Structure and fluorescence of photonic colloidal crystals

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1 Introduction

1.1 Spontaneous emission

It is now commonly accepted that spontaneous emission is not an immutable property of the emitter, but it depends on the density of modes of the light field at the location of the emitter. This dependence was originally noted by Purcell and it is embodied in Fermi's Golden Rule. According to the Golden Rule, the rate of emission can be interpreted as the product of the square of the transition matrix element with the density of states. In this picture, the transition dipole moment of the emitter couples to the zero-point fluctuations of the electric field. The change in spontaneous emission can also be understood semiclassically, as an impedance of the surrounding medium or as a back action of the environment on the emitter. Experimentally, the influence of the density of modes was first demonstrated by Drexhage in 1966, in his measurements of the excited state lifetime of europium ions at various distances from a metallic mirror. More recently, the field of quantum optics has witnessed a flourishing of sophisticated experiments, demonstrating that the spontaneous emission rate can be enhanced or reduced with respect to vacuum by placing emitters in a high-quality resonant or non-resonant cavity, respectively. For light, currently no more than partial suppression is achieved (lifetimes extended by up to a factor of 2 in refs. 3, 7), in small volumes, and in a narrow wavelength range. Photonic crystals promise the complete suppression of spontaneous emission over extended spatial volumes and large bandwidths.

1.2 Photonic crystals

Photonic crystals are three-dimensional periodic dielectric structures in which the refractive index varies on lengths of the order of the wavelength of light. The propagation of light in such photonic materials is analogous to the well-known wave-like propagation of electrons in crystalline solids. The periodic structure gives
rise to Bragg diffraction, that is associated with stop bands for propagation in certain directions. If the light is very strongly coupled to the crystal, a photonic band gap is expected, a frequency band in which no light can propagate through the crystal in any direction. One of the most important consequences of photonic band gaps is that spontaneous emission of excited atoms with a transition frequency in the gap is inhibited.\textsuperscript{9,15} This inhibition of emission is expected to lead to novel phenomena in optics and quantum optics\textsuperscript{9,12} and may serve as the basis for lasers without threshold\textsuperscript{16} and highly efficient light emitting diodes.\textsuperscript{17}

### 1.3 Photonic band structure

In Fig. 1.1 we show the dispersion relation, the relation between the wavevector $k$ and the frequency $\omega$, both of a homogeneous medium and of a photonic crystal. In the homogeneous medium, the optical modes are plane waves with a linear dispersion relation, the straight lines $\omega = ck$. In analogy with the electron wave-functions in a crystalline solid, the optical modes in a periodic material are Bloch waves, functions that have the periodicity of the lattice with an additional phase factor $\exp(ik \cdot r)$.\textsuperscript{13,14} Periodic structures can diffract a wave, changing the wavevector by a reciprocal lattice vector; the dispersion relation of the diffracted wave is indicated by the straight line dispersion relation that is shifted by a reciprocal lattice vector $G$. The two waves correspond to an incident and a reflected wave. The straight lines intersect at the edge of the Brillouin zone. In photonic crystals, the variation of the refractive index causes splittings at the edge of the Brillouin zone,
Bragg reflection occurs when light reflected from a set of lattice planes interferes constructively; the extra path length indicated by the thick line equals an integral number of wavelengths.

producing bands separated by stop gaps. Bloch waves with frequencies in the bands resemble normal plane waves. Toward the edge of a band, the Bloch waves become standing waves. The nodes of the low frequency mode occur predominantly in the high refractive index material, the modes of the high frequency mode occur in the low refractive index material. Waves with frequencies within the stop gaps are Bragg reflected and cannot propagate through the crystal.

1.4 Bragg reflection

Bragg reflection plays a prominent role in optical experiments on photonic crystals. It occurs whenever there is constructive interference of waves reflected from a set of lattice planes, as illustrated in Fig. 1.2. The reflection appears only for specific wavelengths $\lambda$ and angles $\theta$, given by Bragg’s law $2d \sin \theta = n\lambda$, where $d$ is the distance between lattice planes and the integer $n$ is the order of Bragg reflection. If a crystal is sufficiently well-ordered that the reflections from many lattice planes interfere constructively, then the Bragg reflection will be very strong, close to 100%. The associated extinction will be very large, increasing exponentially with sample thickness. Light cannot propagate in the direction of a Bragg reflection: the Bragg reflections correspond to the stop gaps in the photonic band structure.

If light is strongly diffracted by the scatterers, then a small number of lattice planes suffice to reflect an incident wave. The wavelength $\lambda$ and angle $\theta$ then do not need to conform to Bragg’s law exactly: the interference still will be constructive for the limited number of lattice planes involved. As a consequence, the Bragg reflections extend over a range of frequencies, corresponding to the width of the stop gaps.
Figure 1.3  Dispersion surface at fixed frequency according to dynamical diffraction theory, in a photonic crystal (—) and in a homogeneous medium (⋯). The arrows indicate the angular width of the stop gap (shaded). The photonic strength $\Psi$ is 0.15. Only perpendicular polarization is shown.

