Investigating Naturally Occurring 3-Dimensional Photonic Crystals

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I certify that all material in this thesis which is not my own work has been identified and that no material has previously been submitted and approved for the award of a degree by this or any other University.

Caroline Pouya
2012
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Abstract

This thesis describes my research into the highly tuned naturally occurring 3D photonic structures that are present on a selection of insects. The experimental and theoretical work presented in this thesis was performed in both the optical and microwave regimes.

The work performed in the optical regime included both the geometric and optical characterisation of the native photonic structures present on the beetle Eupholus magnificus and the butterfly Parides sesostris. The native photonic structures of these organisms were probed in order to determine their photonic responses and also to ascertain their geometries and structural classes. In cases where the geometry of a photonic crystal system has been determined, I have performed additional theoretical analysis of the structure to establish how it might be optimised for a particular optical function. The overall aim of the work performed in the optical regime is to further the understanding of the photonic structural designs present on a selection of beetles and butterflies, by both identifying and characterising their underlying structural geometries and consequent photonic responses.

Eupholus magnificus is a species of weevil that produces its coloured appearance from photonic structures that are present on its outer wing casing, producing a striped coloured pattern. The photonic structures that I discovered were present on this weevil were found to be contrasting in structural order. I used a wide-ranging variety of experimental and theoretical techniques in order to perform an extensive electromagnetic and structural characterisation of these contrasting structures. The two contrasting photonic mechanisms employed by E. magnificus were found to produce a similar optical response in terms of angle-independent colour whilst reflecting different coloured hues.

Parides sesostris is a species of butterfly that uses a gyroid photonic crystal structure, contained within scales, to produce green coloured patches on the dorsal side of its wings. In addition to this, P. sesostris uses embellishments to its scale morphology in order to produce a highly tuned
angle-independent optical response. The optical effects brought about by these structural embellishments were investigated with optical experimental techniques and they were found to diffusely scatter light and aid iridescence suppression. In addition to this, theoretical modelling was performed on a variety of gyroid geometries. The gyroid photonic structure found in the wing scales of *P. sesostris* was determined to be highly optimised to reflect the largest range of frequencies possible from this geometry, also aiding iridescence suppression. In addition to this, the arrangement of gyroid arrays within each scale was determined to produce the highest intensity possible by using the smallest possible number of unit cells.

In addition to the optical characterisations of the organic naturally occurring photonic structures found on these organisms, I also synthetically replicated the three fundamental naturally occurring triply periodic bicontinuous cubic photonic crystal structures for experimental and theoretical electromagnetic characterisation in the microwave regime. The microwave regime was selected to perform the characterisation as a high-resolution fabrication method can be employed in order to produce millimetre-scale structures, suitable for probing in this wavelength regime. A high resolution fabrication method is an absolute requirement for accurately replicating the complex geometries of constant mean curvature structures and retaining a high level of detail. I have electromagnetically characterised these three structures with the aim of gaining a better understanding of their polarisation-dependent photonic stop-band responses. Specifically, I have identified the origin of, and the dispersion of, photonic stop-bands produced by each unique structural geometry. I have principally focused on the characterisation of the electromagnetic responses of these structures, how they differ from each other and also why a linear polarisation dependence arises from these 3D photonic structures. In addition to this I have related the electromagnetic responses of these structures to analogous optical structures that naturally occur on the wings of the butterfly *P. sesostris* and elytra of the weevil *E. magnificus*. With this I aimed to gain a better understanding of the origin of the optical effects they provide the host biological system. This includes the characterisation of the gyroid photonic crystal structures, chosen to mimic that found in *P. sesostris* wing scales. The results from this were also subsequently used in the optical optimisation examination performed on the *P. sesostris* gyroid.

Finally, I have investigated a dynamic aspect of the 3D gyroid photonic crys-
tal, formed from a constant mean curvature surface. A compliant gyroid structure was fabricated for analysis in the microwave regime and a systematic compression force applied to it. I have measured the electromagnetic response of this compliant gyroid at each compression distance. Alongside this, I used theoretical modelling to electromagnetically characterise an analogous system under compression. In doing this I have identified the origin of the novel and complex photonic band-shifting behaviour produced by this 3D geometry.
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Chapter 1

Thesis overview

Some of the most vivid colours and patterns are those found in nature; bright coloured hues and striking optical effects are extremely common in certain insects, birds, aquatic life and even in flora. Structural colour produces the brightest and most optically diverse coloured appearances found in nature and has attracted the attention of scientists since the 17th century [1]. Hooke [1] and Newton [2] first identified the presence of structural colour in birds, in particular the iridescence from peacock and duck feathers. Since these early discoveries, the development of electromagnetic theory and the invention and continuing resolution improvements of electron and optical microscopes have led to an improved understanding of the mechanisms that result in the structurally coloured appearances in some animals and flora. Photonic structures similar to those found in nature are being used in many technological applications including optical fibres [3] [4] and LEDs [5]. In addition to their uses in technology, photonic structures are being implemented in pigment-free cosmetics [6] and even in fabric design [7]. The stunning iridescent blue colour of the Morpho genus of butterfly has recently inspired the Teijin Fibres Corporation to create a fabric named Morphotex [7] that mimics the structure and optical coloured appearance of the Morpho butterflies. This fabric is fade-proof and environmentally friendly as it contains no chemical pigments or dyes [7].

The interest in and characterisation of photonic crystals has only seen a surge in development over the last 50 years. As nature has had hundreds of millions of years to evolve highly tuned photonic structures suitable for performing a particular optical function, it is logical to take inspiration from the structures nature provides. Not only are they often highly tuned for a particular function, but they are also self-assembled. The ability to control the formation of optical structures in a self-assembling manner is widely considered as a great fabrication advantage. For these reasons, bio-mimetic photonic structures are being developed for use in an increasing number of applications.

This thesis describes my research into naturally occurring 3D photonic structures.
Some of these structures are present on a selection of insects including butterflies [8] [9] [10] [11] [12] [13] and beetles [14] [15]. The work presented in this thesis has taken place in both the optical and microwave regimes. The work performed in the optical regime included in-depth studies into the photonic structures and the subsequent electromagnetic responses of the native structures present on the weevil *Eupholus magnificus* and the butterfly *Parides sesostris*. This was undertaken with a wide variety of experimental techniques and also theoretical modelling. In addition to this I have synthetically replicated the three fundamental naturally occurring bicontinuous cubic photonic crystal structures and characterised their electromagnetic responses in the microwave regime. The most ubiquitous of these naturally occurring structures, the gyroid structure, was also fabricated as a compliant array on the millimetre-scale. This dynamic structure was also experimentally and theoretically characterised electromagnetically whilst under deformation forces.

### 1.1 Thesis outline

This thesis presents an investigation into many naturally occurring photonic systems that exist in both butterflies and beetles. The native, organic structures have been analysed and optically characterised alongside structural analysis, enabled by the used of electron microscope imaging. In addition to this, the characterisation of three synthetic replicas of naturally occurring photonic crystals has been undertaken. This was done with the aim of furthering the understanding of both the general photonic responses of these structures and also the colour production methods from analogous photonic structures found on beetles and butterflies. This has also inspired the investigation and characterisation of the electromagnetic response of synthetic 3D photonic crystal structures under deformation.

Chapter 2 reviews the progress in the field of structural colour in nature. The work presented in this thesis focuses on 3D photonic crystal geometries, including those found on beetles (Coleoptera) and butterflies (Lepidoptera). In this chapter an overview of 1D, 2D, 3D ordered and disordered photonic structures found on Coleoptera, Lepidoptera, aquatic life and flora is presented. The variety of photonic geometries present on a wide range of life forms and the diversity of associated coloured appearances is highlighted in this chapter. The formation of triply-periodic bicontinuous cubic structures is also discussed in this chapter.

Presented in chapter 3 are the mathematical and physical theories behind electromagnetic interactions with dielectric media. The theory of reflection and transmission from a single interface is presented and developed to include reflection and transmission from a thin film. The sections that follow include the principles behind photonic crystal
1. Thesis overview

theory. Here the behaviour of electromagnetic fields within periodic dielectric media is presented by both a mathematical and physical analysis. Photonic crystal theory describes the origin of the photonic band-gap and consequently the origin of structural colour. Using this theory, it is possible to determine how varying the geometry or the refractive index contrast of a periodic dielectric system can result in the change of its band-gap response. By changing the refractive index contrast of the system it is possible to achieve an increase or decrease in the width of the photonic band-gap and therefore the width of the frequency range reflected from the system. By altering this or the geometry of the periodic system it is possible to alter the angle-dependence of the reflected frequency band. This may result in a highly iridescent coloured appearance or, if tuned correctly, a ‘full-and-complete band-gap’ can result, where a particular range of frequencies are always reflected over all angles. A new breed of photonic geometries with ‘quasi-order’ are also discussed in this chapter [16]. These structures offer the suppression of iridescence from low index-contrast media.

The experimental and theoretical methods employed to collect the data presented in this thesis are outlined in chapter 4. Here, an introduction to optical microscopy and spectroscopy methods are described along with a description of the scanning electron microscopy (SEM) and focused ion beam (FIB) milling technique that was used to characterise the natural photonic systems. The ion beam and electron microscopy methods were used concurrently in order to capture detailed high-resolution images of the photonic structures present within weevil scales. A description of the ‘imaging scatterometer’ is also presented in this chapter. The scatterometry method is a recent development by Stavenga et al. [17] and allows for the imaging of the full-scattered hemisphere from a photonic sample. When used alongside the other methods described in this chapter, these experimental methods allow for the full optical and geometric characterisation of photonic structures present on Lepidoptera and Coleoptera. In this chapter a description of the millimetre fabrication technique used to replicate three triply periodic bicontinuous cubic photonic crystals for use in the microwave regime is also outlined. Alongside this, a description of the experimental microwave set-up used to electromagnetically characterise the synthetic structures is presented. The final sections of this chapter describe the theoretical methods that were used in conjunction with these experimental techniques in order to characterise the naturally occurring photonic crystal structures. Here, the finite element method modelling procedure is outlined alongside a description of the systems used in the theoretical models in order to replicate the environment of specific experimental set-ups.

Chapter 5 describes the experimental and theoretical investigation into the electromagnetic response of the three fundamental naturally occurring bicontinuous cubic photonic crystal structures; based on the P-, D- and G-surfaces. The three photonic
crystal structures were fabricated on the millimetre length-scale for electromagnetic characterisation in the microwave regime. Both experimental and theoretical transmission data were collected from these structures over an extensive incident polar and azimuthal angle range. The structures were designed to produce transmission stop-band widths that were analogous to the corresponding reflection band-gaps. From these experimental and theoretical data, the origin of each stop-band and its associated dispersion was identified. The data was taken using transverse electric (TE) and transverse magnetic (TM) linearly polarised incident radiation. The novel finding in this work appears with the presence, identification of and quantification via concentration factor analysis of linear polarisation-dependent stop-band widths for all three of the 3D photonic geometries under investigation. In addition to this characterisation, an investigation into the linear polarisation conversion brought about by the chiral G-surface structure, or ‘gyroid’, is presented at the end of this chapter.

Chapter 6 describes a detailed study of the 3D photonic structures present on the outer wing casings (elytra) of the weevil *Eupholus magnificus*. Many different experimental techniques were employed to perform this characterisation, including optical microscopy and spectroscopy, FIB milling and SEM imaging, scatterometry, fast Fourier transform analysis, Voronoi image analysis and configurational entropy calculations alongside theoretical modelling. The concurrent use of such a vast array of techniques allowed for the extensive characterisation of the optical function and geometry of the photonic structures present on this weevil. In the course of this work, this weevil was found to use two contrasting photonic structural mechanisms in order to produce the coloured appearance of the two different coloured bands present on its elytra. The structures were found to be contrasting in geometric order and consequently possessed a different level of rotational symmetry in each case. Although the coloured hues produced by the two different structural classes were different, the overall optical effect of an angle-independent coloured appearance was achieved in both cases. The co-existence of such structural order on a single organism and the use of such contrasting structural classes to produce the same optical effect is a feature that is extremely rare in nature.

Chapter 7 outlines the experimental and theoretical work performed on the butterfly *Parides sesostris* in the optical regime. The work presented in this chapter predominantly investigates the iridescence suppression within the wing scales of *P. sesostris*. The new optical experimental data directly explores the role and function of a surface structure that is present on individual wing scales. The theoretical work presented in this chapter examines how the gyroid photonic crystal structure present in these scales is optimised in order to suppress iridescence whilst concurrently producing a saturated and intense coloured appearance. The optimisation of the photonic crystal geometry within *P. sesostris* wing scales was previously overlooked by other workers in this field.
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as a method used by the butterfly to suppress iridescence.

