave vector $k_s$ lies mainly in the plane perpendicular to the applied field.
For the ordinary and the extraordinary cases we have two different differential cross sections: \([d\sigma/d\Omega]_e\) and \([d\sigma/d\Omega]_o\). For both cross sections we can write

\[
\frac{d\sigma}{d\Omega} = \sigma_0 (k_i R)^4 A(\delta, \alpha, \theta, \gamma, ...),
\]

(4.12)

where \(\sigma_0\) is the geometric cross section \((\sigma_0 = \pi R^2)\) and \(R\) the droplet radius. \(A(\delta, \alpha, \theta, \gamma, \epsilon_p, \epsilon_e, \epsilon_o, R, k)\) is a function of the angles \(\delta, \alpha, \theta, \gamma\) involved in the three-dimensional scattering process and depends also on the dielectric constants of the PDLC, on the droplet radius \(R\) and on \(k = k_i - k_s\); \(A\) is the normalized differential cross section. For a complete treatment see ref. [16].

We can calculate \(A(\delta, \alpha, \theta, \gamma,...)\) assuming that the incoming light is extraordinary polarized. For this particular case, which means to impose \(\alpha = 90^\circ\), we can write the two normalized differential cross sections as:

\[
A_e \propto \frac{1}{(Rk)^6} \left[ \frac{\epsilon_e - \epsilon_o}{3\epsilon_p} \sin^2 \theta \cos \gamma \cos \delta - \sin \delta \cos \theta \sin \theta \right]^2 \sin^2 \gamma
\]

(4.13)

\[
A_o \propto \frac{1}{(Rk)^6} (\frac{\epsilon_o}{\epsilon_p} - 1)
\]

(4.14)

Fixing all the parameters except \(\delta\) we obtain the normalized cross sections
depicted in fig. 4.14 (a). $A_e$ is peaked around $\delta = 0^\circ$ and $\delta = 180^\circ$. For $\delta = 90^\circ$ the cross section goes to zero. This means that the light is preferentially scattered in directions that conserve the extraordinary polarization, while the scattering is inhibited for the directions that change the polarization from extraordinary to ordinary. $A_e$ has a behavior that is very close to $\cos^2 \delta$. $A_o$ is zero for every angle, if we choose a perfect matching between $n_o$ and $n_p$.

We can now calculate the distribution of the scattered light by a nematic PDLC droplet. We choose an unpolarized incoming wave vector orthogonal to the nematic director. We obtain a distribution of light scattered by the droplet that is plotted in fig. 4.14 (b). The distribution for the angle $\delta$ is peaked around $-15^\circ$ (near forward scattering) and $160^\circ$ (near back scattering). The major part of the light is scattered with an extraordinary polarization. When $\delta$ increases we find a region from $60^\circ$ to $90^\circ$ where the scattered light is suppressed.

The single scattering analysis give us a clear picture for the elastic light scattering from a nematic droplet of a PDLC.

- Ordinary polarized incoming light: No scattering event is observed if $n_o = n_p$.

- Non-ordinary polarized incoming light: The droplet scatters the light preferentially around $\delta = 0^\circ$ (forward scattering) and $\delta = 180^\circ$ (back scattering). The scattered light is mainly extraordinary polarized. The ordinary channel is strongly inhibited.

The above considerations are made for an ideal system, where the coupling between the nematic director and the electric field was considered complete. Besides we have chosen perfect matching for $n_o$ and $n_p$. In a real sample these two hypotheses cannot be fulfilled. However if we choose $n_o - n_p = 0.03$ (a realistic estimate) $A_o$ is still two orders of magnitude smaller than $A_e$. So the extraordinary channel will always result dominant [16]. We can now apply these concepts to our situation, where a gain medium is dissolved in the PDLC.
Figure 4.14: (a): Normalized differential scattering cross sections $A_e$ and $A_o$ in function of the scattering angle $\delta$. The incoming wave vector is extraordinary polarized. $A_e$ is similar to $\cos^2 \delta$. The probability that the incoming light is scattered at $\delta = 0^\circ$ and $\delta = 180^\circ$ is high. On the other hand the cross section tends to zero when we approach $\delta = 90^\circ$. $A_o$ is zero in this case because $n_o = n_p$. (b): Distribution of the scattered light for an incoming wave vector orthogonal to the nematic director with an arbitrary polarization. The forward scattering and the back scattering are favored. The scattered light has a dominant component of extraordinary polarization.
4.4.4 PDLC as a quasi-two-dimensional random laser system

The scattering cross sections presented in section 4.4.3 are for the single scattering from a nematic droplet. We can generalize the results to a multiple scattering system in a qualitative way. The resulting transport for a PDLC random laser is schematically depicted in fig. 4.15. The field is applied along the z axis. Without external field (fig. 4.15 (a)) the scattering is isotropic and the PDLC behaves like a regular diffusive random laser. The PDLC therefore emits its energy in all directions and with random polarization. When the electric field is applied, the nematic director is aligned and multiple scattering takes place for extraordinary polarized light and mainly in the x-y plane. In fig. 4.15 (b) a random walk of extraordinary light is shown for the high electric field case. A spontaneously emitted photon with extraordinary polarization and a wave vector that lies in the x-y plane will perform such anisotropic random walk, which will allow for the gain to become larger than losses and for the random laser action to be set in. For each scattering event, the forward and the back scattering directions are the more favorable, as shown in fig. 4.14 (b). The diffusion is in practice confined in the x-y plane. On the contrary if the spontaneously emitted photon has an ordinary polarization, it will see a transparent medium and will exit the sample without being scattered.

The dye-doped polymer dispersed liquid crystal at high electric field has a particular advantage concerning the optical excitation of the dye. Usually in random lasers the optical excitation is more difficult than in regular lasers, due to the scattering of the pump beam. The probability for light to be absorbed by a random laser is proportional to the transport mean free path. For an electric field aligned PDLC, due to the absence of scattering for propagation perpendicular to the sample, the dye can be optically excited at near 100% efficiency: the excitation beam is almost completely absorbed. This higher efficiency in the high field case leads to an even stronger lasing effect compared to the isotropic three-dimensional case, as was seen in fig. 4.12.

The high field provides an efficient multiple scattering mechanism and basically confines the light to an anisotropic random walk in the x-y directions.
Figure 4.15: Schematic representation of the random laser action in an active PDLC system. \( \mathbf{k}_i \) and \( \mathbf{k}_s \) represent the incoming and scattered wave vectors and \( \mathbf{P}_i \) and \( \mathbf{P}_s \) the related polarization vectors. (a): Multiple light scattering in absence of the electric field. The liquid crystal droplets are randomly oriented and there is no global anisotropy in the system. Light transport follows a regular isotropic diffusion process. (b): A strong electric field \( \mathbf{F} \) is applied in the \( z \) direction, and the nematic director in the liquid crystal droplets aligns along the field. Multiple light scattering takes place for the extraordinary polarization channel and preferably in the \( x-y \) plane.
This confinement is enhanced even more by Fresnel reflection at the front and rear sample (the critical angle for total internal reflection is 42.5°). The application of the electric field makes the PDLC random laser go from a three-dimensional diffusive system to a two-dimensional one. We observe a change of the dimensionality of the light transport mechanism.

Considerations for the 2D-transport in the PDLC random laser can be done also starting from the fundamental condition of reciprocity in Maxwell’s equations. For high field values, the spontaneous emitted light that travels along the z axis crosses the system without being scattered (it sees a transparent medium). Vice versa, the extraordinary emitted light that travels in the x-y plane is scattered in this plane and cannot be scattered in the z direction.

### 4.4.5 Anisotropic and polarized emission

The model presented in the previous section implies that the emitted light has to be polarized. One expects that extraordinary polarized photons will be scattered and therefore strongly amplified due to the mismatch between $n_e$ and $n_p$, while ordinary polarized photons will not. This means that we would measure narrow emission spectra mainly in the extraordinary polarization channel.

We can collect the light emitted from various positions from our samples. Fig. 4.16 depicts a section of the PDLC film, where the electric field $F$ is applied along the z axis. Our detector can collect the emitted light from the sample when $\varphi = 0^\circ$ (back reflected emission) or when $\varphi = 90^\circ$ (transverse emission).

When the electric field is applied a light wave is amplified in our PDLC random laser, if it is extraordinary polarized. This means that it has to travel inside the PDLC with a $\mathbf{k}$ vector orthogonal to the field and a polarization vector parallel to it. So to detect an extraordinary polarized emission, we have to place our detector in the transverse configuration, as shown in fig. 4.16. In this case we need a polarizer to distinguish between ordinary and extraordinary channels. A sheet polarizer was put in front of the detector for
CHAPTER 4. PDLC RANDOM LASER

Figure 4.16: Experimental geometry for emission measurements on a PDLC random laser. The electric field is applied along the z axis. The emission can be collected in back reflection ($\varphi = 0^\circ$) or in a transverse configuration ($\varphi = 90^\circ$).

this reason. The axis of the polarizer could be parallel to the z axis for the extraordinary detection or parallel to the y axis for the ordinary detection. From the model presented in the previous section, we expect in the back reflection configuration ($\varphi = 0^\circ$) no difference between the two polarization channels. While if $\varphi = 90^\circ$, we expect to measure narrow banded emission for the extraordinary channel.