1.5 Dynamical diffraction

If the interaction between light and a photonic crystal is very strong, the stop gaps in all directions will overlap, creating a band gap. Spontaneous emission at frequencies within a band gap will be inhibited. If the interaction is not so strong, then the stop gaps will cover only part of the available directions for emission, as indicated in Fig. 1.3. The modification of the spontaneous emission rate will be proportionally smaller.

A clear illustration of the connection between the stop gaps and the spontaneous emission rate is provided by dynamical diffraction theory (as opposed to kinematical diffraction, ordinary Bragg reflection). The theory considers reflections at a fixed wavelength. In free space, the wavevector $k$ traces out a sphere of radius $k = \omega/c$ at fixed frequency. The intersection of this sphere with a plane is shown in Fig. 1.3 as a circle. The dynamical diffraction theory usually considers two such circles, corresponding to the incident and the reflected wave. The centers of the circles are one reciprocal lattice vector $G$ apart. At the intersection of the spheres the dispersion curves split, due to the interaction between the waves. The splitting produces a stop gap, like in Fig. 1.1, but as a function of diffraction angle instead of frequency. The stop gaps cover only a small range of directions, unless the light is very strongly coupled to the photonic crystal.
One would expect that light emitted in the direction of a stop gap is attenuated, whereas the light can propagate perfectly well in other directions. This propagating light is observed outside the crystal, as we show in chapter 5. Contrary to expectations, light is observed to emerge also in the direction of the stop gaps. This light originates from emission in the other directions. The emitted light is scattered in the direction of stop gaps by a small concentration of defects that always occur in any crystal. As a result, light is observed even in the direction of stop gaps. In the presence of a photonic band gap, the scattered light is strongly attenuated because the stop gaps extend over all directions. Thus the spectrum of sources inside photonic crystals reveals unambiguously whether a photonic band gap has been achieved. Furthermore, the scattering relates the photonic crystals to the disordered photonic materials: the periodic structure of a photonic crystal could facilitate the localization of light, vigorously pursued in multiply scattering media.

1.6 Photonic strength

The interaction strength between light and a photonic crystal can be conveniently expressed by a parameter $\Psi$ defined as the ratio of the optical volume per particle – the polarizability $4\pi\alpha$ – to the physical volume per particle $V$. This concept of photonic strength applies both for dielectric media and for atoms in optical lattices. For dielectrics, the spatial variation of the refractive index appears in the polarizability $4\pi\alpha$ via the ratio $m$ of the refractive indices of the particles and the surrounding medium. As an illustration we have plotted this photonic strength $\Psi$ for polystyrene and silica spheres in water as a function of filling fraction $\phi$ in Fig. 1.4. In the same plot, we also show the width of the lowest stop gap obtained from numerical band structure calculations. It turns out that the photonic strength $\Psi$ closely approximates the stop gap width. This supports the merit of $\Psi$ as a measure of the strength of interaction between light and a crystal.

The coupling strength $\Psi$ between light and photonic crystals has a clear optimum as a function of the volume fraction $\phi$ occupied by the spheres. With increasing volume fraction, the coupling first increases because of the increasing size of the scatterers; at higher volume fractions it decreases because the crystal scatters less efficiently. At high sphere densities the roles of the spheres and the liquid are reversed: the light is diffracted by the liquid in between the spheres and the spheres act as background medium. To illustrate this, we have also plotted the photonic strength parameter $\Psi$ with an inverted refractive index ratio in Fig. 1.4. This photonic strength more closely approximates the numerically obtained widths at high densities.
1.7 Making photonic crystals

Yablonovitch was the first to demonstrate the feasibility of creating a photonic band gap for microwaves, using a structure of drilled holes.\textsuperscript{9,23} Although disputed at first,\textsuperscript{24,25} the existence of microwave band gaps is now firmly established. Yablonovitch suggested to use the same approach to create a photonic band gap for visible light. Indeed photonic structures have been realized for far infrared wavelengths, by etching instead of drilling the holes,\textsuperscript{26} but the etching technique is not readily extended to submicron length scales; current nanotechnology focuses mainly on patterning two-dimensional surfaces rather than making three-dimensional structures.\textsuperscript{27} Nevertheless, heroic attempts have been made to create three-dimensional crystals by etching. The largest structure to date measures 16 stacked two-dimensional layers comprising one unit cell.\textsuperscript{28} Creating large three-dimensional regular structures of dielectric scatterers with wavelength size has proven to be a major technological challenge. Our approach is to use self-organizing colloidal suspensions of small spheres.