Chapter 8 describes a detailed study examining the electromagnetic response from a compliant and tunable gyroid photonic crystal. In this chapter, a gyroid comprised of a rubber polymer and air was electromagnetically characterised in the microwave regime when under a compressive force. Previously published work on tunable photonic crystals have concentrated predominantly on 1D and 2D geometries. This work investigates the tunable response of a 3D, interconnected structure. The symmetry of the 3D gyroid is such that there exists multiple orientations throughout the geometry that possess periodic effective planes, each of which gives rise to a photonic stop-band. Consequently, the deformation of a 3D structure in one direction can ultimately alter the plane spacing of a number of these periodicities. This results in the ability to control the response of a number of stop-bands by applying a force in a single direction. When under compression in a direction perpendicular to the incident beam, the electromagnetic response of the gyroid was found to comprise a novel red- and blue-shifting stop-band behaviour. In particular, an overlap of two stop-bands that observed similar dispersion properties when uncompressed separates into two individual stop-bands when under compression.

Finally, a summary of the results and conclusions of the experimental and theoretical work carried out and described in this thesis is presented in chapter 9. I have also included scope for future work that has developed from the work presented here. In some cases initial theoretical modelling has been presented and prototype samples fabricated. I have also included a list of publications including papers, oral presentations and poster presentations that have arisen from the work presented in this thesis.
Chapter 2

Introduction - structural colour in nature

2.1 Introduction

The mechanisms behind the production of colour from incident white light can be classified in two broad categories; the production of colour via chemical processes, such as pigments and dyes, and colour production via photonic structures. The production of colour through the use of a chemical pigment arises from the scattering of white light from a material alongside the selective absorption of certain wavelengths, specific to the material in use [18]. Consequently, the colour observed from such a material is highly diffuse and is independent of viewing angle. The production of colour via pigment can be obtained by straightforward colouring procedures and so pigmentary colour is used in the majority of industrial colouring treatments. However, pigmentary colour does not possess the varying array of optical effects that are possible to achieve through the alternative colour production method, namely, by producing colour from photonic structures. Structural colour arises from the use of sub-micron structures that are often arranged in a periodic manner on a length-scale comparable to the wavelength of light [19] [18] [20]. In this case, colour is produced by interference effects that arise from the geometric arrangement of the structure [18] [20]. The preference to reflect constructively interfered wavelengths strongly from such a photonic structure can result in the observation of extremely intense and vivid colours, without the use of a chemical pigment. Not only are these colour reflections extremely intense, but they generally do not fade, unlike pigmented materials. In addition to this, iridescent effects can also be observed from photonic structures. The simplest case of structural colour arises from a 1D multilayer arrangement of thin films that possess alternating high and low refractive indices, such as a soap bubble or an oil film on water. After performing observations
from soap bubbles in 1704, Newton noted: ‘If a bubble be blown with water first made tenacious by dissolving a little soap in it, tis a common observation, that after a while it will appear tinged with a great variety of colours’ [2].

The earliest studies of structural colour are attributed to Hooke and Newton. In Micrographia [1], Hooke identified the colours produced from peacock and duck feathers arose from structural colour, as opposed to pigment. He predicted that the arrangement of the structure responsible for such colour arose from a periodic arrangement of cuticle and air, due to the change of colour observed when water infused into the feathers. This analysis was confirmed 39 years later by Sir Isaac Newton in his book ‘Opticks’ [2]. Over one hundred years later, the theories behind electromagnetic interaction with media were established by James Clerk Maxwell. This lead Lord Rayleigh to develop the theory behind regularly stratified media [19] in 1917 where he even hypothesised the presence of such regularly stratified media in naturally occurring samples such as beetles and butterflies [19]. In 1987 Yablonovitch first suggested the possibility of three dimensional ‘band-gaps’ arising from photonic crystal structures that were periodic in three-dimensions [21].

Although the presence of structural colour in animals was first realised in 1665 by Hooke [1], nature has been evolving photonic structures for hundreds of millions of years [22]. Since the early discovery of structural colour in 1665, a wide range of animals have been discovered to produce their colour via structural mechanisms. The variety of identified structures range in geometry, rotational symmetry, level of order and disorder and, ultimately, the resulting visual effects. The evolution of these naturally occurring structures have resulted in highly tuned mechanisms for performing a particular optical phenomenon and biological function. Scientists believe the need for specific coloured appearances are due mainly to mating, signaling, defense or camouflage purposes [23] [24] [25] [26]. In 1859 Charles Darwin published the first edition of his book ‘On The Origin of Species’ [27]. This work presented Darwin’s theory of evolution through natural selection and concepts of variation, particularly intra-species variations as the result of environmental differences. It was discussed in Darwin’s work that many animals, including butterflies, had developed coloured appearances that mimicked a more noxious animal [27]. Around the time of Darwin’s publication an English naturalist, Henry Walter Bates, contributed valuable insight into the evolving world Darwin had described. His findings involved variations among the Heliconius butterflies. Many of the samples he collected had novel survival mechanisms in-built into the patterns and colours on their wing surfaces. Many non-toxic samples displayed patterns and colours that mimicked a more dangerous organism, to which Bates proposed the better imitators would be less likely to be preyed upon due to their more harmful appearance [28] [26]. Bates described his findings as ‘a most beautiful proof of the theory of natural
2. Introduction - structural colour in nature

The patterns from the Heliconius butterflies occur through the use of colour pigmentation and through structural colour. As the chemical processes that are necessary to produce some coloured hues, such as greens and blues, are unavailable to the majority of the animal kingdom, structural colour may be employed to produce the coloured hues that are unavailable by pigmentation. In order to achieve the desired colour reflection response the most appropriate photonic structure, or the use of a novel adaptation of a simple structure, must be utilised. Over the millions of years that structural colour has had to evolve, many novel and elaborate mechanisms for producing a specific optical effect to perform a specific function have been developed in nature.

Photonic structures, or ‘photonic crystals’, can range from 1D, 2D and 3D periodic structures to quasi-ordered photonic crystals, which possess larger degrees of rotational symmetry than are obtainable from ordered geometries. Although, generally, iridescence is observed from periodic micro-structures, if the geometry of the structure and its compositional materials are tailored appropriately, angle-independent colour reflections may be obtained. In this chapter, a variety of novel, naturally occurring photonic structures that have formed in insects, birds, aquatic animals and flora are discussed.

2.2 1-dimensional structures in nature

There exist many different variations of structures that are periodic in one dimension. Examples of 1D structures that induce structural colour include diffraction gratings and 1D multilayers. Nature has adopted many variations of these 1D structural mechanisms in order to produce colour. In this section, an outline of a selection of such 1D structures that have evolved in natural organisms including the wings of butterflies, the outer wing casings, or ‘elytra’, of beetles, and examples of flora are presented.

2.2.1 1D structural colour in beetles

The 1D multilayer is the most commonly occurring photonic structure in beetles. Their formation occurs in the development of their outer surface, or ‘exoskeleton’, where chitinous material is secreted from the epidermis of the beetle. Chitin is a relatively transparent material, with refractive index of $n = (1.56 \pm 0.01) + (0.06 \pm 0.01)i$. The chitinous material, once secreted from the deposition zone, is hardened in layers over the surface of the beetle, or ‘endocuticle’. The secreted material is ejected in parallel layers with varying amounts of chitin and proteins in order to create an alternating refractive index system. If a periodic structure is formed on
2. Introduction - structural colour in nature

Figure 2.1: A schematic diagram showing the three-layered system of beetle cuticle formation. Layers of cuticle, containing varying amounts of chitin, are ejected from the deposition zone. The top layer, or 'epicuticle', often possesses the multilayer structure that interacts with optical wavelengths of light in order to produce interference effects [32].

Figure 2.2: The beetle *Chrysochroa raja*, (a), has a predominantly green metallic coloured appearance, with the addition of orange stripes. The colour of this beetle is produced by a regular multilayer system (b) [33]. (b) A transmission electron microscope image obtained from the epicuticle of the orange striped region of *C. raja* clearly shows this multilayer system. Scale bars: (a) 10 mm, (b) 200 nm. (Images courtesy of J. Noyes and P. Vukusic [33]).
a length scale comparable to the wavelength of light, interference effects will occur from
the reflections at each material interface. The colour of the resultant interference effect
is determined by the optical thickness of each layer within the system: the wavelength
of reflected light is scaled proportionally with the optical thicknesses and, therefore, the
lattice constant of the system [18] [20]. The layered system generally consists of three
main zones, presented in figure 2.1; the endocuticle, exocuticle and epicuticle, with the
epicuticle at the top surface of the beetle [32]. On top of the epicuticle is a protective
waxy over-layer [34] [32] [31]. It is the epicuticle, at the top surface of the three layered
system, that generally contains the optical multilayer system [34] [32]. Often, beetles
that possess a multilayer photonic structure produce a metallic optical appearance due
to their smooth outer surface. An example of this is the beetle *Chrysochroa raja*, pre-
sented in figure 2.2(a). The jewel-like coloured appearance of *C. raja* is produced by
a regular multilayer system, figure 2.2(b), and consequently is highly iridescent [33].
Some beetles have been identified to possess similar multilayer systems without the
use of chitin. Schultz and Rankin [37] determined that the multilayer structural sys-
tem on the exocuticle of tiger beetles (Cicindelinae) comprised non-chitinous epicuticle
alternated with ultra-thin layers of melanin [31].

2.2.1.1 Tiger beetles (Cicindelinae)

Beetles, and all natural organisms that possess a structural colour mechanism, have
limited materials available to them for the production of the photonic systems they
possess. Due to the, generally, low refractive index contrast of the compositional ma-
terials in which this limitation results, most regular multilayer systems in nature are
highly iridescent. However, some beetles, such as tiger beetles, require a non-iridescent,
appearance that allows them to blend in to their surrounding environment. It has been
shown that tiger beetles exhibit an anti-predator defense in their coloured appearance,
as it has been observed that they often exhibit structural colours that are directly cor-
related with the geographical variation in the colour of soils on which they live [38] [39]
[40]. Consequently the morphology of the multilayer structures of many tiger beetles
have been modified in order to develop a novel method to appear as a uniform diffusely
coloured hue over all observed angles. The elytra of many Cicindelinae are covered in
closely packed arrays of dimples that result from deforming their exoskeleton surface.
As the exoskeleton of the beetle contains a standard multilayer structure, the dim-
pling of its surface provides the multilayer with a graded periodicity from the centre
to the edge of each ‘bowl’-like shape [37]. The resultant optical effect this induces,
in the near-field, is a variation in the reflected wavelength that is dependent upon
the position across each individual dimple. Consequently, in the far-field, additive or
pointillistic colour mixing occurs from the many different colour reflections produced across each dimple [41]. The overall observed optical appearance is a non-iridescent blend of reflected colours from the array of dimples that results in a matte brown or green coloured appearance, dependent on the individual analysed sample [41].

2.2.1.2 Polarising reflectors

Similar bowl-shaped multilayers have been discovered to be present on the elytra of other beetles including *Plusiotis boucardi* [42], *Chrysina boucardi* [31] and *Chrysina gloriosa* [43]. The bowl-shaped multilayer systems are arranged in a roughly hexagonal form on the surface of *P. boucardi, C. boucardi* and *C. gloriosa*. In these instances, the chitin fibres that form the layers of the multilayer bowl system are arranged throughout the system in a helical manner. The layers are deposited such that one rotation of the helix is approximately equal to one optical wavelength [42]. Therefore, in addition to the multilayer reflections produced by the multilayer bowl, this chiral mechanism produces a circularly polarising reflector. When circularly polarised light is incident upon the structure, light reflected from the beetle maintains its original handedness [42]. This conservation of handedness is a result of circularly polarised light interacting with an optic-axis possessing the same handedness [44] [42]. This type of circular polariser has been likened to a cholesteric liquid crystal structure [44] [45] [42].