The results of the measurements, with a detector in transverse configuration, are plotted in fig. 4.17. The pump energy was 3.5 mJ and the spot size of the beam 1.6 mm. The measurements were performed increasing the electric field for the two polarization channels. In fig. 4.17 (a) the integrated intensity of the emission peaks (output energy) is plotted in function of F. The triangles represent the extraordinary polarized light, while the dots represent the ordinary one. The extraordinary channel grows with the field and a polarization ratio of 2 is reached at maximum field. The ordinary channel remains roughly constant. The PDLC random laser emits polarized light with controllable degree of polarization. For $F = 0$ kV/cm the random laser emis-
Figure 4.17: Total output energy and bandwidth for the emission in the x direction for the two polarization channels (triangles: extraordinary polarization, dots: ordinary polarization), in function of the applied field. The excitation power is 3.5 mJ. (a): The emitted light becomes gradually extraordinary polarized when the field is increased. The increase of the total intensity (sum of both polarization channels) is consistent with the increase of the efficiency of the absorption of the pump beam. (b): The peak narrowing, caused by the electric field, is observed for both polarization channels.
sion is not polarized, for the two channels we have roughly the same amount of emitted energy. For $F = 120$ kV/cm the light is preferentially emitted with extraordinary polarization. If we sum the output energy from the two channels at $F = 0$ kV/cm and $F = 120$ kV/cm, we observe an increase of the emitted energy of 35% when the high field is applied. This can be explained by the fact that the pump beam at high $F$ is absorbed better by the sample, as explained in section 4.4.4.

Fig. 4.17 (b) shows the bandwidth for the two polarization channels versus the electric field. For both channels the emission is well below the threshold value of 50 nm. It means that apparently extraordinary and ordinary are mixed during the random walk inside the sample. The model describes only in a qualitative way what happens in a PDLC, as already said. A Monte Carlo simulation would be necessary to understand better the anisotropic transport in our random laser.

The polarized emission is visible only if our detector stays at $\varphi = 90^\circ$. If we change $\varphi$ we observe always narrow emission and we cannot distinguish between ordinary and extraordinary light. This is in agreement with our model; only light emitted from the plane x-y can be polarized. Note that this is a remarkable property for a disordered light source based on random lasing.

The model predicts also that the emission of light has to be anisotropic, in the sense that the major part of the emission should be radiated in the x-y plane. We have measured that at maximum field $F = 120$ kV/cm the total emission in the x direction increases by 60% with respect to $F = 0$ kV/cm, while at $\varphi = 0^\circ$ (z direction) the total emission increases only by 16%. This behavior is another signature of the anisotropic emission diffusion process.

For the PDLC random laser we can now conclude that it possesses several new features with respect to the “classic” diffusive random laser [19, 20]:

- **Temperature tuning**: Due to the nematic-isotropic phase transition the random laser can be switched between two states. It goes above thresh-

---

1 The little difference between the two channels is due to a residual memory effect in the PDLC. The system possesses a memory of the previous application of $F$. This effect is well-known for PDLCs [18].
old in the nematic phase and below threshold in the isotropic phase.

- **Electric field switching**: The electric field aligns the nematic droplets and we observe a change of the diffusion dimensionality in our system. The random laser goes from a 3D isotropic diffusive state at \( F = 0 \) kV/cm to a quasi-2D anisotropic diffusive state at \( F = 120 \) kV/cm. In the last case the multiple scattering becomes highly anisotropic.

- **Anisotropic emission**: At \( F = 120 \) kV/cm the emission is anisotropic. The light is emitted preferentially in the plane orthogonal to the applied field.

- **Polarized emission**: The emitted light from the x-y plane is extraordinary polarized. We have control over the degree of polarization via the electric field.

To enhance more the 2D transport behavior and hence the anisotropic emission for our system we need to overcome the main limitation for the PDLC random laser. This is the thickness of the samples. To reach the critical volume we have used a sample of 1 mm thickness, which is difficult to synthesize. A typical thickness for PDLCs is about 50 \( \mu \)m [7]. For a film of 1 mm it is difficult to obtain a uniform polymerization. This creates defects in the structure that limit the action of the external electric field upon the droplets alignment. To overcame this problem we have to reduce the critical thickness \( L_{cr} \) (see eq. 4.8). Reducing \( L_{cr} \) means that we need a medium with smaller gain length \( \ell_g \) than DCM special. An option could be to use high gain nano-particles (ZnO for example) dispersed in the nematic droplets. In this case we can reduce the sample thickness to 50-100 \( \mu \)m and grow a PDLC random laser with a lower numbers of defects.
Bibliography


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Chapter 5

Random Multilayers

Porous silicon is a suitable material to build up random multilayer structures. 1D random systems present always a finite localization length. In this chapter time-resolved measurements are reported to investigate the properties of the states of a 1D random system. The time response of a localized state was characterized by a strong reduction of the group velocity and by a slow exponential decay. But the main contribution to the resistance of a random system is not due to localized states but to necklace states. A necklace state extends over the whole sample and hence is not localized. It is formed by $N$ resonances. A necklace state has a time response characterized by a strong reduction of the group velocity, but since it is not a localized state, the decay is very fast. 1D random multilayers can be used also to study the random laser action in one dimension. A little modes competition was experimentally observed, but due to losses channels present in our samples the random laser was always below threshold.
CHAPTER 5. RANDOM MULTILAYERS

5.1 Porous silicon

The interest on porous silicon was started at the beginning of ’90, when Canham proposed this structure and measured high values for the photoluminescence of a porous silicon layer at room temperature [1]. Bulk silicon is not a good light emitter, the photoluminescence efficiency is $10^{-6}$. This happens because bulk silicon is a semiconductor with an indirect band gap, which means that the maximum of the valence band and the minimum of the conduction band in the Brillouin zone have not the same $k$ value. Porous silicon is formed by Si nano-crystals. In this case the electrons and the holes are strongly confined and hence the radiative recombination rate is strongly increased with respect to bulk Si. For porous Si the photoluminescence efficiency is $10^{-1}$ [2, 3].

The technological interest in porous silicon stays in applications for light-emitting devices. The advantage is that porous silicon can be easily integrated into Si devices. But another application emerged recently for porous silicon. It is the possibility to grow 1D multilayers structure, where two layers with different porosity can be stacked alternatively to produce, for example, a 1D photonic crystal [4]. The porosity can range from 20% to 80% and for each value we have a different effective refractive index $n_{eff}$ for a single layer. To evaluate the refractive index for a single layer we can use the Bruggeman formula [5]:

$$f_{\text{air}} \frac{\epsilon_{\text{air}} - \epsilon_{\text{eff}}}{\epsilon_{\text{air}} + 2\epsilon_{\text{eff}}} + f_{\text{Si}} \frac{\epsilon_{\text{Si}} - \epsilon_{\text{eff}}}{\epsilon_{\text{Si}} + 2\epsilon_{\text{eff}}} = 0,$$  \hspace{1cm} (5.1)

where $f_{\text{air}}$ and $f_{\text{Si}}$ are respectively the fractions of air and silicon that are present in a layer ($f_{\text{Si}} = 1 - f_{\text{air}}$).

Multilayer structures are commonly grown with chemical vapor deposition (CVD) technique. This technique is very time consuming (1 day is required to grow a multilayer with 30-40 layers) and also necessitates an expensive apparatus. Porous silicon offers a cheapest alternative. It is possible to grow structures until 400 layers in 3 hours. The disadvantage for porous silicon is
Besides 1D photonic crystals, various structures can be produced with porous silicon, using two layers with different porosity. Fig. 5.1 shows same examples of multilayer systems. The first one is the distributed Bragg mirror (DBR), in other words a 1D photonic crystal, where the layers of type \( A \) and \( B \) are stacked alteratively. The second is an optical microcavity. The microcavity \( AA \) is sandwiched between two DBRs and it confines the light to a small sample volume. An ideal cavity would confine light indefinitely (that is, without loss) and would have resonant frequencies at precise values. Deviation from this ideal condition is described by the cavity \( Q \) factor, which is proportional to the confinement time in units of the optical period \([6]\). The third example of fig. 5.1 is the Fibonacci quasi-crystal. A Fibonacci quasi-crystal is a deterministic aperiodic structure that is formed by stacking two different compounds \( A \) and \( B \) according to the Fibonacci generation scheme: \( S_{j+1} = [S_{j-1}S_j] \) for \( j \geq 1 \), with \( S_0 = [B] \) and \( S_1 = [AB] \). The transmission spectrum of a Fibonacci system has forbidden frequency regions, called pseudo band gaps, similar to the band gap of a photonic crystal \([7]\). The last example is a random multilayer system, where \( A \) and \( B \) are randomly arranged. This type of structure is the argument of this chapter.
5.1.1 Preparation of porous silicon multilayers