![Figure 1.4](image)

**Figure 1.4** Photonic strength parameter $\Psi$ (---) and relative (111) stop gap width $\Delta\omega/\omega$ (---) as a function of density, for fcc lattices of polystyrene or silica spheres in water (refractive index contrast $m = 1.59/1.33 = 1.20$ and $m = 1.45/1.33 = 1.09$). The photonic strength is obtained using $m$ at low densities and $1/m$ at high densities. The stop gap widths result from numerical band structure calculations.
1.8 Colloidal crystals

Colloids are very suitable to realize photonic materials since they naturally possess the right size and spontaneously form bulk three-dimensional crystals. The periodicity of the material makes Bragg reflections appear as a beautiful iridescence. Colloidal crystals can be produced artificially, but they also occur naturally. A familiar example is the precious gem opal, which consists of silicate particles. An example of such a crystal is shown in Fig. 1.5.

It is crucial to know the structure of self-organizing photonic colloidal crystals, since their optical properties are intimately connected to the crystal structure. For dilute or index matched colloids, the crystal structure is accurately known, but not for dense colloids with strong refractive index variations, desirable for photonic crystals. The strong interaction between photonic crystals and light causes multiple scattering which hampers structure determination by light scattering or other optical methods. Therefore, we have performed a synchrotron small angle x-ray scattering study, see chapters 7 and 8. We observe large numbers of x-ray Bragg diffraction peaks of photonic colloidal single crystals. The colloidal particles order in face centered cubic (fcc) structures, with a high degree of localization about their lattice sites. This is an excellent starting point for photonic band gap crystals. These results have both encouraged the search for materials with a full photonic band gap based on colloids, and they have stimulated interest in x-ray diffraction as a tool for colloid research.
Colloidal spheres can be doped with fluorescent dye molecules\textsuperscript{32,33} to observe the influence of photonic band structure on the spontaneous emission. Fluorescent dyes are very suitable because of their high quantum efficiency and ease of excitation. Fluorescent dye molecules are sensitive not only to the photonic band structure however; they are also affected by chemical interactions with their environment\textsuperscript{34} and they influence each other directly via nonradiative electromagnetic interactions when they are close together, see chapter 3. In the study of spontaneous emission in photonic crystals, these interactions are intolerable so low dye concentrations and appropriate shielding of the dye molecules are essential.

We have specially prepared silica spheres with a suitably low dye content to study photonic effects. From these colloidal spheres, we have grown crystals with wide stop bands. The stop gaps extend over $\sim 15$ nm in wavelength, a substantial part of the dye’s emission spectrum. The crystals have dimensions up to 0.5 mm, so they affect the density of modes over an extended spatial volume. The screened Coulomb interaction of our charged spheres provides considerable flexibility: the density of the crystals can be tuned via the ionic strength of the suspending liquid. The crystal densities are optimal from a photonic point of view, see Fig. 1.4, and the stop gaps in the photonic band structure overlap with the dye's emission spectrum.

1.9 The optimal photonic crystal

The strength of the interaction between light and a photonic crystal depends critically on the relative spatial variation of the refractive index. Creating a complete photonic band gap requires both a sufficiently large refractive index contrast $m$, a suitable crystal structure, and an optimal filling fraction, see Fig. 1.4. Initially the fcc crystal structure was considered the best candidate, since this structure has the most spherical Brillouin zone.\textsuperscript{9,23} However, it turned out that for spherical scatterers on an fcc lattice there is no band gap between the lowest bands due to a polarization degeneracy. Early theoretical investigations considered only scalar waves. Light has a polarization however, so one should consider vector waves for accurate photonic band structure calculations. It turns out that creating a band gap for vector waves is much more challenging than for scalar waves.\textsuperscript{23,35} Calculations for a fcc lattice of spherical scatterers indicate that a band gap will open up between the 8th and the 9th branch of the dispersion relation for refractive index ratios $m > 2.9$.\textsuperscript{31,36} The optimal filling depends on the refractive index contrast. As a rule of thumb, the optical path lengths in the high and low index materials should be equal, to enhance interference. As a consequence, a proportionately lower density of high index material is favorable.

Very recently a new class of strongly photonic crystals has been developed,\textsuperscript{37,38}
having the appropriate density of high index material and a favorable connected structure. The crystals are made by filling the voids in an artificial opal with a solid of high refractive index and subsequently removing the opal. In this way, crystals of air spheres in titania (TiO$_2$) could be synthesized. These three-dimensional crystals currently hold the record of the strongest photonic interaction, almost forming a band gap. The fabrication technique is rapidly becoming the method of choice for the synthesis of strongly photonic crystals, as it holds great promise for the near future. Experiments are underway to make air-sphere crystals of semiconductors, with a refractive index of more than 3, which would open up a full photonic band gap at optical frequencies.

References