2.2.1.3 1D broadband reflectors in beetles

The typical multilayer arrangement of alternating layers of a specific thickness comprised of different media generally produces a single narrow band colour reflection that is highly iridescent. The broadband nature of a standard multilayer reflector can be altered by adapting the structure in one of three different methods [30] [31]. The three classifications of multilayer stack that reflect in a broadband manner are a chirped stack, figure 2.3(a), where the optical thickness of each layer is arranged as a gradient throughout the depth of the stack, a combination of multilayers, figure 2.3(b), and a multilayer structure comprising randomly sized layers, figure 2.3(c) [30] [31]. In each case the optical thicknesses of the component layers differ greatly, and no clear single periodicity is present, consequently resulting in the reflection of a variety of wavelengths from the structure. In addition to this, the large range of reflected wavelengths results in a reduction in the angle-independence of the reflected colour. By tuning the chirped stack appropriately it is possible to obtain broadband coloured hues such as gold, white or silver. Only the first of the three broadband reflecting systems have been discovered in beetles. The chirped stack was discovered in the scarab beetles *Plusiotis resplendens* [46], *Anoplognathus parvulus* [30], and *Chrysina chrysagyrea* [31]. The colours pro-
2. Introduction - structural colour in nature

2.2.2 1D structural colour in Lepidoptera

2.2.2.1 *Morpho rhetenor*

The *Morpho* genus of butterfly is widely celebrated for the striking and bright blue coloured appearance present on its dorsal wings, as presented in figure 2.4(a). The extremely intense and bright coloured appearance of the *Morpho* wings enables long range intra-species communication [35], and is said to be visible up to half a mile away from an observer [35] [47]. Such bright and intense colour reflections are only achievable with the use of structural colour. The extremely intense blue coloured appearance originates from an arrangement of 1D photonic structures present within wing scales. The wing scales, such as those displayed in figures 2.4(b) and (c), appear to have long ridges running along the length of the scales. The ridges are periodic and possess a pitch of 500-600 nm and the height of the ridges is approximately 1.4 µm [35] [48]. In studies by Vukusic et al. [35] and Kinoshita et al. [48], the many structural mechanisms that aid the relatively angle-independent blue colour reflections from many of the *Morpho* butterflies were identified.
Figure 2.4: The blue coloured appearance of the dorsal wing of the butterfly *Morpho rhetenor*, (a), is produced by photonic crystal arrays that are present within scales arranged on its wing surface, (b) and (c). The surfaces of individual wing scales possess periodic ridges, (d). A TEM cross-section through a scale reveals that the periodic surface ridges result from an array of Christmas tree-like structures, (e) and (f). Each ‘Christmas tree’ structure is a 1D periodic multilayer array. Scale bars: (a) 4 cm, (b) 100 µm, (c) 70 µm, (d) 3 µm, (e) and (f) 600 µm. (Images courtesy of P. Vukusic [35][47].)
A cross-section through a typical *M. rhetenor* scale, presented in figure 2.4(e) and (f), reveals that the periodic surface ridges arise from the apex of 1D Christmas tree-like structures within each scale. The role and function of the 1D Christmas tree structures and ridging were determined by Vukusic et al. in 1999 [35] with a follow up study by Kinoshita et al. in 2002 [48]. They reported that the multilayer Christmas tree structure, within a surface ridge, produces constructive interference, resulting in the selective reflections of a narrow range of blue wavelengths. The peak reflectivity from these scales was determined to occur at a wavelength of 450 nm [35] [49]. However, the periodic nature of the Christmas tree structure alone would result in a highly iridescent appearance, which is not observed from the butterfly. Instead, the wings of *M. rhetenor* appear blue over an extremely large angle range. In 1999, Vukusic et al. [35] identified that each Christmas tree multilayer possessed a tilt with respect to the scale substrate. The tilted nature of these structures increases the diffuse nature of reflected light from them by creating a large spread over the angle at which blue colour reflections would be observed [35]. Kinoshita et al. [48] deduced that the ridge height throughout a scale is not constant, and is almost randomly distributed. Kinoshita et al. [48] added that the irregularity in the ridge height aids this uniform coloured appearance over a large angle range. The irregularity of the ridge height causes a more diffuse and broadband reflection due to the elimination of interference between the ridges [48]. The intensely bright colours seen from the wings of *M. rhetenor* originates from the large number of layers within each 1D multilayer system, due to the high reflectivity this produces [48]. In addition to this, the wing scales are arranged on top of a dark wing substrate. The dark appearance of the wing can be observed around the edge of the butterfly wing in figure 2.4(a). The highly absorbing, melanin-rich wing substrate absorbs any transmitted wavelengths, consequently enhancing the observable reflected colour purely from the multilayer structures [50]. These adaptations of a 1 dimensional structure ultimately result in a highly tuned photonic system that acts to produce the highly intense and vivid uniform blue coloured appearance associated with the *Morpho* butterflies, something that is unobtainable from pigment alone.

### 2.2.2.2 *Papilio palinurus* and *Papilio ulysses*

Two Swallowtail (*Papilio*) butterflies have also been identified to exhibit novel structural colour through the use of a 1D multilayer system. These are *Papilio palinurus* [54] [51] [52], presented in figure 2.5(a), and *Papilio ulysses* [51] [52], presented in figure 2.6(a). A modified 1D photonic structure is present within their wing scales as shown in figures 2.5(b) and figure 2.6(b) for each respective example. The scale morphology in each case comprises dimpled concavities which consequently distort the underlying
Figure 2.5: (a) The Swallowtail (*Papilio*) butterfly *Papilio palinurus*. The wings of *P. palinurus* are covered in scales that possess a 1D photonic structure. (b) An image, obtained by scanning electron microscopy, of a typical wing scale from *P. palinurus* shows that an array of concavities cover each scale. (d) A cross-section through such a dimpled array reveals the deformed multilayer structure underlying each concavity. A retro-reflection from an incident light beam results in a shorter wavelength reflection from the edges of the concavities and a regular normal incidence multilayer response from the central region. Consequently, optical microscopy imaging, (c), reveals blue annuli surrounding yellow colour centres. Scale bars: (a) 20 mm, (b) 65 µm, (c) 10 µm, (d) 1 µm. (Images courtesy of P. Vukusic [51] [52] [53]).
2. Introduction - structural colour in nature

Figure 2.6: (a) The Swallowtail (Papilio) butterfly *Papilio ulysses*. The wings of *P. ulysses* are covered in scales that possess a 1D photonic structure. (b) An image, obtained by scanning electron microscopy, of a typical wing scale from *P. ulysses* shows that an array of concavities also cover each scale in a similar manner to that of *P. palinurus*. (d) A cross-section through such a dimpled array reveals the deformed multilayer structure underlying each concavity, possessing shallower walls with a smaller incline when compared to that observed in *P. palinurus* scales. The shallow nature of the *P. ulysses* walls results in the absence of a retro-reflection from the side walls. Consequently, optical microscopy imaging, (c), reveals no distinct coloured annuli surrounding the colour centres. In this instance, the coloured appearance results purely from the blue colour centres. Scale bars: (a) 20 mm, (b) 120 µm, (c) 10 µm, (d) 1 µm. (Images courtesy of P. Vukusic [51] [52] [53]).
multilayer structure into bowl shapes, similar to that observed in the tiger beetles discussed in section 2.2.1.1. Cross-sections through such concavities are presented in figures 2.5(d) and 2.6(d) for *P. palinurus* and *P. ulysses*, respectively. The spacing of each layer in the 1D structure of *P. ulysses* results in blue coloured reflections, while the larger plane spacing from that of *P. palinurus* results in a green coloured hue. However, the respective inclination of concavity walls on the wing scales of each butterfly brings about a more interesting difference in optical response. The concave dimples of *P. ulysses* are relatively shallow in comparison with *P. palinurus*. The inclination of the sides of the concavities are approximately 45° for *P. palinurus* [51] and 30° for *P. ulysses*. The deeper, steeply inclined walls of *P. palinurus* result in a retro-reflection occurring from the surrounding walls of each concavity. Such a retro-reflection results in the annuli observed in the optical microscopy image presented in figure 2.5(c) [51] [52]. The blue annuli, surrounding the yellow colour centres, result from the retro-reflection effect and the yellow colour centres result from normal incidence reflection. The blue, shorter wavelength reflections of the annuli arise due to the larger angle upon which light is incident on the multilayer present under the inclined walls, resulting in a blue shift from the yellow hues observed at normal incidence [51] [52] [47]. An additive mixing process occurs between the resulting yellow and blue reflected wavelengths in order to produce a green overall coloured appearance, due to the pointillistic colour mixing process, described in section 2.2.1.1 [51] [52]. As the concavities shown in 2.6(d) do not possess walls that are as steeply inclined as in *P. palinurus*, there is no presence of distinctly different coloured annuli in the corresponding optical images presented in figure 2.6(c) [47]. Therefore the colour reflections produced from the wings of *P. ulysses* result primarily from the blue colour reflections that originate from the centre of each concavity.

### 2.2.3 1D structural colour in flora

Colour production via structure is not limited to animals in the natural world, but also exists in many cases of flora. Many plants use structurally-assisted colour by implementing diffraction and multilayer structures alongside pigmentation in order to appear as distinguishable as possible to a large variety of insects. The visible spectral range of insects differs to that of humans [55] [56]. In particular, bees are capable of seeing most of the visible spectrum and also deep into the UV sector of the electromagnetic spectrum [55] [56]. Consequently, due to their visual spectral range, the way in which bees see and distinguish vegetation appears extremely different to human perception of the same environment. In some cases bark, soil, stone and leaves may appear indistinguishable from the petals of a flower to an insect as they all reflect weakly across the
whole range of the insect’s visual spectrum \[57\] \[56\]. Consequently the bright colours of flower petals, that act to attract pollinating insects, may not be distinguishable from the surrounding vegetation to a rapidly moving insect. The addition of an iridescence-inducing structure alongside the pigmented colour of some petals have been identified in many floral samples \[58\] \[59\] \[56\]. *Mentzelia lindleyi* is a pigmented flower which appears yellow to normal human vision. In addition to the yellow pigment, there exists a diffraction grating on its surface which diffracts predominantly UV wavelengths of light \[59\]. Human photoreceptors can not detect the UV iridescence it causes, yet insects, including bees, possess photoreceptors that are sensitive deep into the UV wavelengths of the electromagnetic spectrum and will be able to detect this diffraction. It is thought this UV ‘coloured’ appearance and patterning, brought about by the diffracting structure, acts to create a bullseye spot for landing pollinators to target certain flowers, including *M. lindleyi* \[56\]. This contrast to surrounding vegetation, and the iridescence induced by a diffraction structure, is particularly useful for attracting the attention of a rapidly moving pollinator, such as a bee, consequently aiding the visualisation of and the attraction to the flower \[56\]. *Tulipa sp.* and *Hibiscus trionum* are additional examples of flora that also possess UV diffraction gratings, aiding their attraction to many animal pollinators \[58\] \[56\].

*Selaginella* is a floral example that benefits from the use of structural colour in an alternative way, \[60\] \[47\] \[56\]. *Selaginella* possesses green leaves when grown in conditions with an abundancy of light. In low light conditions *Selaginella* was found to appear blue, possessing iridescent blue colour reflections from its leaves. In 1984, Hebant and Lee discovered that this iridescent appearance originated from the development of a dual layer multilayer system on the low light sample, not found in the usual green variety \[60\]. Transmission electron microscopy revealed each layer was approximately 80 nm thick. This system was determined to act as an anti-reflective coating by reflecting blue wavelengths from the leaves and by aiding the transmission of red wavelengths, necessary for photosynthesis, into the leaves \[60\] \[56\].

### 2.3 2-dimensional structures in nature

Animals and flora possessing photonic crystals that exhibit 2D periodicity are very uncommon, however, some 2D structures have been discovered to exist in water animals and birds. The most studied of which are the 2D photonic structures found in peacock feathers. Newton was the first to hypothesise about the presence of a photonic crystal array in peacock feathers. In his publication ‘Opticks’ \[2\] in 1704, he noted: ‘The finely colour’d feathers of some birds, and particularly those of peacock’s tails, do, in the very same part of the feather, appear of several colours in several positions of the
eye, after the very same manner that thin plates were found to do, and therefore their colours arise from the thinness of the transparent parts of the feathers; that is, from the slenderness of fine hairs, or Capillimenta, which grow out of the sides of the grosser lateral branches or fibres of these feathers’ [2]. The actual underlying 2D photonic structure that generates the colour observed from peacock feathers was later confirmed by scanning electron microscopy analysis.

2.3.1 2-Dimensional structures in birds

The male peacock *Pavo cristatus* is well known for its striking display of coloured feathers, particularly its characteristic iridescent blue feathers and the yellow-green ‘eye’ patterning it possesses. The optical patterns on the tail feathers of the male peacock are often displayed in mating rituals and also as a warning display to competing animals [61]. The coloured appearance of peacock feathers originates from a 2D photonic crystal structure contained within feather barbules that emanate from the central feather stem [62] [63]. Inside each barbule exists a 2D array of melanin fibre rods that arrange along the length of the barbules in a square packing configuration [62] [64]. The melanin rods possess a length ranging from 0.52 µm, with rod diameters of 130 nm for blue feathers and 140 nm for yellow feathers [62]. The lattice constants of the rod arrays are 150 nm for blue feather and 190 nm for yellow feathers [62] [63]. The highly ordered arrangement of 2D melanin rods arranged in air results in the iridescent optical response observed from the feathers [62].