The starting point for the growth of a porous silicon multilayer is a wafer of p$^+$-type (0.01 Ω·cm) doped Si, with [100]-oriented substrates. The wafer is placed in a bath of aqueous hydrofluoric acid (HF) and electrically connected to a brass electrode. The other electrode, made of platinum, is put into the HF bath and a current generator is used. Applying a current density $J$ between electrodes, the ions $\text{F}^-$ react with the holes of the doped Si and the pores grow. The time in which a certain $J$ value is applied defines the thickness of the layer. Our samples were grown with a typical optical thickness of $\lambda_0/4$, where $\lambda_0$ is the wavelength at which our structures were centered and was $\lambda_0 = 1450$ nm. The optical thickness is $n_i d_i$, where $n_i$ is the refractive index of a generic $i$ layer and $d_i$ its physical thickness. Hence

$$d_i = \frac{\lambda_0}{4n_i}.$$  \hspace{1cm} (5.2)

Changing the current density one can modulate the pores size and hence the porosity. Our samples had two types of layers: $A$ with high porosity and $B$ with low porosity. High porosity $\lambda_0/4$ layers were obtained with a current density of 50 mA/cm$^2$ for a time of 5.9 s; they had an effective refractive index $n_A \sim 1.4$. Low porosity $\lambda_0/4$ layers were obtained with $J = 7$ mA/cm$^2$ for 21.5 s, which resulted in an effective refractive index $n_B \sim 2.1$. The typical size of the pores ranged from 50-100 nm and since the silicon wafer used had [100]-oriented substrates, the pores grew perpendicular to the surface of the sample. In 2-3 hours every multilayer structure can be grown (for details see ref. [8]).

With HF etching it is possible to obtain porous systems that have at maximum 400 layers. The main disadvantage in using HF acid is that the samples present a natural drift in the porosity (so also in the index of refraction). The first layer grown stays in contact with HF for all the time necessary to grow the whole structure, while the last one only for some seconds. It is clear that this overexposure to HF for the first layers generates a gradient in the porosity from the first to the last layers. For 110 layers structure, the porosity drift is
of the order of 8% in our case [9].

Fig. 5.2 shows a picture of a random porous silicon multilayer. Our samples\(^1\) were free-standing, without silicon substrate. To produce a free-standing sample an anodic electropolishing current pulse (0.4 A/cm\(^2\) for 2 s) was applied at the end of the growth process to detach the structure from the substrate. After the drying in air, the structures were pasted on a plastic holder with a hole, thus obtaining free standing air-porous silicon-air structures. The availability of free standing structures allowed to perform transmission measurements for our samples in contrast with the more commonly used reflectivity measurements [10].

### 5.2 Transmission measurements

As discussed in section 1.3, the Anderson localization for photons is due to spatially random optical potential. For a 3D sample the Ioffe-Regel criterion \(k\ell_t \leq 1\) defines a critical transport mean free path \(\ell_{cr} = 1/k\), below which photons with \(\lambda = 2\pi/k\) are localized in the system. The dimensionality of a disordered medium is a crucial parameter for Anderson localization. For 1D and 2D systems any degree of disorder will lead to a finite localization length [11, 12], while in 3D systems a certain critical degree of disorder is

\(^1\)The samples were grown at the University of Trento.
needed before localization will set in. Here we are interested in 1D disordered systems, so a finite localization length is expected.

Transmission of disordered samples will decay exponentially following \( T = T_0 \exp(-L/\xi) \), where \( \xi \) is the localization length and \( L \) the sample thickness. So an estimate for \( \xi \) can be done by transmission measurements. We studied 7 types of 1D random structures, where the number of layers ranged from 60 to 350. The sequence for 350 layers was randomly generated and to build up samples with a lower number of layers the sequence was cut off. The two layers A and B had an optical thickness of 1450 nm and mean refractive indices \( n_A \approx 2.1 \) and \( n_B \approx 1.4 \). Transmission measurements were performed using a tungsten lamp with \( \sim 200 \) \( \mu \)m spot size. To detect the transmission we have used a 250i Chromex monochromator coupled with a PbS detector, that allowed to cover a spectral range from 1000 nm to 2000 nm.

In fig. 5.3 four transmission spectra for the samples with 350, 250, 150 and 60 layers are shown\(^2\). First, what we can observe is that the peaks become more narrow if the sample thickness is increased. This means that the states become more localized in the system when thickness increases. This is a consequence of a finite localization length. If a sample has a thickness smaller than \( \xi \) the states are not localized, but extend over the whole sample and so they are broad in transmission. If the thickness is bigger than \( \xi \), the states result localized and hence the transmission peaks are narrow. The other feature pointed out in fig. 5.3 is the decreasing of the peaks transmission when the number of layers increases. This is a consequence of the scattering losses present in porous silicon multilayers. Absorption for our samples is negligible in the spectral range where transmission measurements were performed [13], but light scattering from the pores and from interfaces between layers not. The estimated scattering loss coefficient \( \alpha_s \) for our samples is \( \alpha_s = 100 \) cm\(^{-1} \) [9].

Beyond the scattering losses, our samples present (as said in section 5.1.1) a natural drift in the refractive index due to HF action. This is also a loss\(^2\)

\(^2\)We will use for the next pages of this chapter the abbreviation R350 for a random multilayer of porous Si with 350 layers, and so on for the other samples.
Figure 5.3: Transmission spectra for the samples R350, R250, R150 and R60. The transmission decreases when the samples become thicker because of scattering losses and refractive index drift.

channel that makes the transmission decrease for thicker samples. This gives a loss drift coefficient of 40 cm\(^{-1}\) [9]. So scattering and drift are the two losses channels and the total extinction coefficient will be \(\alpha = 140\) cm\(^{-1}\).

The transmission formula \(T = T_0 \exp(-L/\xi)\) for disordered systems refers to the transmission taken at a fixed wavelength. To estimate the transmission at a fixed \(\lambda\), we need to average over all the possible realizations of the disorder for each sample. In other words we need, let’s say, 100 samples with 100 different disorder realizations for each thickness. So totally 700 samples if we want to analyze 7 different thickness. This is experimentally unrealistic.
What we can do, since each sample has a large number of peaks, is to take the average over $\lambda$. We know that

$$<\ln T(\lambda)> = -\frac{L}{\xi + \varsigma},$$

where $\varsigma = 1/\alpha$ is the extinction length.

Fig. 5.4 shows the $<\ln T(\lambda)>$ in function of the thickness of the samples. Taking $\varsigma = 71 \mu m$, the fit gives a localization length $\xi = 14\pm4 \mu m$. This means that our sample R60, that has a thickness of 12.8 $\mu m$, do not have localized states. For the others, from R100 to R350, localized states are present since their thickness is larger than $\xi$. The confidence interval for the average of $\ln T$ (shown in fig. 5.4 as error bars) was obtained making many transmission measurements on a 250 layers sample. Due to lateral inhomogeneities of porous silicon samples the average of $\ln T d\lambda$ isn’t a constant for spectra taken from different point on the sample; the standard deviation of the average of $\ln T$
5.3 Transfer matrix approach: ξ formula

To treat analytically a multilayer structure we can use the transfer matrix approach. We can start considering a single layer with thickness \( d \) and with an effective refractive index \( n_{\text{eff}} \), surrounded by air. We supposed here to have a non magnetic (\( \mu = \mu_0 \)), isotropic and homogeneous material. To simplify the following formulas we assume normal incidence for the light on the system. If we consider an incident plane wave on the layer, we can calculate the reflected and transmitted components of the electric and magnetic fields. Let be \( E^+ \) and \( B^+ \) the transmitted components and \( E^- \) and \( B^- \) the reflected ones. For plane waves, the magnetic and electric fields are related by

\[
B^+ = \gamma E^+ \quad \quad B^- = \gamma E^- ,
\]

where \( \gamma = c/n_{\text{eff}} \).