In addition to peacock feathers, another bird *Pica pica*, more commonly known as the black-billed magpie, also produces structural colour with the use of a 2D photonic crystal array [65]. The feather barbules of *P. pica* form a ribbon shape. The barbule emerges from the central feather barb with the flat side of the ribbon-shape barbule oriented perpendicular to the plane of the feather. At a few micrometres away from the barb the orientation of the barbule twists so that the flat side is in the plane of the feather [65]. Each barbule contains an array of cylindrical air holes arranged in a hexagonal array in a keratine and melanin material matrix [65]. The yellow-green tail feathers of *P. pica* possess a lattice constant of 180 nm between neighbouring cylindrical channels, with diameter of each channel being 50 nm and length being in excess of 1.5 µm [65]. In a study by Vigneron et al. this structure was theoretically determined to produce a first-order reflection that is centred about the wavelength of $\lambda = 564$ nm, which agreed well with the experimentally determined reflected wavelengths [65]. However, the blue tail feathers of *P. pica* possess a lattice constant of 270 nm. This is a vastly greater lattice constant than that discovered within the yellow-green feathers. Such an increase in lattice constant will induce a red-shift of the first order reflected
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Figure 2.7: Transmission electron micrographs displaying cross-sections taken from different sites along the length of the bristles from the Pherusa sp. polychaete worm at (a) 1 $\mu$m, (b) 2 $\mu$m, (d) 5 $\mu$m and (e) 5 $\mu$m along the bristle. (c) A cross-section through a bristle from the Pherusa sp. polychaete worm. The polycrystalline hexagonal arrangement of chitinous rods is clearly visible. This is in contrast to the monocrystalline arrangement of hexagonally arranged rods within the bristles of the Aphrodite polychaete worm, (f). Scale bars: (a) 1 $\mu$m, (b) 2 $\mu$m (c) 1 $\mu$m (d) 5 $\mu$m (e) 5 $\mu$m (f) 2 $\mu$m. (Images courtesy of T. Trzeciak and P. Vukusic [66].)

Wavelengths. In the same report by Vigneron et al. [65], this larger lattice constant was theoretically modelled and blue wavelengths of 423 nm were determined to be reflected as second order reflections as a ‘second Brillouin-zone boundary gap reflectance’. The first order reflectance lies outside of the human visible range, in the infra-red wavelength regime. Typically it might be expected for the lattice constant to be reduced in order to induce a blue shift of first order reflections, such as that observed from the lattice constants present within the feathers of the male peacock. Therefore this is a novel and unconventional mechanism for reflecting smaller wavelengths, but is likely to be beneficial to the black-billed magpie and may form in this manner as it simply can not produce structures with smaller lattice constants.
2.3.2 The 2D photonic structure of *Pherusa sp.*

Polychaete worms are marine animals that live throughout all depths of the oceans. The polychaete worm *Pherusa sp.* has fibrous bristles that appear iridescent in nature. A 2D array of chitinous rods are arranged within the bristles in a polycrystalline array of hexagonal symmetries [66], presented in figures 2.7(a)-(e). Previously, Vukusic and Sambles reported of another polychaete worm, *Aphrodite*, which possessed a highly periodic monocrystalline 2D array of rods arranged with hexagonal symmetry [47], presented in figure 2.7(f). The polycrystalline structure of *Pherusa sp.* is thought to have emerged through the introduction of defects in the formation of the bristles, consequently deforming the arrangement of rods from the monocrystalline arrangement observed in the *Aphrodite* system. The packing fraction of rods remains approximately constant throughout the length of the *Pherusa sp.* bristles, yet the pitch of the hexagonal structure decreases towards the tip of the bristles, which have a smaller bristle diameter, although the change does not occur proportionally, shown in figures 2.7(a)-(e). Despite the tapering of the tips of the bristles, the pitch of the structure remains in a range that will produce an optical response. In order to do this, some of the rods terminate before reaching the tip of the bristles [66].

2.4 3-dimensional structures in nature

3D photonic structures have the capability of producing a highly isotropic geometry, due to their periodicities spanning all three dimensions. This provides scope for producing angle-independent colour reflections from a photonic structure. However, naturally occurring structures that are produced within animals and flora are produced with limited availability of materials. Consequently, novel methods for producing angle-independent colour reflections are often employed in nature, in order to suppress the iridescence inherent in 3D photonic structures with low refractive index contrasts.

2.4.1 *Callophrys rubi*

The ventral wing of the butterfly *Callophrys rubi* displays a diffuse green coloured appearance, shown in figure 2.8(a), while the dorsal side remains brown, shown in figure 2.8(b). This results in a green coloured appearance when the butterfly is in a resting position [10]. The dorsal side of *C. rubi* is covered in wing scales that are hundreds of microns in length. Contained within each wing scale is a 3D photonic crystal structure. The geometry of the photonic crystal structure present in the wing scales of *C. rubi* has been highly debated in literature. In 1975 Morris, [67], thought the structure to be a simple cubic 3D array of air spheres in a matrix of cuticle, and later Ghiradella...
Figure 2.8: The ventral, (a), and dorsal, (b), sides of the butterfly *Callophrys rubi*. The ventral wing surface is covered in scales that are hundreds of microns in length and contain a gyroid 3D photonic crystal structure (c). The gyroid array is arranged with a depth comprising approximately four unit cells. Scale bar: (c)1 µm. (Images courtesy of P. Vukusic.)
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and Radigan, [68], proposed that the structure was better defined by a face-centred cubic network. In 2008 it was described by Michielsen et al. to be a ‘gyroid’ photonic structure [9] [10]. The gyroid structure present in the butterfly wing scales of C. rubi is comprised of an interconnecting periodic array of chitin and air labyrinths with a lattice constant of $a = (311 \pm 5) \text{ nm}$ [12]. The gyroid structure possesses two chiral axes; both a left- and a right-handed helix is present along the [100] and [111] axes, respectively [12] [69]. The presence and exact nature of these chiral axes were tomographically mapped fully in 3D space by Schröder-Turk et al. in 2011, providing further evidence and information regarding the chiral gyroid structure present in this butterfly [12]. Consequently, this structure has been shown to display significant circular dichroism effects for blue and ultraviolet light [69]. It has been hypothesised that this circular dichroism effect might imply the presence of some biological photoreceptors that are sensitive to circular polarisation in insects [69]. The gyroid structure is a self-assembled structure that is produced by a surface of minimum energy that divides the two interconnecting labyrinths of different media, discussed later in section 2.6.1. The presence of this self-assembling photonic structure has inspired research into their formation in butterfly wing scales [11]. Their self-assembling nature makes the gyroid an attractive candidate for the mass-fabrication of 3D photonic structures.

2.4.2 Weevils

Curculionidae, or ‘weevils’, are from the order of Coleoptera. Many weevils have been identified to possess 3D photonic crystal structures on their elytra. Eupholus is a genus of weevil that possesses a large variation in coloured appearance and patterning between species. Figure 2.9 displays three weevils from the Eupholus genus: (a) Eupholus margificus [14], (b) Eupholus schoenherri pettiti and (c) Eupholus loriae. All three weevils produce their coloured appearance through the use of a 3D photonic crystal structure contained within scales that are positioned over the dark melanin rich elytra. Scale bars: 4 mm.

Figure 2.9: A selection of three weevils from the Eupholus genus: (a) Eupholus magnificus [14], (b) Eupholus schoenherri pettiti and (c) Eupholus loriae. All three weevils produce their coloured appearance through the use of a 3D photonic crystal structure contained within scales that are positioned over the dark melanin rich elytra. Scale bars: 4 mm.
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Figure 2.10: (a) A scanning electron micrograph displaying a broken scale from the yellow coloured elytral band of the weevil *Eupholus magnificus*. Within the scale is a 3D photonic crystal structure. The 3D nature of the highly ordered structure is visible by the fracturing that has occurred from this scale. (b) A scanning electron micrograph displaying two neighbouring intra-scale structural domains. Each of these juxtaposed domains possess the same 3D photonic crystal geometry but are arranged at different orientations with respect to neighbouring domains. Scale bars: (a) 2.5 µm, (b) 1 µm.

Figure 2.11: Colour-producing scales from the (a) *Eupholus magnificus* [14], (b) *Eupholus schoenherri pettiti* and (c) *Eupholus loriae* weevils. All three weevils produce their coloured appearance using a 3D photonic crystal structure that is arranged in domains within the scales. Each domain comprises the same 3D photonic crystal structure but is rotated to a different orientation with respect to neighbouring domains. This is observed optically in the near-field as juxtaposed intra-scale domains that appear as different coloured hues. Scale bars: 50 µm.
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*magnificus*, (b) *Eupholus schoenherri pettiti* and (c) *Eupholus loriae*. In contrast to the 1D systems present on the elytra of beetles discussed in section 2.2.1, their structural colour is produced by a 3D photonic crystal mechanism that is arranged in domains within elytral scales. A scanning electron micrograph image taken from a scale obtained from the yellow elytral band of *E. magnificus* is presented in figure 2.10(a). Here the 3D nature of the structure is clearly visible due to the way in which the scale has fractured. Figure 2.10(b) presents a scanning electron micrograph image obtained from an intra-scale region that contains a domain boundary, also obtained from the yellow elytral band of *E. magnificus*. Optical microscopy images of the scales present on the elytra of *Eupholus magnificus*, *Eupholus schoenherri pettiti*, and *Eupholus loriae* are presented in figures 2.11(a), (b) and (c), respectively. Where a domaining approach of an ordered photonic crystal is present within elytral scales, each intra-scale domain possesses the same 3D photonic crystal structure arranged at a different orientation with respect to neighbouring domains. The 3D photonic crystal structure present in each scale comprises chitin, \( n = 1.56 \), and air. Ordered photonic crystals with a low refractive index contrast are iridescent despite being 3-dimensional in nature and consequently more isotropic than 1D or 2D structures. The lowest refractive index contrast possible to reflect a specific wavelength range over all angles from an ordered photonic crystal occurs for the diamond structure and has a value of approximately 2 [70]. Due to the iridescent nature of these 3D photonic structures, the optical effect produced from each intra-scale domain manifests as a different observable colour in the near-field, as seen in figures 2.11(a), (b) and (c). However, when viewed macroscopically the colour reflections from each intra-scale domain add together to produce a single average colour, similar to the pointillistic colour mixing process described in section 2.2.1.1. This results in an angle-independent coloured appearance of a single average coloured hue, something that is not achievable through the use of these ordered 3D photonic crystal structures alone. This is another example of the novel methods nature uses in order to produce the desired optical effects through photonic structures.

2.4.3 *Dynastes hurcules*

Another example of a beetle that possesses a 3D photonic crystal system is *Dynastes hurcules*, also known as the Hercules beetle [71] [72]. The coloured hue of *D. hurcules* differs according to the humidity of its surrounding atmosphere. When the beetle is in a dry atmosphere it appears as a khaki-green colour, yet when the atmosphere reaches a high humidity state this coloured hue disappears and the beetle appears black [71]. The green colour of *D. hurcules* is produced from an open porous layer located 3 \( \mu m \) below the cuticle surface. The layer consists of a spongy multilayer positioned under a
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Protective wax cover [72]. The multilayer is comprised of air and chitin [72]. Penetrating through the multilayer is an array of vertical columns, perpendicular to the cuticle surface, consequently providing a rigidity to the layered air-chitin array. The separation between the layers of the 1D structure and the separation of the perpendicular columns are comparable, and both strongly interact with light. This consequently forms a composite 3D photonic crystal structure. In addition to this, the outer cuticle of the beetle possesses many straight cracks directly above the composite 3D photonic structure [72]. It has been hypothesised that the surface cracks allow water to penetrate into the multilayer, consequently wetting the structure. This results in the diminishing of the green colour observed from D. hurcules when in a very humid atmosphere. However, the exact conditions for the transformation to a black appearance are still unknown and under investigation [72].

2.5 Disordered structures producing broadband colour reflections

Highly ordered photonic structures have the ability to selectively reflect a narrow wavelength band. By increasing the level of disorder present in a photonic structure, it is possible to achieve a broadening of this reflected wavelength band. Nature has developed many different scattering mechanisms that induce broadband scattering of white light, and have been discovered within many animals such as butterflies and beetles and also in flora.

2.5.1 Beetles

The scarab beetles Cyphochilus and Lepidiota stigma and the beetle Calothyrza margaritifera, a member of the Cerambycidae, have been shown to possess highly contrasting methods for scattering a broad-band of optical wavelengths from their elytral scales [73] [74]. These beetles are presented in figures 2.12(a), (c) and (e), respectively. Each beetle produces its white coloured appearance by use of a disordered array of optical scatterers contained within scales that sit upon their exoskeleton, shown in figures 2.12(b), (d) and (f).

The disordered intra-scale scattering systems used by Cyphochilus and L. stigma employ a connected network of randomly oriented filaments, whereas the scattering mechanism within the C. margaritifera beetle comprises a disordered arrangement of discrete solid spheres [73] [74]. The broadband nature of the resultant scattering from each of these structures differs greatly. The reflectance from each beetle was experimentally measured and theoretically modelled by Luke et al. [73] [74] in order to deter-
Figure 2.12: A selection of white beetles including two scarab beetles, (a) *Cyphochilus* and (c) *Lepidota stigma* and one beetle member of the Cerambycidae, (e) *Calothyrza margaritifera*. The exoskeleton of each beetle is covered in scales that vary in shape and size. (b) The scales of *Cyphochilus* are plate-like and similar to that of *L. stigma*, (d). (e) The scales from *C. margaritifera* are more hair-like in comparison. Each scale contains a random array of filaments or particles that give rise to extremely broadband scattering, hence their white visible appearance. Scale bars: (a), (c) and (e) 1 cm, (b), (d) and (f) 500 µm. (Images courtesy of S. M. Luke [73].)
mine the efficiency of optical scattering from each beetle. The broadband reflectance produced by *Cyphochilus* was experimentally measured to possess a distinctly bright intensity when compared to that from the other two beetles, particularly *L. stigma* which was determined to produce the lowest reflectance of the three beetles. Luke et al. investigated the effect of changing the filling fraction, scattering centre diameter and scatterer spacing of these three scattering systems with the use of theoretical modelling. It was discovered that the filling fraction used by the *Cyphochilus* beetle was optimum for scattering the brightest broadband reflectance possible with the filamentary system used. In addition to this *Cyphochilus* and *C. margaritifera* were both shown to have optimum scattering centre sizes which consequently produce the maximum amount of optical scatter possible for their respective scattering mechanisms. The size of scattering centres used by *L. stigma* did not lie in a theoretically determined optimum range, and so may account for the lower experimentally determined reflectance. All beetles were shown to possess an optimum scatterer spacing and no optical crowding was present in any scales.

Mie theory modelling and experimental scattering data obtained by Luke et al. [73] [74] indicated that scattering centres with a diameter of 200-300 nm and concurrent scattering particle separation of approximately 500 nm provides an optimal size and spacing for producing the maximum possible scattered intensity. All three beetle species under investigation had diameters and spacings within these ranges, implying structural optimisation is present in these species at varying levels. It was discovered that the disordered structure within *Cyphochilus* scales exhibits the most efficient broadband optical scatter of the three beetles under investigation [73] [74]. The theoretical modelling performed on the *Cyphochilus* beetle implies this efficiency is due to the size of scattering centres, filling fraction and scatterer spacing present within this beetle [73] [74]. *Cyphochilus* scales have a thickness of approximately 5 µm. The efficiency of optical scatter produced by an ultra-thin system has inspired research into ultra-thin optical coatings for the paper [75] and fabric industry [76].

2.5.2 Flora

*Leontopodium nivale* subsp. *alpinum*, also known as ‘edelweiss’, is a flowering perennial herbaceous plant which can be found at altitudes of up to 3400 m, generally in the Alps [77]. The entirety of the plant is covered with hollow filamentary hairs which gives the plant its characteristic white appearance. The hairs are arranged in a disordered ‘criss-cross’ manner over the plant [77]. On the surface of each filamentary hair exists a highly diffractive surface structure comprising highly ordered filaments [77]. This surface structure induces optical diffraction, which can be explicitly observed in the
near-field as a variety of colours across each hair. However, when viewed in the far-field, the summation of these diffracted colours over the many disordered, criss-cross arrangement of filaments, results in a very broadband white appearance. In addition to this, it was reported that the covering fleece of filamentary hairs protects the plant from dehydration and cold [77]. Furthermore, the diffracting surface structure of the filaments also reflects wavelengths in the UV regime, consequently protecting the plant from harmful ultraviolet radiation. This is particularly beneficial to this plant as it is generally found at very high altitudes where UV radiation from the sun is stronger [77].

2.6 Self-assembly in nature

With the increasing desire for mass fabrication of photonic crystals, particularly 3D photonic crystals, the mechanisms behind the natural formation of photonic crystals are under intense research. Nature has developed many efficient photonic crystal structures, and other photonic mechanisms, that perform specialised and highly tuned optical functions that are required by the host organisms. These naturally occurring structures are generally self-assembled. The self-assembling fabrication approach is particularly attractive in technological applications of photonic crystals where the precise mass-fabrication of a particular geometry is required. Consequently, understanding the self-assembly mechanisms inherent in the production of naturally occurring photonic crystals may aid the synthetic development of similar structures for technological use. The fabrication methods used in photonic crystal production are structure-dependent. For instance, the formation of multilayer structures through layer-by-layer deposition has been reported in many beetle samples and does not prove an obstacle for synthetic replication on the optical scale. However, there is little known about how animals self-assemble their 2D or 3D photonic structures. Self-assembling minimal surfaces are found to exist in many different scenarios and naturally form highly ordered structures. In most cases they do not form on the optical length scale, but on smaller length scales such as in synthetic lipid or copolymer systems [78] [79] [80]. However, a selection of minimal surface or constant mean curvature structures that self-assemble on larger length scales, and in some cases on the optical length-scale, have been discovered in biological cell membranes [81]. There have recently been discoveries of many examples of insects which use minimal surface or constant mean curvature structures on the optical scale, such as the gyroid found in the butterfly *C. rubi* discussed in section 2.4.1. The gyroid is thought to be the most commonly appearing self-assembled structure in nature [82] [80]. Consequently, its discovery as a photonic crystal structure on insects has inspired research into their self-assembled formation on the optical length-scale [83] [11].
2.6.1 Minimal surfaces

The term ‘minimal surface’ is commonly used when discussing surfaces of minimal energy, particularly within lipid-water mixtures where a surfactant has been added. Due to the hydrophobic nature of lipid molecules, oil and water can not mix without the use of an amphiphilic surfactant which has both a hydrophilic head group and a hydrophobic tail group [80]. The amphiphilic surfactant can then sit in between the two materials in a state of minimum energy, allowing the two to mix. A minimal surface is defined as having zero mean curvature [80]. More generally, a surface of constant mean curvature (CMC) is a surface which has a constant mean curvature, not limited to zero. A minimal surface or CMC surface divides two regions of space, often forming two completely separated interconnecting labyrinths. Such a system is referred to as ‘bicontinuous’. A triply periodic bicontinuous structure is one which is periodic in all three dimensions [80]. Triply periodic bicontinuous structures have the potential to form 3-dimensional periodic arrays which are particularly significant as a prospect for 3D photonic crystal array fabrication. CMC structures have been discovered to exist in a variety of naturally occurring scenarios on different length-scales, including lipid-water-surfactant mixtures [84], beetles [85], butterflies [9] and even in mammalian skin [83] [86]. Gyroid [87] and double gyroid [88] structures have already been utilised in the production of semi-conductors for use in solar cells, on a smaller length scale than photonic crystals. However, similar synthetic structures have not yet been fabricated on optical length-scales using self-assembly mechanisms. Recent studies have suggested that the formation of the gyroid in butterfly wing scales starts in the larval stage of the butterfly’s growth [8] [11]. The process involves membrane folding of the cellular plasma membrane and the intracellular smooth endoplasmic reticulum [8] [89] [11]. The membrane folding process creates a pentacontinuous network [11]. Chitin is then ejected from the plasma membrane into an extracellular network. This chitin is then hardened. After the cell is formed, the plasma membrane and the smooth endoplasmic reticulum membrane dies, leaving a single chitin network behind in the geometry of a gyroid network [8] [11].

2.7 Applications of photonic crystals

The biological world has evolved a diverse range of novel photonic structures that are highly tuned to perform a range of optical functions. In studying this variety of naturally occurring structures, our understanding of function, fabrication and novel geometries may benefit the technological world. Photonic crystals are the subject of rapidly increasing interest due to the potential they offer in many aspects of optics-based
applications. The ability to control and direct electromagnetic radiation, particularly specific wavelengths of visible light, is highly attractive in many technology sectors. In addition to this, the optical effects they offer are being utilised in cosmetics [6], fabrics [7] and in holographic design. Communication technology has benefited from the adaptation of optical fibres to include ordered photonic crystal arrays [3] [4] which increase efficiency when compared to traditional fibre optics. By use of an optical fibre comprised of a photonic crystal array with a continual defect, or symmetry breaking element, running along the central axis of the fibre, light of a particular wavelength can be reflected by the crystal and consequently guided through the fibre [3] [90] [4] [91] [92]. In many cases, optical fibres are formed using 2D structures similar to that of the polychaete worms discussed in section 2.3.2, [47] [91] [66], where an array of rods runs along the length of the fibre in order to create a highly efficient reflecting surface. This communication method produces a highly efficient method for transferring optical data. Other uses for optical photonic crystal structures range from uses in lasers as highly efficient reflectors [93] [94] to the use of high efficiency quasi-ordered photonic crystals in light emitting diodes (LEDs) [5]. In the case of photonic crystal lasers, tunable photonic crystals are being developed in order to produce a variation in the wavelength response of the laser [93] [94]. In addition to this, tunable photonic crystals are currently being investigated for their use in light modulation for optical communications, display, and data storage applications [95]. Tunable devices with the ability to reflect light over the entire visible spectrum when an external input causes deformation of the structure are beginning to be fabricated and are currently under investigation [96].

2.8 Conclusion

A brief overview of some of the many structural colour mechanisms that exist in nature is presented in this chapter. The existence of 1D, 2D and 3D ordered structures has been outlined, with a selection of examples of each case described in detail. In addition to this, some examples of disordered structures have also been highlighted. Examples of organisms that possess these photonic mechanisms are varied and include insects, such as butterflies and beetles, aquatic life, birds and flora. The requirement for colour by these natural samples, that may not be accessible by pigmentation, have led to some elaborate and novel adaptations to traditional 1D, 2D or 3D ordered structures. These photonic structures have been developed predominantly for enhancing appearance, signaling, anti-predatory or camouflage purposes in animals. Photonic structures have been discovered in flora for the purpose of signaling to pollinators and also for aiding photosynthesis in dark conditions. Natural organisms such as these do not have a variety of materials available to them and so high refractive index contrast media are not
generally accessible to them. In order to achieve the required optical effect necessary for survival, an organism may have to overcome this refractive index contrast limitation using a novel structural approach. This is particularly applicable to organisms that require an angle-independent coloured appearance. Periodic photonic crystal structures comprised of low refractive index contrast media generally produce an iridescent optical response. Arranging a single iridescent structure in juxtaposed domains, each possessing a different structural orientation with respect to neighbouring domains, results in reflected wavelengths that are domain-dependent. When viewed macroscopically an additive colour mixing process results and a single average coloured hue is observed. Additive colour mixing is a procedure that is utilised in butterflies and beetles, when using 1D, 2D and 3D ordered photonic structures. The overall additive colour is often angle-independent, something that is usually unobtainable from an ordered photonic crystal structure comprised of low refractive index media alone.

The applications of photonic crystals in the technology sector are wide-ranging and may benefit from a self-assembly approach to mass fabrication. Obtaining a better understanding of the self-assembling mechanisms involved in the production of naturally occurring photonic crystals may improve our current mass-fabrication methods. As nature has been developing photonic structures for hundreds of millions of years, the range of photonic structures present in insects, birds and flora are often very varied in geometry and provide highly tuned optical responses. The variety of photonic structures present in the natural world provides us with an abundance of structures to study in order to better understand how and why they produce their associated optical effects. In addition to this, naturally occurring photonic structures commonly comprise novel mechanisms that are highly tuned to perform a particular optical function and occasionally to compensate for the limited materials available to them. This diverse variety of novel systems and approaches to structural colour found in the natural world has inspired many branches of structural bio-mimetic designs in the technological sector [7] [75] [76] [6].
Chapter 3

Theory

3.1 Introduction

The intensity of electromagnetic reflections from, or transmission through, a boundary
that separates media of different permittivities is defined by the Fresnel equations [18].
When multiple interfaces are present, creating a multilayer system, the reflections from
each interface interfere constructively or destructively in accordance with the phase
difference between each reflected wave. This generates a wavelength-dependent reflection
response. The strong, constructively interfered reflections of certain wavelengths
forms the basis of structural colour. The range of wavelengths reflected from the system
are prohibited to propagate through the structure. Consequently a ‘gap’ forms in the
range of wavelengths that are allowed to propagate through the system. The range of
wavelengths reflected from the system is termed the ‘photonic band-gap’. Alternatively
this range of wavelengths, if different in various directions, is termed the ‘stop-band’.
The allowed modes that form just above the maximum and below the minimum fre-
cquency of the photonic band-gap set up within the structure as standing wave modes.
The configuration of these two standing wave modes within a system of mixed media
directly determines the width of the photonic band-gap due to the corresponding en-
ergy of each mode. The width of the photonic band-gap varies with factors such as
system geometry, refractive index contrast of constituent materials and polarisation of
incident light. The analysis of the electromagnetic field profiles of transmitted modes
at the edge of the band-gap enables the physical and mathematical determination of
its origin and consequently how differences in band-gap width arise.