The variables that propagate through the layer are the total electric field \( E = E^+ + E^- \) and the total magnetic field \( B = B^+ + B^- \). These are continuous at the interfaces. If we consider that, from one side of the layer to the other, a plane wave experiences a phase shift \( \delta = 2\pi n_{\text{eff}} d/\lambda \), we can easy find (see ref. [15] for details):

\[
\begin{pmatrix}
E_a \\
B_a
\end{pmatrix} = \begin{pmatrix}
\cos \delta & i\sin \delta/\gamma \\
i\gamma \sin \delta & \cos \delta
\end{pmatrix} \begin{pmatrix}
E_b \\
B_b
\end{pmatrix}.
\]

If we have a system formed by \( N \) layers, this technique can be iterated. We can relate the field on the very first layer with the one on the very last through a \( 2 \times 2 \) matrix, that is the product of transfer matrices relating fields on adjacent interfaces.

\[
\begin{pmatrix}
E_1 \\
B_1
\end{pmatrix} = \mathcal{M}_1 \cdot \mathcal{M}_2 \cdots \mathcal{M}_N \begin{pmatrix}
E_N \\
B_N
\end{pmatrix} = \mathcal{M}_T \begin{pmatrix}
E_N \\
B_N
\end{pmatrix}.
\]
CHAPTER 5. RANDOM MULTILAYERS

The knowledge of elements of $\mathcal{M}_T$ allows us to obtain both transmittance and reflectance, once the parameter $\gamma$ for the medium that surrounds the system is provided (we will call it $\gamma_0$), through formulas

$$t = \frac{2\gamma_0}{\gamma_0 m_{1,1} + \gamma_0^2 m_{1,2} + m_{2,1} + \gamma_0 m_{2,2}},$$

$$r = \frac{\gamma_0 m_{1,1} + \gamma_0^2 m_{1,2} - m_{2,1} - \gamma_0 m_{2,2}}{\gamma_0 m_{1,1} + \gamma_0^2 m_{1,2} + m_{2,1} + \gamma_0 m_{2,2}},$$

where $m_{i,j}$ are the elements of the transfer matrix 5.5. Note that from the measurements we obtain $T = |t|^2$ and $R = |r|^2$.

Multiplying a large number of $2 \times 2$ matrices is a very comfortable way to make computer numerical simulations (calculous can be made, in principle, with any given precision) but does not really give us the physical picture of what it is happening. In disordered systems can thus be convenient to search for average properties in order to better understand the physic involved. To do this we start defining a different kind of transfer matrices (from now on, in order to avoid confusion, we will refer to this latter type as scattering matrices), that relate the total field entering and going out from the two sides of a layer

$$\begin{pmatrix} E_1^+ \\ E_1^- \end{pmatrix} = \frac{1}{\bar{t}} \begin{pmatrix} \frac{1}{t^*} & \frac{1}{r} \\ \frac{-r*}{t} & \frac{1}{t} \end{pmatrix} \begin{pmatrix} E_0^+ \\ E_0^- \end{pmatrix} = X_1 \begin{pmatrix} E_0^+ \\ E_0^- \end{pmatrix}. \quad (5.9)$$

Iterating this formula we can obtain the scattering matrix relating the field entering and going out from the two sides of the whole sample.

$$\begin{pmatrix} E_N^+ \\ E_N^- \end{pmatrix} = X_1 \cdot X_2 \cdots X_N \begin{pmatrix} E_0^+ \\ E_0^- \end{pmatrix} = \tilde{X} \begin{pmatrix} E_0^+ \\ E_0^- \end{pmatrix}. \quad (5.10)$$

Note that transmittance and reflectance parameters of a single layer can be easily calculated through transfer matrices $\mathcal{M}$.

Assuming that all layers are statistically independent from each other and

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$^3$The following calculation were performed by Jacopo Bertolotti for his undergraduate thesis.
5.3. **TRANSFER MATRIX APPROACH: ξ FORMULA**

that all of them follow the same statistic, the ensemble averaging operation becomes much easier:

\[
\tilde{X}_{i,j} = \left[ \prod_{n=1}^{N} X_n \right]_{i,j} = \left[ \prod_{n=1}^{N} X_n \right]_{i,j} = \left[ \left( X_n \right)^N \right]_{i,j}.
\] (5.11)

This allows us to make the ensemble average on the scattering matrix of a single layer and then to make the \( N \)th power of it.

In our case the system is made of two different kinds of layers A and B, but with the same optical thickness and each layer have a 50% to be either A or B kind. Note that it does mean that the phase shift between two interfaces is always the same, independently from the reflective index of the layer itself. We can thus infer that, all frequencies that are integer multiple of \( 2c\lambda_0 \), will resonate in all layers and thus will see the system as fully transparent. As a consequence those wavelength are not localized, because they do not see the disorder at all.

Instead of taking the single layer as a logical unit we decided to take a set of equal layers (let’s say of the A kind) surrounded by two layers of the other kind (let’s say B). Neglecting the rightmost and leftmost layers, who are in contact from one side with air, it is always possible to define such thick layers which have a physical thickness \( \mathcal{N} \) times (with \( \mathcal{N} \in \mathbb{N} \)) the thickness of a single layer and thus \( \bar{d} = \lambda_0\mathcal{N}/4n \). For our statistics it can easily be seen that to find \( \mathcal{N} = 2 \) is half as likely as to find \( \mathcal{N} = 1 \) and so on. The transfer matrix for such structures (let’s assume of the A kind) can be written as:

\[
\mathcal{M}_A = \begin{pmatrix}
\cos \delta_A & i \sin \delta_A \\
\gamma_A \sin \delta_A & \cos \delta_A
\end{pmatrix},
\] (5.12)

where \( \delta_A = 2\pi \frac{d_A}{\lambda} = 2\pi \frac{\lambda_0}{4n_\lambda} \mathcal{N}_A \) and \( \gamma_A = n_A/c \).

With the assumption that the surrounding medium is of type B we can use equations 5.7 and 5.8 to obtain
\[ t_A = \frac{1}{\cos \delta_A + i \left( \frac{n_B^2 + n_A^2}{2n_An_B} \right) \sin \delta_A} \quad (5.13) \]

\[ r_A = \frac{i \left( \frac{n_B^2 - n_A^2}{2n_An_B} \right) \sin \delta_A}{\cos \delta_A + i \left( \frac{n_B^2 + n_A^2}{2n_An_B} \right) \sin \delta_A} \quad (5.14) \]

and from here

\[ X_A = \cos \delta_A \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + i \sin \delta_A \begin{pmatrix} -\frac{n_B^2 + n_A^2}{2n_An_B} & -\frac{n_B^2 - n_A^2}{2n_An_B} \\ -\frac{n_B^2 - n_A^2}{2n_An_B} & \frac{n_B^2 + n_A^2}{2n_An_B} \end{pmatrix}. \quad (5.15) \]

The matrix \( X_A \) is symmetric for the exchange of A with B.

When we do the ensemble average over this matrix, we have to average both over all possible \( N \) (with the proper weights) and over all possible reflective indices (that are just two, \( n_A \) and \( n_B \)). For any fixed \( N \) we notice that \( \delta_A = \delta_B \), and thus we can write (angular brackets denote the weighted average over all possible \( N \)):

\[ \langle X \rangle = \left< \cos \delta \right> \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \left< i \sin \delta \right> \begin{pmatrix} -\frac{n_B^2 + n_A^2}{2n_An_B} & -\frac{n_B^2 - n_A^2}{2n_An_B} \\ -\frac{n_B^2 - n_A^2}{2n_An_B} & \frac{n_B^2 + n_A^2}{2n_An_B} \end{pmatrix}. \quad (5.16) \]

Because the off-diagonal terms are antisymmetric in the exchange of A with B, they cancel out upon averaging on the reflective index.

To calculate the dimensionless resistance of a multilayer \( \varrho = 1/|t|^2 \), we need to write down the \( X_{S1}^{(2)} \) (defined by Pendry in ref. [14]) scattering matrix that contains \( r \) in his central term\(^4\)

\(^4\)in a non absorbing medium one can write

\[ \left| \frac{r}{t} \right|^2 + \frac{1}{|t|^2} = \left| r \right|^2 + \frac{1}{|t|^2} = \frac{2 - |t|^2}{|t|^2} = 2\varrho - 1 \]
5.3. TRANSFER MATRIX APPROACH: ξ FORMULA

\[
X_{S1}^{(2)} = \begin{pmatrix}
\frac{1}{(r^2)^2} & \frac{2r}{|t|^2} & \frac{(r^2)^2}{t^2} \\
\frac{r^*}{(t^2)^2} & \frac{|r|^2}{(t^2)^2} & \frac{r^*}{t^2} \\
\frac{-r^*}{t^2} & \frac{-r^*}{t^2} & \frac{1}{t^2}
\end{pmatrix}
\]

(5.17)

that, for a A type layer, is

\[
X_{S1}^{(2)} = \begin{pmatrix}
-\frac{(2i\alpha n_B \cos \delta_A + \alpha \sin \delta_A)}{4n_A^2 n_B^2} & \frac{i\beta \sin \delta_A (\cos \delta_A - i \sin \delta_A \alpha)}{n_A n_B} & -\beta^2 \sin^2 \delta_A \\
\frac{i\beta \sin \delta_A (\cos \delta_A - i \sin \delta_A \alpha)}{2n_A n_B} & 2\cos^2 \delta_A - 1 + 2\alpha^2 \sin^2 \delta_A & \frac{i\beta \sin \delta_A (\cos \delta_A - i \sin \delta_A \alpha)}{2n_A n_B}
\end{pmatrix}
\]

\[
\left(\begin{array}{cc}
\ldots & 0 \\
0 & 2 < \cos^2 \delta > - 1 + 2 \left(\frac{n_A^2 + n_B^2}{2n_A n_B}\right)^2 < \sin^2 \delta > \\
\ldots & \ldots
\end{array}\right).
\]