In this chapter, the theory of the interaction of light with periodic dielectric media
is discussed. Photonic crystal theory is presented through the analysis of field distribu-
tions in periodic photonic systems [20], which quantitatively describes the origin of the
photonic band-gap. This mathematical analysis is presented alongside physical electro-
magnetic principles which, collectively, fully describe the origin of photonic band-gap properties.

3.2 Reflection of electromagnetic waves at an interface

In optical systems, the geometry of an interface upon which light is incident will determine the nature of reflected light. Light incident on an optically smooth interface will result in a mirror-like specular reflection, namely \( \theta_i = -\theta_r \), where \( \theta_i \) is the angle of incidence and \( \theta_r \) is the reflected angle, both measured from the surface normal [18]. In addition to the reflection that occurs, a component of incident light will also be transmitted through the interface. The transmitted light is refracted by an amount determined by the refractive index contrast of the media within which light is propagating. The relationship that governs this is Snell’s law:

\[
n_1 \sin \theta_1 = n_2 \sin \theta_2, \tag{3.1}\n\]

where \( n_1 \) and \( n_2 \) are the refractive indices of the material on the incident side of the interface and the transmitted side of the interface respectively, \( \theta_1 \) and \( \theta_2 \) are the angle of incidence and the transmitted angle, respectively [18]. The reflection and transmission coefficients that determine the amplitude of reflected or transmitted light are determined by the refractive indices of the media on either side of the interface. They are also dependent on the angle of incidence and the polarisation of the incident light. Such polarisation dependence arises from the fundamental continuity conditions that must be conserved across a boundary. According to Gauss’s theorem [97], normal components of electric displacement, \( \mathbf{D} \), and magnetic induction, \( \mathbf{B} \), are conserved on passing a boundary. In addition to this, according to Faraday’s law [97], tangential components of the electric field, \( \mathbf{E} \), and magnetic field, \( \mathbf{H} \), are conserved. Using these boundary conditions, it is possible to obtain the reflection and transmission coefficients for the case where the electric field vector is in the plane of incidence, transverse magnetic (TM), and for the case where the electric field vector is perpendicular to the plane of incident light, transverse electric (TE). The amplitudes of reflected and transmitted TM or TE polarised light from an interface are presented by the Fresnel reflection and transmission coefficients, shown below:

\[
\begin{align*}
r_{\parallel} &= \frac{E_{r,\parallel}}{E_{i,\parallel}} = n_2 \cos \theta_1 - n_1 \cos \theta_2 \quad \text{for TM}, \\
r_{\perp} &= \frac{E_{r,\perp}}{E_{i,\perp}} = -\frac{n_1 \cos \theta_1 - n_2 \cos \theta_2}{n_1 \cos \theta_1 + n_2 \cos \theta_2} \quad \text{for TE}. \tag{3.3}
\end{align*}
\]
where \( r_\| \) and \( r_\perp \) denote the fraction of incident electric field that is reflected for TM and TE polarised light respectively \[18\]. The intensity of the reflected light of each polarisation can be written as

\[
R_\perp = r_\perp^* r_\perp = \frac{\sin^2(\theta_1 - \theta_2)}{\sin^2(\theta_1 + \theta_2)}, \quad (3.6a)
\]

\[
R_\| = r_\|^* r_\| = \frac{\tan^2(\theta_1 - \theta_2)}{\tan^2(\theta_1 + \theta_2)}, \quad (3.6b)
\]

The functional response of each of these reflection coefficients differs greatly. This results in a distinct difference in the reflection responses of TM and TE polarised light when the incident angle is altered. Equation 3.6a, for the case of TE polarised light, can never equal zero as, according to Snell’s law, \( \theta_1 \neq \theta_2 \). Equation 3.6b, for the case of TM polarised light, may equal zero when \( \theta_1 + \theta_2 = \pi/2 \). When this condition is satisfied, TM polarised light is purely transmitted and only TE polarised light can be reflected. When this condition is met, the incident light is at the Brewster angle \( (\theta_1 = \theta_B) \) \[18\].

Using Snell’s law (equation 3.1), the Brewster angle can be expressed as

\[
\theta_B = \arctan \left( \frac{n_2}{n_1} \right). \quad (3.7)
\]

### 3.2.1 Thin film interference

The Fresnel reflection coefficients for a single interface may be adapted to obtain reflection coefficients from a two interface system. The two interface system comprises three layers of different refractive indices: an incident medium, \( n_1 \), the thin film medium, \( n_2 \), and the exit medium, \( n_3 \), depicted in figure 3.1. The sum of the reflection coefficients from the first interface, the second interface and the many possible back reflections from within the thin film, will reveal a new set of thin film Fresnel equations. The thin film Fresnel equations are dependent on the path difference, and therefore the phase difference, between the multiple reflections from each of the two layers. Therefore an additional phase variable is present for all reflections with the exception of the reflection that occurs from the first interface only. The derivation that follows is for the amplitude coefficient of reflection of a thin film \[98\] \[99\].

As light impinges on the first interface of a thin film system (figure 3.1), a fraction of
3. Theory

Figure 3.1: A schematic diagram of the possible reflection and transmission processes that occur at the interfaces of a thin film. Light that is incident upon the first interface can either be reflected, $r_{12}$, or transmitted, $t_{12}$. These respective fractions of reflected and transmitted light are defined by the Fresnel equations, equations 3.2-3.5 in section 3.2 and are polarisation-dependent. The light that is transmitted may incur additional reflections from the second interface. A number of reflections may occur within the thin film before a second transmission, $t_{21}$, occurs. Due to the presence of a second interface in the system, the relative phase of reflected and transmitted waves from each boundary must be considered in order for the overall reflection amplitude to be calculated.
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Figure 3.2: A schematic diagram showing how two waves reflected from the two interfaces of a thin film may result in a phase difference. The optical path difference of the two waves can be calculated by trigonometric analysis by consideration of the two reflected angles, refractive indices of the two media and the thickness of the thin film. From this the phase difference can be calculated and is presented in equation 3.9.

When light is reflected, \( r_{12} \), and the rest is transmitted, \( t_{12} \). These amplitude coefficients are simply those discussed previously in section 3.2, defined by equations 3.2-3.5. They each remain polarisation dependent. A fraction of the transmitted light will either transmit through the second interface or undergo a reflection from it, \( r_{23} \). It may then transmit back through the first interface, \( t_{21} \), or experience a number of similar reflections within the thin film. There are, therefore, a series of possible reflection and transmission processes that may occur between the two interfaces of a thin film. Due to the introduction of a second interface into the system, the relative phase of reflected waves from each boundary must be considered. The phase difference, \( \Delta \phi \), of two waves is simply written as

\[
\Delta \phi = k \times OPD \pm \pi, \quad (3.8)
\]

where \( k \) is the wavenumber in the incident medium and \( OPD \) is the optical path difference, equal to \( 2n_2 d \cos \theta_2 \) for the case shown in figure 3.2 [18]. The additional \( \pi \) term arises from the relative phase change between the two interfering waves reflected from each boundary, where one reflection has occurred from a low-to-high refractive index. This relative phase change arises when the thin film is surrounded by the same medium. For a thin film this phase difference is given by

\[
\Delta \phi = k \cdot 2n_2 d \cos \theta_2 \pm \pi \Rightarrow (m + 1) \frac{2\pi}{\lambda} n_2 d \cos \theta_2 \pm \pi, \quad (3.9)
\]

where \( \theta_2 \) is the transmitted angle with respect to the surface normal, as shown in figure 37.
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3.2, and \( m \) is the number of internal reflections within the thin film and determines the optical path within the film. The variable, \( m \), will always be an odd integer for any beam that is included in the calculation of the total reflection coefficient for a thin film, with the exception of beam \( r_{12} \). If \( \delta = \frac{2\pi}{\lambda} n_2 \cos \theta_2 \), the reflection coefficient that represents the summation of all contributing reflections, along with their corresponding phases, can be represented as the series presented below:

\[
A_r = r_{12} + t_{12} r_{23} t_{21} e^{-i2\delta} + t_{12} r_{23}^2 r_{21} t_{21} e^{-i4\delta} + t_{12} r_{23}^3 r_{21}^2 t_{21} e^{-i6\delta} + \ldots \quad (3.10)
\]

Such an expression can be represented as an infinite series:

\[
A_r = r_{12} + t_{12} r_{23} t_{21} e^{-i2\delta} \sum_{j=0}^{\infty} (r_{23} r_{21})^j e^{-i2j\delta}. \quad (3.11)
\]

In this case \( j = n - 1 \) where \( 2n = (m + 1) \) and \( n \) is the order number of the reflected beam. The sum of a geometric series has the property of \( \sum_{j=0}^{\infty} (r)^j = \frac{1}{1-r} \), and so equation 3.11 may be rewritten as

\[
A_r = r_{12} + \frac{t_{12} r_{23} t_{21} e^{-i2\delta}}{1 - r_{23} r_{21} e^{-i2\delta}}. \quad (3.12)
\]

From the Fresnel reflection equations 3.2 and 3.3 for a single interface, it is evident that \( r_{ij} = -r_{ji} \). Equation 3.12 can, therefore, be expressed as

\[
A_r = r_{12} + \frac{t_{12} r_{23} t_{21} e^{-i2\delta}}{1 + r_{23} r_{21} e^{-i2\delta}}. \quad (3.13)
\]

By rearranging equation 3.13, a total reflection amplitude coefficient for a thin film, purely in terms of individual reflection coefficients, can be obtained and is presented in equation 3.14 below:

\[
A_r = \frac{r_{12} + r_{23} e^{-i2\delta}}{1 + r_{23} r_{12} e^{-i2\delta}}. \quad (3.14)
\]

This result presents the reflection amplitude from a thin film. Each of the terms used in the derivation are Fresnel amplitude coefficients from a single interface, each possessing the polarisation of the incident light. As a result, equation 3.14 applies to both TM or TE polarisations. The reflected intensity can, again, be represented as \( R = A_r^* A_r \), which yields the reflectivity of a thin film and is presented below in equation 3.15:

\[
R = \frac{r_{12}^2 + r_{23}^2 + 2 r_{12} r_{23} \cos(2\delta)}{1 + r_{23}^2 r_{12}^2 + 2 r_{12} r_{23} \cos(2\delta)}. \quad (3.15)
\]
The distinct difference between the reflectivity equations for a single interface, 3.6b and 3.6a, and a thin film, 3.15, is the introduction of phase dependent terms. Consequently, the preferential reflections of certain wavelengths result through constructive interference.

### 3.2.2 Constructive interference and iridescence

Light incident on a thin film at normal incidence produces reflected, or transmitted, intensity maxima for certain incident wavelengths that are determined by the path difference and, therefore, the resulting phases of combining reflected waves. The phase difference, $\Delta \phi$, described by equation 3.9 will equal an even multiple of $\pi$ for constructively interfered reflected waves and an odd multiple of $\pi$ for constructively interfered transmitted waves. Increasing the angle of incidence in a thin film alters the optical path difference. The optical path difference varies as $\cos \theta_2$, and so by increasing $\theta_1$, and therefore $\theta_2$ according to Snell’s law (equation 3.1) and as shown in figure 3.2, the optical path difference decreases. Therefore in order for the constructive interference condition to hold, the incident wavevector must increase (equation 3.9) and so the wavelength must decrease. The phenomenon which results is called iridescence, namely, the change in reflected wavelength by changing the angle of incidence. This property can not be achieved through pigmentedary colour, but is unique to structural colour. The physical origin of the iridescence produced by a multilayer can be determined by analysing the wavevector response produced from a periodic array when the angle of incidence is changed. The following treatment explores the effect that non-normal incident waves have on the reflected wavelength by the use of trigonometry and momentum conservation.

An incident wave at normal incidence to a multilayer, which has periodicity purely in the $\hat{z}$-direction, will have a wavevector $k_0 = k_z$, with no $\hat{x}$-component. In this case, the incident light is traveling purely in the direction of the periodicity of the structure. At an angle, $\theta_1$, away from normal incidence, as shown in figure 3.3, this is no longer the case. The incoming wavevector may then be considered as component parts in $x$ and $z$, with the magnitudes of each related as

$$ k_0^2 = k_x^2 + k_z^2, \quad (3.16) $$

where $k_x$ and $k_z$ are the $\hat{x}$- and $\hat{z}$-components of the incident wavevector, $k_0$, respectively. At normal incidence, the incident wavevector is directed purely along the direction of periodicity of the multilayer and there is no $\hat{x}$-wavevector component. As the angle of incidence, $\theta_1$, increases, $k_x$ also increases. However, the wavevector in the direction of periodicity, $k_z$, must be equivalent in both cases in order for the appropri-
ate interference conditions to be realised. Applying this increase in $k_x$ and maintaining an unchanged $k_z$ in equation 3.16 results in the apparent increase of $k_0$. Namely, a larger incident wavevector, or smaller wavelength, is required when incident angle is increased in order to observe the same constructive/destructive interference effects. Consequently, for a constructively interfered reflection, the reflected wavelength from the multilayer also reduces when incident angle is increased by the conservation of momentum. In turn, this produces the phenomenon of iridescence which manifests as a decrease in reflected wavelength when the incident angle is increased from the surface normal to the multilayer.

In semi-infinite systems with no inherent absorption associated with the constituent materials, the frequencies over which this reflection of particular wavelengths exists, is referred to as a photonic band-gap. If this band-gap is large enough, there may be a range of frequencies that are always reflected over all incident angles, $\theta$. This is known as a complete band-gap [20]. For the cases of 2D and 3D photonic crystal structures, there may be many different directions or orientations within the structure that have associated periodicities. The resonances that are required for the production of a photonic band-gap may occur in each of the multiple directions of the structure that have a periodic nature. If a complete photonic band-gap is to occur in a 2D or 3D structure, each direction through the crystal that holds a periodicity must support a band-gap that contains that same frequency, or frequency range. These periodic directions are dictated by the symmetry of the photonic crystal, in particular the points of high-symmetry inherent in the geometry of a given photonic crystal which can be determined by the first Brillouin zone of the structure. The direction between two points of high-symmetry within a particular geometry indicates a direction through the crystal that possesses a unique structural periodicity. In these directions, effective periodic geometric planes give rise to photonic band-gaps. The photonic band-gap along each direction of high symmetry can be represented on a band diagram. Figure 3.4 presents the photonic band structures of two 2D hexagonal arrays of rods in air. The structures that produce the band structures in figures 3.4(a) and (b) differ only by the refractive indices of the rods which are (a) $n = 1.56$ and (b) $n = 2.9$. The high symmetry points $\Gamma$, $M$ and $K$ of the structure have been identified on the band diagram and also in the inset of figures 3.4(a) and (b) where the first Brillouin zone of the structure has been depicted. The corresponding band-gaps along each symmetry direction are clearly identifiable in the band diagrams presented in figures 3.4(a) and (b). The width of each photonic band-gap along each symmetry direction widens when the refractive index contrast of the system increases. As a direct result from this, the structure with refractive index contrast of $n = 2.9$ has a complete band-gap, whereas the structure with a low refractive index contrast does not.
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Figure 3.3: A multilayer comprising media of differing refractive indices reflects a selective band of wavelengths, determined by the geometry of the structure. The wavelength band that is reflected from the system changes when incident angle is changed. The angle-dependence of the reflected wavelengths from a multilayer can be determined by considering the component parts of the incoming wavevector. At normal incidence the incoming wavevector is purely in the direction of periodicity. However, at a non-normal incident angle the incoming wavevector has component parts in both the direction of periodicity and the \( \hat{x} \)-direction. The wavevector in the direction of periodicity, \( \hat{z} \), must be equivalent in both cases in order for the appropriate interference condition to be realised. Due to the additional \( \hat{x} \) component in the non-normally incident case, a larger incoming wavevector, or smaller wavelength, is required. Consequently, the reflected wavelength from the multilayer reduces when incident angle is increased.
3. Theory

Figure 3.4: The band structures of a 2D hexagonal photonic crystal of dielectric rods with refractive indices of (a) $n=1.56$ and (b) $n=2.9$ in air. Photonic band-gaps appear in both instances and are represented by a grey shaded area. A complete photonic band-gap is present in (b) where the refractive index contrast is high. The insets represent (left) the 2D hexagonal array of dielectric rods and (right) the Brillouin zone of the 2D photonic crystal structure and the points of high symmetry have been labelled.

Photonic crystal theory describes the physical mechanisms behind determining the width of a photonic band-gap via mathematical analysis. The following section presents both the mathematics and the physics of the origin of the photonic band-gap.

3.3 Photonic crystal theory

The photonic crystal theory that follows is undertaken using the simplest periodic photonic crystal, a 1D multilayer, as an example. The theory applies to multi-dimensional photonic crystals, where there may exist periodicities along various symmetry directions within the photonic crystal geometry. Both the mathematics, through eigenvalue analysis [20], and the physics of the photonic band-gap is presented. The majority of the mathematical eigenvalue analysis regarding photonic crystal theory was initially developed by Yablonovitch [21] and John [100] in 1987. The mathematical eigenvalue analysis considers photons impinging on a periodic photonic structure as an analogy with electrons within a periodic potential in solid state physics. The mathematical eigenvalue analysis that follows employs this mathematical analogy and is predominantly inspired by the full mathematical analysis presented by Joannopoulos [20]. In addition to this, this section also explores the equivalent physical concepts behind the
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photonic band-gap by implementing general electromagnetic theory and principles [97] [18].

3.3.1 Dispersion

The dispersion of a homogeneous material is determined by its permittivity and dictates how the phase velocity of incident light is perturbed by a material. The dispersion associated with a linearly dispersive material, with refractive index $n$, is determined by the relation

$$\omega(k) = \frac{ck}{n}, \quad (3.17)$$

where $\omega$ is the angular frequency, $k$ is the wavenumber and $c$ is the speed of light in free-space. The dispersion diagram presented in figure 3.5(a) displays the dispersion of three linearly dispersive materials with refractive indices $n_1 < n_2 < n_3$.

The first Brillouin zone of a periodic structure defines the smallest region in $k$-space that can fully define the structure when repeated. The Brillouin zone boundary of the structure can be labelled on the $k$-axis of its associated dispersion diagram. In the reduced zone scheme (figure 3.5(b)) the dispersion curve that lies outside of the first Brillouin zone can be folded back to lie within the first Brillouin zone. The dispersion diagram can be thought of as the band structure of the system, where the band-index denotes the Brillouin zone from which each ‘band’ originates. The dispersion of the non-periodic material, $n_1$, has been displayed in the reduced zone scheme in figure 3.5(b) where the band index has been labelled. The periodicity needed to define a Brillouin zone boundary has been assigned to the material although the refractive index throughout the structure remains constant in this case. When two materials with different refractive indices are arranged in a multilayer with this same periodicity, the band diagram changes drastically at the structure’s Brillouin zone boundary, as depicted in figure 3.6 [20]. These changes arise due to the interference effects that are now present and attributable to the periodic nature of the 1D array of thin films. The dispersion of the multilayer, presented in figure 3.6, therefore displays the presence of photonic band-gaps.

The exact electric field distributions within a periodic refractive index system determine the size of the photonic band-gap. The mathematical and physical theory that follows is based on the eigenmode analysis of electromagnetic waves in mixed, periodic, dielectric media. From this, it is possible to determine such field distributions and, ultimately, the origin of the photonic band gap.
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Figure 3.5: (a) The dispersion of 3 individual materials with refractive indices of $n_1$, $n_2$ and $n_3$ where $n_1 < n_2 < n_3$. (b) The dispersion of a single material represented in the reduced zone scheme. The Brillouin zone boundaries are labelled at $\frac{-\pi}{a}$ and at $\frac{\pi}{a}$ and are determined by the unit cell lattice constant, $a$, of the structure. When represented in the reduced zone scheme, the dispersion can be referred to in terms of ‘bands’. The band number denotes the Brillouin zone from which it originates. [20].

Figure 3.6: The band diagram of a 1D photonic multilayer structure comprising periodic media of differing refractive indices. Photonic band-gaps appear at the Brillouin zone boundaries where standing waves are set up within the system. The position and width of the photonic band-gap is determined by the geometry of the structure including lattice constant, filling fraction and refractive index contrast. [20].
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3.3.2 Maxwell’s equations and the master equation

Maxwell’s equations define the complex relationship between electric $E(\mathbf{r}, t)$ and magnetic $H(\mathbf{r}, t)$ fields that vary with space, $\mathbf{r}$, and time, $t$ [97]. In order to be evaluated by Maxwell’s equations, such electric and magnetic fields can be represented by equations 3.18a and 3.18b below:

$$H(\mathbf{r}, t) = H(\mathbf{r})e^{-i\omega t}, \quad (3.18a)$$

$$E(\mathbf{r}, t) = E(\mathbf{r})e^{-i\omega t}. \quad (3.18b)$$

Although these fields are represented as a monochromatic ansatz, the linearity of Maxwell’s equations justifies their use. The fundamental forms of Maxwell’s equations may be manipulated in order to describe how electromagnetic radiation behaves in particular systems. Naturally occurring photonic crystal structures, such as those found on butterflies and beetles, are purely comprised of dielectric media. When applied to mixed, dielectric, non-magnetic, isotropic and lossless media and ignoring any material dispersion, Maxwell’s equations can be written in the following form

$$\nabla \cdot H(\mathbf{r}, t) = 0, \quad (3.19a)$$

$$\nabla \cdot [\epsilon(\mathbf{r})E(\mathbf{r}, t)] = 0, \quad (3.19b)$$

$$\nabla \times E(\mathbf{r}, t) + \mu_0 \frac{\partial H(\mathbf{r}, t)}{\partial t} = 0, \quad (3.19c)$$

$$\nabla \times H(\mathbf{r}, t) - \epsilon_0 \epsilon(\mathbf{r}) \frac{\partial E(\mathbf{r}, t)}{\partial t} = 0, \quad (3.19d)$$

where $\epsilon_0$ is the permittivity of free space and $\mu_0$ is the permeability of free space [20]. These equations hold in SI units. The variable $\epsilon(\mathbf{r})$ defines the spatial dependence of the permittivity within the system and is, therefore, the variable that defines the periodicity of the structure. Equations 3.19a and 3.19b represent the transversality requirement. By applying the two remaining Maxwell’s equations, 3.19c and 3.19d, to the electric and magnetic fields previously defined by equations 3.18a and 3.18b, the following relations are obtained:

$$\nabla \times E(\mathbf{r}) - i\omega \mu_0 H(\mathbf{r}) = 0, \quad (3.20a)$$
\[ \nabla \times \mathbf{H}(\mathbf{r}) + i \omega \epsilon_0 \epsilon(\mathbf{r}) \mathbf{E}(\mathbf{r}) = 0. \]  
(3.20b)

Along with the transversality requirement, equations 3.20a and 3.20b fully describe the behaviour of electromagnetic radiation in the system defined by \( \epsilon(\mathbf{r}) \). It is possible to combine equations 3.20a and 3.20b to form a single master equation [20]. Dividing equation 3.20b by \( \epsilon(\mathbf{r}) \) and taking the curl of the resulting equation results in the following Hermitian relation:

\[ \nabla \times \left( \frac{1}{\epsilon(\mathbf{r})} \nabla \times \mathbf{H}(\mathbf{r}) \right) + i \omega \epsilon_0 \nabla \times \mathbf{E}(\mathbf{r}) = 0. \]  
(3.21)

On substituting equation 3.21 into equation 3.20a, and using the relation \( c = \frac{1}{\sqrt{\epsilon_0 \mu_0}} \), it is possible to obtain the master equation presented in equation 3.22, below:

\[ \nabla \times \left( \frac{1}{\epsilon(\mathbf{r})} \nabla \times \mathbf{H}(\mathbf{r}) \right) = \left( \frac{\omega}{c} \right)^2 \mathbf{H}(\mathbf{r}). \]  
(3.22)

The master equation is purely in terms of magnetic field, \( \mathbf{H}(\mathbf{r}) \), and fully describes the behaviour of a magnetic field in a system defined by \( \epsilon(\mathbf{r}) \) [20]. The electric field solutions can be obtained from this master equation by applying equation 3.20b. The master equation is in the form of a classic eigenmode problem and so can be expressed as an eigenvalue equation, explicitly:

\[ \hat{\Theta} \mathbf{H}(\mathbf{r}) = \left( \frac{\omega}{c} \right)^2 \mathbf{H}(\mathbf{r}). \]  
(3.23)

The master equation determines the allowed modes, \( \mathbf{H}(\mathbf{r}) \), that can exist with a frequency eigenvalue of \( \omega \) within a mixed dielectric system. The operator \( \hat{\Theta} \) includes the periodicity properties of the photonic structure, defined by \( \epsilon(\mathbf{r}) \). The allowed modes, \( \mathbf{H}(\mathbf{r}) \), are permitted to exist within the structure and can, therefore, be transmitted through the system. Prohibited modes will be reflected from the structure.

### 3.3.3 Mathematical and physical consequences of the master equation

The master equation is often constructed in terms of the magnetic field in order for it to remain Hermitian [20]. Hermitian operators have the property that

\[ \int d^3 \mathbf{r} \mathbf{A}^*(\mathbf{r}) \cdot \hat{\Theta} \mathbf{B}(\mathbf{r}) = \int d^3 \mathbf{r} (\hat{\Theta} \mathbf{A}(\mathbf{r}))^* \cdot \mathbf{B}(\mathbf{r}). \]  
(3.24)

The integral over all space of a dot product of two fields, \( \mathbf{A}(\mathbf{r}) \) and \( \mathbf{B}(\mathbf{r}) \), in this way is called the ‘inner product’ [20]. For simplicity, the inner product of two variables may
be given the following notation:

$$\int d^3r (\hat{\Theta} A(r))^* \cdot B(r) = (\hat{\Theta} A, B).$$ \hfill (3.25)$$

Therefore, the Hermitian identity of equation 3.24 can be rewritten as

$$(A, \hat{\Theta} B) = (\hat{\Theta} A, B).$$ \hfill (3.26)$$

Utilising this property of Hermitian operators in the mathematical analysis of the master equation, assists the determination of the origin of the photonic band-gap.