(5.18)

A nice property of this matrix is that \([X_{S1}^{(2)}]_{2,2}^{N} = [X_{S1}^{(2)}]_{2,2}^{N}\) and so we are uninterested in all terms but the central one. We can now write:

\[
\bar{\varrho} = \left(\frac{1}{2} \left[X_{S1}^{(2)}\right]_{2,2} + \frac{1}{2}\right)^N = \left(\frac{1}{2} \left(2 < \cos^2 \delta > - 1 + 2 \left(\frac{n_A^2 + n_B^2}{2n_A n_B}\right)^2 < \sin^2 \delta > \right) + \frac{1}{2}\right)^N \quad (5.19)
\]

\[
= \left(< \cos^2 \delta > + \left(\frac{n_A^2 + n_B^2}{2n_A n_B}\right)^2 < \sin^2 \delta > \right)^N.
\]

We have to evaluate \(< \cos^2 \delta >\) and \(< \sin^2 \delta >\). Here we meet the problem that these averages do not converge to a number but to a function of \(\lambda\). This can be expected since we already noticed that there are some resonating frequencies.
that see the whole system as fully transparent and in those cases the resistance dropped to zero. Anyway in our wavelength range of interest (from 1000 nm to 2000 nm) both functions are almost flat, spanning from 0.6 to 0.66 for \( < \sin^2 \delta > \) and from 0.33 to 0.4 for \( < \cos^2 \delta > \).

We can see that the average resistance of our samples is expected to grow exponentially with \( N \), note that \( N \) is the number of logic units in the sample (our thick layers) not the number of A or B layers in them, which is denoted by \( \mathcal{N} \).

We can estimate the localization length \( \xi \) through:

\[
\xi = \frac{L}{\ln \frac{d}{\rho}} = \frac{2N < \mathcal{N} > \langle d \rangle}{\ln \left( < \cos^2 \delta > + \left( \frac{n_A^2 + n_B^2}{2n_A n_B} \right)^2 < \sin^2 \delta > \right)^N} \]

\[
= \frac{4 \langle d \rangle}{\ln \left( < \cos^2 \delta > + \left( \frac{n_A^2 + n_B^2}{2n_A n_B} \right)^2 < \sin^2 \delta > \right)} .
\]

In our case \( \langle d \rangle \approx 214 \text{ nm} \), \( N = 1 \), \( < \mathcal{N} > = 2 \) and thus we obtain

\[
\xi = 9 \pm 1 \text{ \mu m} .
\]

This is in good agreement with the measured localization length \( \xi_{\text{exp}} = 14 \pm 4 \text{ \mu m} \), even if in eq. 5.20 the losses channels are not included (it is not so trivial to introduce them in the previous formulas).

### 5.4 Time-resolved measurements

To understand the behavior of localized states present in our random multilayers, we have investigated the time evolution of a short laser pulse (FWHM \( \sim 250 \text{ fs} \)) transmitted through them.
5.4. TIME-RESOLVED MEASUREMENTS

The setup used for time-resolved measurements is shown in fig. 5.5 and it is based on the optical gating technique. Two laser lines were used: a Ti:Sa laser (\(\lambda = 810\) nm, pulse width \(\sim 100\) fs) as the delay line and an optical parametric oscillator (OPAL) (tunable from 1400 to 1600 nm, pulse width \(\sim 200\) fs) as the reference line (where the sample was inserted). The pulses repetition rate was 82 MHz. The delay line could be moved at steps of 2 \(\mu\)m. The two laser beams were then converted in a single beam by a non linear crystal (BBO-crystal), using frequency up-conversion (the resulting beam had \(\lambda = 530\) nm and FWHM \(\sim 250\) fs; it is the cross-correlation signal). The step resolution of the setup was 7 fs. The resolution for the decay times was 250 fs; we could not measure decay times faster than the cross-correlation. The resulting signal was processed by electronics to get the time evolution of the...
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OPAL pulse in the random sample. At the same time the setup allowed also to measure transmission spectra of the samples, using a beamsplitter after the sample. The source light in this case was the OPAL pulse, broad \( \sim 14 \text{ nm} \), that excited the samples. So we measured only a limited spectral region (\( \sim 25 \text{ nm} \)) of samples transmission, but the advantage was that we knew exactly the shape of the peaks from which we measured the time response. The resolution for transmission spectra was 0.5 nm, since we used an InGaAs single array of photodiodes coupled with 250i Chromex in spectrometer configuration.

This setup is very similar to the one for the diffusion measurements presented in section 4.4.1. In that case we collected the light diffused by the sample and we analyzed it by a streak camera, that is a sort oscilloscope that measures the time evolution of the signal. In this case, without the help of the streak camera, we had to use two laser pulses to measure the time response, giving 10 times more temporal resolution with respect to the setup of section 4.4.1. Note that here we measured the transmission evolution and not the time evolution of the diffused light.

5.4.2 Time response for 1D random multilayers

Time-resolved measurements were taken for each sample, changing the central wavelength of the OPAL, in steps of 5 nm. In this way we have obtained a complete scan for the random structures from 1400 to 1600 nm, measuring both the time response and the integrated transmission. In fig. 5.6 the transmission, obtained from the OPAL pulse, for the R200 sample is shown. This results in a plot formed by superposed spectra, because each spectrum corresponds to a certain central wavelength of the OPAL. On the right y axis of the figure the delay time \( \Delta \tau \) of each pulse is plotted, in function of the OPAL wavelength used for the measurements. The delay time represents the center of mass of the pulse that exits from the sample. In this case the delay is very pronounced reaching 1000 fs. The gray gaussian represents the OPAL pulse (spectral width of 14 nm), which can be moved to scan the transmission peaks. In the depicted case the OPAL pulse is centered at 1510 nm.
5.4. TIME-RESOLVED MEASUREMENTS

Figure 5.6: Transmission for the sample R200 obtained moving the OPAL pulse at steps of 5 nm. On the right y axis the delay time $\Delta \tau$ is plotted in function of the OPAL central wavelength. $\Delta \tau$ represents the calculated center of mass of the time response. The plot shows also the OPAL pulse (FWHM $\sim 14$ nm). In this case the OPAL excites two transmission peaks.

From ref. [7, 16] we know that

$$\Delta \tau = \frac{v(0)}{v_g(\omega)} = \frac{c}{v_g(\omega) n_{eff}}, \quad (5.22)$$

where $v(0)$ is the phase velocity and $v_g(\omega)$ is the group velocity for the transmitted pulse. A large $\Delta \tau$ means a large group velocity reduction with respect to the phase velocity. For the investigated spectral range for R200 in fig. 5.6, the maximum reduction is measured for $\lambda = 1545$ nm, where $v_g(\omega)/v(0) = 0.15$, and the transmission spectrum reveals only the peak centered at 1555 nm. We are exciting only one state. This state is responsible for this strong group velocity reduction.

Fig. 5.6 shows a typical behavior for a random multilayer. With the OPAL pulse we always excite one transmission peak if it is enough isolated with respect to the others, or we can excite two states if they are enough close
Figure 5.7: Time-resolved measurements for the R200. (a): The OPAL wavelength is 1510 nm. We are exciting two states (see fig. 5.6). We observe oscillations due to a beating effect between the two peaks. (b): OPAL wavelength at 1550 nm. We excite a single resonance, see fig. 5.6. In this case the light intensity decays exponentially, with a time constant $\tau = 1050$ fs. The gray curve is the exponential fit.

to each other. For the samples R60 and R100 the time-resolved measurements did not give any appreciable results, because the transmission peaks were larger (> 14 nm) than the OPAL pulse. From the point view of the laser pulse this means that the samples were homogeneous.

Fig. 5.7 shows the time response for the sample R200 when the OPAL wavelength is 1510 nm (a) and when it is 1550 nm (b). In fig. 5.7 (a) we are exciting two peaks (see also fig. 5.6) and a beating between the two is observed. The beatings happen when we have a superposition of harmonic oscillations at different frequencies, but close to each other. This is a phenomenon well-known in acoustic. In our case the period of beating oscillations $\Delta T$ is 740 fs. From the transmission spectra we know that the two peaks are 10 nm distant. The spacing in wavelength is simply connected to the spacing in time by $\Delta \lambda = (\lambda^2/(c \cdot \Delta T))$. From a spacing of 10 nm we find a time spacing of 760 fs, meaning that the observed oscillations are due to the beating between
5.4. TIME-RESOLVED MEASUREMENTS

Figure 5.8: Sample R150. (a): Transmission spectrum of a single resonance taken with the OPAL pulse. (b): Time response for the transmission peak in (a). In this case the pulse is not delayed, $\Delta\tau \approx 0$ and the decay is very fast, $\tau < 250$ fs.

The peaks (the first at 1506 nm and the other at 1516 nm) measured in transmission. Moving the OPAL pulse to 1550 nm we excite only one peak. The resulting time response is shown in fig. 5.7 (b), where the beating is replaced by a pure exponential decay with a decay time $\tau = 1050$ fs (the gray curve in the plot is the exponential fit).

Another example of a typical behavior for our samples is depicted in fig. 5.8. The transmission spectrum for the sample R150 is shown in (a). The peak in this case has a transmission less than 1% and it is broad (the FWHM is $\sim 10$ nm). The time response for this peak is plotted in fig. 5.8 (b). The OPAL pulse in this case crosses the sample as it is homogeneous. The transmission peak is too broad. The shape of the time response is more or less gaussian, with a FWHM of 250 fs. The pulse is exactly the cross correlation signal shifted from $t = 0$ by $L_{\text{eff}}/c$. So in this case $\Delta\tau \approx 0$ and the decay time $\tau$ is very fast compared to the one of fig. 5.7 (b).

We can compare the two different temporal behaviors for 1 single peak depicted in fig. 5.7 (b) and in fig. 5.8 (b). In the first case we have a
transmission of 4%, with a FWHM of 2.5 nm. This gives an exponential
time evolution, with $\Delta \tau = 1017$ fs and $\tau = 1050$ fs. In the second case the
transmission peak reaches 0.6%, with a FWHM is 10 nm. This gives a time
response with $\Delta \tau = 0$ fs and $\tau$ below the setup resolution. Both are random
generated microcavities. For a microcavity we can define the cavity quality
factor $Q$, that is

$$Q = \frac{\nu}{\Delta \nu}.$$  \hspace{1cm} (5.23)

For the first case $Q_1 = 620$ while for the second $Q_2 = 150$.

In general for an optical cavity, the electromagnetic field is (see e.g. ref.
[17] for details):

$$E(t) = E_0 \exp \left( -t/2\tau_c + i\omega t \right),$$  \hspace{1cm} (5.24)

where $\tau_c$ is the lifetime of photons in the cavity. If we make the Fourier
transform of $E(t)$, we obtain that the transmission spectrum has a lorentzian
lineshape with a width $\Delta \nu$ equal to

$$\Delta \nu = \frac{1}{2\pi \tau_c}.$$  \hspace{1cm} (5.25)

In time-resolved spectra we measure the intensity of the electric field $I = |E|^2$, so for a cavity we have

$$I(t) = E_0^2 \exp \left( -t/\tau_c \right).$$  \hspace{1cm} (5.26)

This means that the field intensity decays exponentially with a characteristic
time constant $\tau_c$, that is the cavity lifetime. So in our case the measured decay
time $\tau$ is the cavity lifetime $\tau_c$ (see fig. 5.7 (b)).

Fig. 5.9 depicts the transmission peak relative to the time response plotted
in fig. 5.7 (b). The resolution of this measurement is 0.5 nm. The data are
fitted with a lorentzian function, giving $2.2 \pm 1$ nm of width. The agreement
between the fit and the experimental points is not so good because of the
experimental resolution. We can compare the linewidth $\Delta \nu$ obtained from
the fit and the one obtained from the time-resolved spectrum. From the fit
5.4. TIME-RESOLVED MEASUREMENTS

Figure 5.9: Transmission peak for the R200. The time-resolved measurement for this state is shown in fig. 5.7 (b). The resolution of the measurement is 0.5 nm. The agreement between the predicted lorentzian lineshape and experimental data are not so good. The fit gives $\Delta \lambda = 2.2 \pm 1$ nm. The cause is the low resolution of the transmission spectrum.

we have $\Delta \nu = 2.7 \cdot 10^{11}$ Hz ($\Delta \nu = \Delta \lambda (c/\lambda^2)$), while from the decay time $\Delta \nu = 1.5 \cdot 10^{11}$ Hz ($\Delta \nu = 1/2\pi \tau_c$). We can trust time-resolved measurements because in this case the step resolution is 7 fs, that is two orders of magnitude larger than $\tau$; while in the transmission measurement $\Delta \nu$ is of the same order of the setup resolution. So we cannot trust it. This means that from the photon lifetime $\tau = 1050$ fs we expect a transmission peak with $\Delta \lambda = 1.2$ nm. The same considerations on $\tau$ and $\Delta \nu$ for the fig. 5.8 cannot be applied, since the transmission cannot be fitted with a lorentzian function and we cannot estimate $\tau$.

We can conclude the comparison between temporal behaviors for single peaks depicted in fig. 5.7 (b) and in fig. 5.8 (b). For the first case $Q_1 = 1290$ (taking $\Delta \lambda = 1.2$ nm) while for the second $Q_2 = 150$. The first is an example of a “good” cavity, with high $Q$ factor. The second is an example of a “bad” cavity, with a low $Q$ factor.
In summary we have shown in this section three examples that characterize the time response for random multilayers.

- **Oscillations**: They are present when the OPAL excite two cavities. They are caused by beatings between the two states.

- **High $Q$ cavity**: Strong delay time $\Delta \tau$ and slow exponential decay.

- **Low $Q$ cavity**: Delay time $\Delta \tau \sim 0$ and no exponential decay.

Obviously there are also cases that lay in between. Moreover the time-resolved spectra very often show oscillations behavior, because of the spectral width of the laser used. Beyond these features, another one very interesting was found that enriches these random systems. It is the presence of *necklace states*.

### 5.5 Necklace states

A 1D random system has in general localized states, that are random generated microcavities. They can be cavities with a low $Q$-value or with a high $Q$-value. They are localized states because at those wavelengths the electromagnetic field is trapped in a finite region inside the system, they do not extend over the whole system. Averaging over all the possible realization of the disorder, at a fixed wavelength, the transmission decays exponentially increasing the sample thickness. We have demonstrated that, for our porous silicon random multilayer systems, the localization length is $14 \pm 4 \, \mu m$.

The localized states are not the main contribution to the total transmission of a disordered system, as one can think. Pendry showed in ref. [14] that the average transmission (means over all possible disorder realizations) is dominated by few rare events called *necklace states*. A necklace state is not a localized state, but it extends over the whole length of the sample. A necklace of order $N$ consists of a series of $N$ internal resonances, slightly shifted in frequency but overlapping. If we look at the intensity of the electromagnetic field inside the system, we find that it decays exponentially for a single resonance, while for a necklace is distributed. The other feature that makes us
distinguish between a single cavity and a necklace is the phase of the electromagnetic field. For a single resonance we observe a jump in the phase of $\pi$, while for necklace state of order $N$ we have a jump of $N\pi$. In transmission a necklace will tend to be a broad gaussian, since it is a superposition of $N$ lorentzians slightly shifted [14].

5.5.1 Artificial necklace states

To understand better the disordered case we have to start from the more simple ordered case. We can use transfer matrices to perform computer simulations. Let’s start with the simple analysis for a single microcavity. The microcavity structure is shown in fig. 5.1. We can have cavities with high $Q$-value, if the cavity is centered in the structure, or cavities with low $Q$-value, if the cavity is near the edges of the structure. The Fourier transform for these two cases is plotted in fig. 5.10. As discussed in section 5.4.2 the high $Q$ cavity has large delay time and slow exponential decay, while low $Q$ cavity has small delay time and a very fast decay. A necklace state is expected to have a very fast decay since it is not a localized state, but a very large $\Delta \tau$; the photons before exit from the system have to rebound from one resonance to the other.

It is instructive to compare a necklace of order $N$ with an ordered system with $N$ degenerate resonances. Information obtained for the temporal response of these artificial necklaces can be useful for the interpretation of time-resolved data on disordered samples.

An example of such an artificial necklace state is shown in fig. 5.11(a), where the scattering states map shows the intensity of the electric field $|E|^2$ in the sample. Six degenerate peaks are present (centered around 1500 nm). The sequence used for the simulation is (4.5 DBR)AA(11.5 DBR)AA(11.5 DBR)....AA (4.5 DBR)$^5$.

$^5$11.5 and 4.5 are the numbers of periods of the DBR. One period is formed by AB.
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Figure 5.10: Fourier transform for the transmission spectra of a high Q microcavity, that has a strong delay $\Delta \tau$ and a slow decay time $\tau$, and for a low Q cavity, which possesses a very fast $\tau$ and $\Delta \tau \to 0$.

Figure 5.11: (a): Scattering map of six degenerate resonances that represent an artificial necklace state. The structure used for the simulation is: $(4.5 \text{ DBR})AA(11.5 \text{ DBR})AA(11.5 \text{ DBR}....AA(4.5 \text{ DBR}))$. (b): The transmission of an artificial necklace of order 6 compared with a single cavity. For the single cavity the lineshape is lorentzian, while for a necklace tends to be gaussian with a high transmission value.
The peculiarity of this sequence of layers is the presence of the two 4.5 DBRs at the beginning and the end of the sample. They allow a good coupling for the incoming and for the exit electromagnetic radiation. If we choose for these two mirrors a period of 11.5 (as for internal DBRs), we obtain a coupled microcavities structure. In this case the resonances are not degenerate but are spitted [10].

In fig. 5.11 (b) the transmission for an artificial necklace of order 6 is compared with the transmission of a single cavity. For a single microcavity the lineshape is lorentzian, while for a necklace it tends to a gaussian, since a necklace is a superposition of lorentzians. The necklace transmission is near to 1 and it is broad with respect to a single state. In transmission an artificial necklace is broad like a low \(Q\)-value cavity, while has a transmission value near to 1 as happens for high \(Q\)-value resonances.

We can simulate the time evolution of a short laser pulse crossing an artificial necklace state. The results of the simulation are plotted in fig. 5.12. In (a) \(\Delta \tau\) is plotted in function of the number resonances present in the sample. We find that the center of mass of the pulse \(\Delta \tau\) is greatly delayed when the number of degenerate resonances are increased. In fig. 5.12 (b) the transmission of an artificial necklace shows a round tip. It is smoothed because is due to a superposition of three resonances. In fig. 5.12 (c) the Fourier transform of the transmitted peak is plotted. We can observe that the decay is very fast.

The artificial necklace is characterized by two main features in the time response:

- Fast decay time \(\tau\). The decay has not exponential behavior as for a low \(Q\) cavity.
- Strong delay for the center of mass. \(\Delta \tau\) increases roughly linearly when the number of resonances increases.

Necklace states are very interesting in random samples, because they contribute dominantly to the total transmission. But the interest for artificial necklaces is limited, because they can be seen as a particular realization of coupled microcavities.
5.5.2 Measured necklace states

To find necklace states for our random sample, we can see if in transmission we obtain a high and broad peak. In our case this is not so obvious because the porous silicon random multilayer suffer from natural drift in the refractive index and from scattering losses. Both reduce the transmission and increase the peaks widths. In time-resolved measurements the things are more simple. If we measure a single peak with a time-resolved spectra with strong delay time and with a very fast decay, as in fig. 5.12 (c), perhaps we have found a
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necklace state.

Figure 5.13: (a): Transmission for the sample R350 around 1570 nm. In the time domain we observe a single peak that has a time response characterized by a strong delay time of 488 fs and by a non exponential decay. (b): Transmission for the sample R250 around 1520 nm. The time-resolved experiment gives a profile that has $\Delta \tau = 388$ fs and no exponential decay. For both peaks the time response is a signature that we are measuring necklace states of order 2 or 3 at maximum.

Fig. 5.13 shows time-resolved and transmission measurements for two peaks for R250 and R350. From transmission measurements we can observe that the lineshape is neither lorentzian nor gaussian. If we zoom over the transmission peaks for each studied sample, it is not so easy to find pure lorentzian peaks. We find usually strange lineshapes. The two transmission peaks in fig. 5.13 are typical for our systems.

The time-resolved measurements show interesting features. First the center
of mass is enough delayed (if we compare it to a low $Q$ microcavity) reaching $\sim 500$ fs and moreover the decay is very fast and not exponential. These two peaks have the main features that characterize necklace states. Only these two peaks have such temporal behavior among all analyzed. We have studied 14 single peaks for 7 samples from R150 to R350 (we had two samples with 200 and 300 layers).

Surely these two peaks are not single resonances, but we do not know from how many resonances they are formed. In fig. 5.12 we calculated for artificial necklace states: $\Delta \tau = 850$ fs for a necklace of order 2 and $\Delta \tau = 1480$ fs for a necklace of order 3. So for the moment we can suppose that our states in R250 and R350 are formed by two or at maximum by three resonances.

5.5.3 Numerical analysis on the R250 sample

One-dimensional systems have the great advantage that the electric field distribution in the sample can be calculated exactly for a given sample realization. Here we focus our attention on the sample R250, in which we seem to observe signs of necklace states. We have to note that we cannot obtain a perfect one-to-one mapping of each layer in the experiment and simulation, because of the experimental samples have a natural drift in the optical thickness and scattering losses. Including both these parameters, it is difficult to simulate our structures exactly. So we perform simulations for an ideal structure.

Fig. 5.14 shows the simulation for the sample R250. In (a) the scattering states map is depicted, while in (b) we have the transmission of the sample. Since the sample is considered ideal, we can reach a transmission near to one. Note that the peaks that have a high transmission value are the ones that resonate in the center of the sample.

We can simulate the structure in a restricted wavelength region as depicted in fig. 5.15. In (a) the scattering states map evidences two high transmission peaks, the first centered around $\lambda = 1012$ nm and the second around $\lambda = 1023$ nm. At first sight the one at 1023 nm seems to be a single cavity, while the one at 1012 nm is formed by two non degenerate resonances with different $\lambda$
values and can be a candidate for a necklace state.

We can than compare these two peaks by taking the Fourier transform of the spectrum (including the phase). The result of the Fourier transform is plotted in fig. 5.15. In (b) the time response for the peak at 1012 nm shows a decay that is not exponential, and it is similar to our measurements presented in fig. 5.13 (b). There is a strong delay, but no exponential decay. Fig. 5.15 (c) shows a temporal behavior that decays exponentially, with a time constant of 1640 fs. From the scattering map and the time-resolved spectrum we can say that the peak at 1023 nm is a single resonance. If we analyze how the phase of the electromagnetic field changes for these two states we observe a jump of π for the single cavity while for the other a jump of 2π. It means that the peak at 1012 nm is a necklace state of order 2.

The simulated necklace state for R250 has a $\Delta \tau = 850$ fs, while the measured one only $\Delta \tau = 388$ fs. Except for this fact the time responses look very similar. We can presume that our necklace states are formed by two resonances, since necklace states of higher order will be characterized by a larger delay time. To measure exactly the order of a necklace state we need a time-resolved setup that allows us to measure also the phase, but here we
Figure 5.15: (a): Zoomed scattering map for R250. Two high transmission peaks are present. (b): Fourier transform for the peak at 1012 nm. Fast decay and a delayed center of mass are the signature of the necklace nature of this peak. The scattering map reveals that this peak is formed by two resonances slightly shifted. (c): Time response of the peak around 1023 nm. The Fourier transform indicates that it is a single resonance.

want only to point out the presence of a necklace and its main properties.

### 5.5.4 The probability to find a necklace state

To confirm that the time responses of fig. 5.13 are relative to necklace states of order 2, we have to make an estimate regarding the probability that a random sample could have necklace states. We are interested to have an order of magnitude for the probability that confirms that the chance to obtain a necklace is not so improbable.

A necklace state of order $N$ is a state where $N$ single resonances are overlapped within their spectral width. We can suppose that our systems have a constant density of peaks $\eta/B$, where $\eta$ is the number of resonances in a spectral interval $B$. If $\Delta\lambda_N$ is the width of a peak formed by $N$ resonances,
the probability for a single resonance to become a necklace of order \( N \) will be:

\[
P_N = (\Delta \lambda_N \eta B)^{N-1}.
\] (5.27)

We are interested on the case where \( N = 2 \). From fig. 5.13 we can estimate the bandwidth of the transmission peaks relative to necklace states and from fig. 5.3 we obtain the value for \( \eta/B \). Considering the sample R250 we have: \( \Delta \lambda_2 = 6 \) nm and \( \eta/B = 20/1000 \) nm\(^{-1} \), so \( P_{2,\text{exp.}250} = 12\% \). From the simulation of the R250 (no drift and no scattering losses) we have a width for the transmission peak of 2 nm and \( \eta/B = 30/1000 \) nm\(^{-1} \), this gives a \( P_{2,\text{th.}250} = 6\% \). The theoretical necklace and the experimental one have a probability to exist that is of the same order of magnitude. For the R250 the time-resolved measurements were performed on 4 single peak and one was a necklace state. Even if we do not have enough peaks to make a statistical analysis a probability of 12\% give us the feeling that the time response of fig. 5.13 (b) is relative to a necklace of order 2. Regarding the R350 sample the transmission of the peak in fig. 5.13 (a) gives \( \Delta \lambda_2 = 3 \) nm and \( \eta/B = 19/1000 \) nm\(^{-1} \). So \( P_{2,\text{exp.}350} = 6\% \).

Necklace states with \( N \geq 3 \) will be more and more improbable because of equation 5.27. In summary the measured time-resolved spectra for R250 and R350 can be considered due to necklace states, since the probability to find a necklace of order 2 is not so small.

5.6 1D random laser action

Random multilayers made of porous silicon can be used also to study the random laser action in one dimension. Since our samples have a localization length \( \sim 16 \) \( \mu \)m, we expect to make lase localized states. The first step to obtain a 1D random laser is to add optical gain to our samples. The simplest way is to infiltrate them using a laser dye dissolved in a solvent. Since the pores of porous silicon range from 50-100 nm, we can be confident about the infiltration.
Random laser action in localized regime for 1D and 2D systems was studied theoretically in last years. Using finite difference time domain analysis, one can see that localized random lasers are formed by random cavities, with different $Q$ values. Increasing the pump energy the random laser goes above threshold, exhibiting a modes competition. Due to different values of $Q$ one laser mode can be amplified more than the others [18, 19]. Note that necklace states have a low $Q$ factor compared with the one of localized states. So they are not expected to lase.

The modes competition for 1D random laser can be studied also using transfer matrices. It is necessary to add a gain coefficient $k_g$ to the phase shift $\delta$ present in the matrix of eq. 5.5. For the sample R300, we can compare the emission spectrum in function of the gain value once we fixed the pump energy. Fig. 5.16 depicts this comparison. The gray curve shows the emission for $k_g = 0.5 \, \text{cm}^{-1}$, while the black curve the emission when $k_g = 50 \, \text{cm}^{-1}$, both normalized to 1. If we look at the heights of peaks around 1040 nm and 1080 nm, the modes competition effect is well visible. The peak at 1040 nm is amplified for low and high gain coefficient. The mode at 1080 is suppressed.

For the experiment we used Styril9 as laser dye (fluorescence centered at 820 nm) and for the solvent ethylene glycol. The dye concentration was 3 mmol/l. The mixture was infiltrated in random samples. It took 10 minutes for the infiltration to occur. We choose ethylene glycol because we needed a solvent that did not evaporate during the measurements. The setup used to collect the emission from this 1D random laser was the same for the PDLC experiment of fig 4.7.

The emission spectra for the R300 infiltrated with Styril9 are shown in fig. 5.17 (a). The pump energy goes from 10 $\mu$J to 63 $\mu$J and the spot size for the pump laser was 1.0 mm. The spectra are characterized by two main peaks at 810 nm and 831 nm. Each of them is formed by other small peaks. Between the two main peaks, one at 822 nm is also visible. From fig. 5.17 (a), at a first sight, we can argue that no modes competition happens for R300. On the contrary analyzing the intensity of each peak in function of the pump energy
5.6. 1D RANDOM LASER ACTION

Figure 5.16: *Transfer matrix simulation of emitted spectra from R300 at which gain was added. Only some modes are amplified for high gain coefficient $k_g$ with respect to the low gain coefficient case. This effect is called modes competition.*

we find something interesting. Fig. 5.17 (b) shows the intensity evolution for some peaks. The modes at 810 nm and at 795 nm for low pump energy are very close, while increasing the energy they are more separated. For the peaks at 769 nm and at 831 nm the same behavior is measured, but in this case it is more pronounced. For the last two modes analyzed in fig. 5.17 (b), we observe that the peak at 822 nm beats the one at 856 nm.

The modes competition is not so pronounced because our system is always below threshold, because of the presence of channels of losses and absorption in our samples. We know that our systems has a losses coefficient $\alpha = 140$ cm$^{-1}$ (see section 5.2). At 800 nm we have also to consider the absorption of the porous silicon. Measurements of absorption at 800 nm gives a coefficient $\alpha_{abs} = 200$ cm$^{-1}$ [13]. So the total coefficient will be $\alpha_{tot} = 340$ cm$^{-1}$. The gain coefficient in our case is $k_g = n\sigma_{em}$ (see section 4.1.4). For Styri9 $\sigma_{em} = 5 \cdot 10^{-21}$ m$^2$ and hence $k_g = 100$ cm$^{-1}$. $\alpha_{tot} > k_g$ which means that the losses overcome the gain.
Figure 5.17: (a): Measured emitted spectra for R300 infiltrated with Styril9 laser dye. The maximum pump energy is 63 $\mu$J, above which the sample results damaged. (b): Modes competition effect for some emission peaks. Note that the peak at 822 nm beats the one at 856 nm. The effect is not so pronounced as in the simulations because our sample is below threshold.
To solve the problem we can think about two solutions:

- Increase the concentration of dye particles. 3 mmol/l is the maximum concentration, since if we add more dye particles they do not solve in ethylene glycol. To obtain \( k_g = \alpha_{tot} \) we need a dye concentration of \( \approx 10 \text{ mmol/l} \). For this particular dye we tried also other solvents, such as methanol, ethanol; but we did not succeed.

- Change the laser dye. We try also with IR26 laser dye (emission spectrum around 1200 nm) but without appreciable results. The quantum efficiency of this dye and in general of infrared dyes is low compared with the efficiency of visible dyes. In this way we avoid absorption, but scattering losses are always present.

A possible solution of the problem can stay in using Erbium implantation instead of laser dye infiltration. \( \text{Er}^{+3} \) emits around 1500 nm and can solve the problem of the absorption but not the one connected to scattering and drift losses.

In conclusion our measurements indicate very interesting effects for a 1D random laser but due to porous silicon and to the solubility of laser dye, our systems do not exhibit a strong modes competition effect, as we expected from fig. 5.16.
Bibliography


Chapter 6

Conclusions

The tunability of photonic systems using liquid crystals was studied in both ordered and disordered cases. The two external parameters that change the scattering proprieties of nematic liquid crystals are the temperature and an external field (can be electric or magnetic). The temperature tuning uses the nematic-isotropic phase transition to make liquid crystals go from an uniaxial to a standard liquid. For an opal photonic crystal it gives the chance to change modestly the dielectric contrast and hence the density of states of the system. For a PDLC random laser the nematic-isotropic phase transition has a more important consequence. The random laser can be switched on and off using the temperature tuning.

Pronounced effects over the transport of light in photonic crystals and in random lasers are present when we consider the field application. For photonic crystals theoretical predictions say that the band gap can be shifted in frequency using the birefringency of liquid crystals. But this is strongly suppressed by the interplay between nematics and the surface of the spheres in which liquid crystals are confined. To tune the band gap by an external field the surface anchoring strength has to be overcame. When the system considered is a PDLC, the droplets mean radius is enough large (≈ 1 µm) for considering negligible the surface anchoring effect. When an external electric field is applied, the emitted light from a PDLC random laser becomes extraor-
ordinary polarized and spatially anisotropic. Moreover, the light diffusion does not take place in three dimensions but we observe a change of its dimensionality, yielding a quasi-two-dimensional random laser action. A 2D random laser is a very promising system since it is transparent in one direction, allowing the pump power to be completely absorbed and also presents a strongly extraordinary polarized emission.

Reducing the dimensionality of the light scattering to one dimension, the light transport is not so trivial to be studied. For a disordered 1D system the localization length is always finite. Such systems possess localized states but also another type of states that contribute dominantly to the resistance of a random sample. The latter are necklace states and are formed by a number $N$ of non degenerate resonances. These states are very interesting for a random 1D system since they are not localized. A necklace state has a time response characterized by a strong delayed center of mass of the pulse and by a fast decay time. The electromagnetic field rebounds from one resonance to the other and this causes strong pulse delay. A necklace state is not localized and so decay is very fast. The probability to find a necklace state is exponential with the power of $N - 1$, so necklace with an high order are very rare, but, higher is the order, larger will be the contribution to the total resistance of the system. Obviously necklace states do not contribute to the random laser action since the cavity quality factor is very small with respect to localized states.
È sempre difficile ringraziare qualcuno e in particolare non so proprio da che parte iniziare. Forse la cosa migliore è seguire un filo cronologico.

Tornando indietro a tre anni fa, quando il Prof. Colocci mi disse che era disponibile un progetto di ricerca sui cristalli fotonici, ne rimasi molto entusiasta. Giustamente me li presentò come l’analogo ottico dei semiconduttori e per me che avevo svolto una tesi su quantum wells di GaN mi sembrò molto sorprendente tale analogia. In questi tre anni di dottorato sono stato seguito dal Dr. Diederik Wiersma, che mi ha trasmesso tanto entusiasmo e anche tantissime conoscenze sui sistemi ordinati e disordinati e mi ha fatto giustamente notare come questi due mondi non sono così distanti, come si può pensare a prima vista.

Per quanto riguarda i miei colleghi e compagni di avventura vorrei ringraziare in particolare il quasi Dr. Riccardo Sapienza, con il quale mi sono particolarmente divertito in laboratorio, la quasi dott. Paola Costantino e il mio primo studente Jacopo Bertolotti. A questo punto la lista si allunga di molto se dovessi citare tutti quelli che lavorano al LENS e quindi vorrei chiudere con il ringraziare il Dr. Sushil Mujumdar per i suoi insegnamenti sui random lasers e sui lucky photons.

Infine, per quel che concerne la sfera privata, all’appello mancano ovviamente i miei genitori e la mia ragazza Valeria, che mi hanno sempre sostenuto e spero mi sosterranno anche nel prossimo futuro.