### 3.3.3.1 Orthogonality

On consideration of two allowed modes, $H_1$ and $H_2$, of a periodic mixed dielectric system, equation 3.23 can be written as

$$(H_2, \hat{\Theta} H_1) = \left(\frac{\omega_1}{c}\right)^2 (H_2, H_1).$$ \hfill (3.27)$$

As the master equation is Hermitian, the identity $(H_2, \hat{\Theta} H_1) = (\hat{\Theta} H_2, H_1)$ holds, and so from equation 3.27 the following equality can be produced

$$(H_2, \hat{\Theta} H_1) = \left(\frac{\omega_1}{c}\right)^2 (H_2, H_1) = (\hat{\Theta} H_2, H_1) = \left(\frac{\omega_2}{c}\right)^2 (H_2, H_1).$$ \hfill (3.28)$$

Rearranging this equality, by considering only terms that contain the two allowed eigenfrequencies, obtains the following relation:

$$(\omega_1^2 - \omega_2^2)(H_2, H_1) = 0.$$ \hfill (3.29)$$

This relation describes one of the key principles behind the origin of the photonic band-gap. It states that either the inner product of the two allowed modes, $H_1$ and $H_2$, will equal zero, or the frequency eigenvalues of the two modes are equal. A photonic band-gap, such as that illustrated in figure 3.6, arises at the Brillouin zone boundary where two allowed modes of a system possess two different eigenfrequencies. Equation 3.29, therefore demonstrates that the inner product of the two allowed modes, $H_1$ and $H_2$, at the edge of a photonic band-gap must equal zero, explicitly

$$\int d^3r H_2^*(r) \cdot H_1(r) = 0.$$ \hfill (3.30)$$

For a single wavevector, the inner product of $H_1$ and $H_2$ can only be zero when the two fields are out of phase by 90°, where they are said to be orthogonal.

The multilayer and associated band diagram presented in figure 3.6 depicts the
dispersion of a photonic band-gap system. The two allowed modes that define the edge of the photonic band-gap, at the Brillouin zone boundary, have been determined to be orthogonal through mathematics. At the Brillouin zone boundary, defined by the structure, the wavevector of the incident light is such that harmonic modes may be set up within the system. Such standing wave states have a group velocity of zero, by definition, therefore this electromagnetic feature is represented on the dispersion diagram as a gradient of zero at the Brillouin zone boundaries [101]. As there are two solutions to a standing wave, depending on the starting phase condition of the wave, there are two points on the dispersion diagram, for a single wavevector, that have a group velocity of zero [101]. The two allowed standing wave modes must be set up within the multilayer with antinodes appearing in either the high permittivity region or the low permittivity region so they do not break the symmetry of the unit cell about its centre. The symmetry of the unit cell dictates where the antinodes of each standing wave can lie, which results in these two modes being orthogonal.

The field profile of each standing wave within the periodic system, determines the energy, and therefore the frequency, of each mode that defines the edge of the photonic band-gap. The frequencies of each mode can be determined by the variational theorem.

3.3.3.2 The variational theorem

The field profiles of the two orthogonal modes, that define the edge of the photonic band-gap, have been determined to possess antinodes in either the high or low permittivity regions of the system. The dielectric region where the majority of the fields are situated is determined by the position of the antinodes of each field profile. This directly affects the corresponding energetics of each mode. To determine which mode is the high, or low, frequency mode the master equation is again employed. The master equation, 3.23, can be written as

\[
\begin{align*}
&\left(\mathbf{H}, \hat{\Theta} \mathbf{H} \right) = \left( \frac{\omega}{c} \right)^2, \\
&\left( \mathbf{H}, \mathbf{H} \right) = \left( \frac{\omega}{c} \right)^2.
\end{align*}
\]

When the left-hand side of this equation is equated to a functional \( F(\mathbf{H}) \), the lowest frequency eigenvalue of the system occurs for the field that minimises this functional. This result is referred to as the variational principle [20]. It is possible to use this result to identify the frequency of each standing wave mode from their field profiles within the system and the relative proportions of fields in the high or low permittivity regions. The numerator on the right hand side of equation 3.31 can be written explicitly as

\[
\left( \mathbf{H}, \hat{\Theta} \mathbf{H} \right) = \int d^3 r \, \mathbf{H}^\ast \cdot \nabla \times \left( \frac{1}{\epsilon(r)} \nabla \times \mathbf{H} \right).
\]

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By substituting rearranged forms of equations 3.20a and 3.20b into equation 3.32, this can be rewritten as

\[ (\mathbf{H}, \hat{\mathbf{H}}) = \int d^3r \frac{\epsilon_0}{\mu_0} |\nabla \times \mathbf{E}|^2. \]  

(3.33)

Similarly, using the scalar triple product and equation 3.20b, the denominator can be shown to be

\[ (\mathbf{H}, \mathbf{H}) = \int d^3r \left( \frac{\epsilon}{\epsilon(r)} \right)^2 \frac{1}{\epsilon(r)} |\nabla \times \mathbf{H}|^2 = \int d^3r c_0^2 \epsilon(r) |\mathbf{E}|^2. \]  

(3.34)

By substituting equations 3.33 and 3.34 into equation 3.31, the following equation purely in terms of electric field, \( \mathbf{E} \), is obtained

\[ \left( \frac{\omega}{c} \right)^2 = \frac{\int d^3r \frac{\epsilon_0}{\mu_0} |\nabla \times \mathbf{E}|^2}{\int d^3r c_0^2 \epsilon(r) |\mathbf{E}|^2} = \frac{\int d^3r |\nabla \times \mathbf{E}|^2}{\int d^3r c^2 \epsilon(r) |\mathbf{E}|^2}. \]  

(3.35)

From this result, it is possible to identify the reciprocal relationship between the frequency, \( \omega \), of the allowed mode and the permittivity, \( \epsilon(r) \), of the dielectric regions which contain the antinodes of the mode. When applied to the configurations of the two orthogonal standing wave modes in a multilayer system, it is evident that the low frequency modes have antinodes positioned in the regions of high permittivity and high frequency modes in regions of low permittivity.

The same result can be described physically, again, by analysis of the dispersion diagram presented in figure 3.6. The two, orthogonal, standing wave modes that define the lower and upper limit of the photonic band-gap are positioned just above the dispersion line for the high permittivity medium (usually a dielectric), and just below the dispersion line for the low permittivity medium (often air). The position of each mode relative to the dispersion lines for each of the multilayer’s constituent materials is directly indicated by where the majority of the fields of each standing wave are situated. Closer to the gamma point, where the periodicity is much smaller than the wavelength of incident light, the periodicity of the structure does not influence an impinging photon, and so the dispersion follows that defined by an effective refractive index of the two materials. The bands that form by standing waves present in either the high permittivity medium or the low permittivity medium are often referred to as the dielectric band and the air band respectively.

3.3.3.3 Field profiles and energy of orthogonal modes

In minimising the variational equation, the lowest energy state of a mixed dielectric system is determined to be within the regions of highest permittivity. This state of
minimum energy is generally the preferred state for a standing wave to concentrate the majority of its fields [102] [20]. The orthogonality constraint concurrently positions the aninodes of the orthogonal modes in the alternative, higher energy state with a node in the high permittivity region [20]. However, due to the preference to sit in a lower energy state, the field profile of the higher energy mode deviates greatly from a standard \( \cos / \sin \) profile. Such deviations become more apparent as the refractive index contrast increases. The field configurations presented in figures 3.7 and 3.8 show how increasing refractive index contrast alters the field profiles of the standing waves set up at the Brillouin zone boundary of a multilayer. For a low refractive index contrast system, figure 3.7, the field profiles of the standing wave modes approximately follow standard \( \cos \) and \( \sin \) profiles. For a high refractive index contrast system, figure 3.8, the field profiles are perturbed from this [20]. The fields of the dielectric mode are confined to the lower energy, high permittivity regions, consequently lowering the frequency of the lower band edge. The air mode, forced to be orthogonal to the dielectric mode, retains a large proportion of its fields in the lower energy, high permittivity region, whilst maintaining an antinode in the low permittivity regions. Consequently, the field profiles of each standing wave mode for a high refractive index contrast system are no longer comparable and the energy density of each standing wave mode differs greatly. The resultant photonic band-gap width from the high refractive-index-contrast system, therefore, is increased. The total, physical energy of each mode determines its frequency. The total, physical energy of an electromagnetic field may be expressed as

\[
U = \frac{\varepsilon_0}{2} \int d^3 r \varepsilon(r) |E(r)|^2.
\]  

(3.36)

The physical energy of each of the modes is determined by both the permittivity and the square of the electric field strength in each region of the mixed dielectric system. Since, for the high refractive index contrast case, the field profiles of each mode differ greatly over each permittivity region, as shown in figure 3.8, the corresponding energy densities will also be distinctly different. The denominator of equation 3.35 depends on the physical energy of the electromagnetic wave and is inversely proportional to the eigenfrequencies of the system. Therefore, the eigenfrequencies of each mode will depend on the local energy density of each field profile as an inversely proportional relationship. The nature of each field profile and associated energy densities will, therefore, give rise to the resulting frequency difference between the two standing wave configurations. This frequency difference will inevitably increase as the refractive index contrast of the system increases.

The concentration of fields in each permittivity region is crucial for determining the frequency difference of each standing wave mode and, therefore, the width of the
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Figure 3.7: Standing waves that configure within a multilayer system comprising alternating permittivities. When the refractive index contrast in a periodic photonic system is low, the field profiles of each standing wave mode appear similar to \( \sin/cos \) waves with maxima in either the high or the low permittivity regions. At the upper edge of a photonic band-gap, or in the ‘air band’, a standing wave is set up with anti-nodes in the low permittivity region. At the lower edge of a photonic band gap, or in the ‘dielectric band’, a standing wave is set up with anti-nodes in the contrasting region of high permittivity. [20].

Figure 3.8: Standing waves that configure within a multilayer system comprising alternating permittivities. In this case the refractive index contrast is high and so the field profile of each standing wave mode deviates greatly from the \( \sin/cos \) waves that set up in the low refractive index contrast system, 3.7. The standing wave that configures with maxima in the high permittivity regions remains approximately sinusoidal. The standing wave with maxima in the low permittivity regions is forced to be orthogonal to the lower energy state and, as antinodes must be present in the low permittivity regions, the field profile deforms greatly from a standard cosine curve. [20].
photonic band-gap. The concentration of fields present in the high permittivity region for each orthogonal mode is called ‘the concentration factor’. The next section discusses the ways in which the concentration factor of a photonic crystal structure may differ when the polarisation or geometry of a structure, particularly within multi-dimensional structure, is altered.

3.3.3.4 Concentration factor

In minimising the variational equation the minimum energy state of an electromagnetic field within a mixed dielectric system was determined to be in the region of highest permittivity. The previous section described the field distributions of each standing wave mode at the edges of the photonic band-gap. Consequently the lowest frequency standing wave mode of the system has antinodes in the high permittivity region, where the majority of the field is concentrated. The orthogonal, higher frequency mode is forced to have antinodes in the low permittivity regions, yet there exists a fraction of high fields in the lower energy, high permittivity region. The frequency of each standing wave mode can be determined by equation 3.35 from each field profile. The concentration factor of an individual field distribution is defined as the fraction of energy of the whole system stored in the electric field within the high permittivity regions of a system. It can be expressed as

\[
Concentration\ factor = \frac{\int_{\epsilon_{\text{high}}} d^3r \epsilon(r) |E(r)|^2}{\int d^3r \epsilon(r) |E(r)|^2}.
\]

(3.37)

The concentration factor of each of the modes that define the edges of the photonic band-gap can be determined from their associated field profiles. The proportion of fields in each of the high or low permittivity regions for an individual field profile determines the energy density and therefore frequency of the mode. The concentration factor of each field profile can directly determine the width of the photonic band-gap.

The boundary conditions discussed in section 3.2 revealed that tangential components of \( \mathbf{E} \) must be continuous when crossing a boundary and normal components of \( \mathbf{D} \) must be continuous. When these boundary conditions are applied to electromagnetic waves impinging on various photonic crystal geometries, it is evident that the geometry and the polarisation of the electric field must be considered when determining the field strength of an electromagnetic wave crossing a boundary. As a direct consequence, the geometry and polarisation of electric field of an impinging electromagnetic field will affect the concentration factors of each standing wave mode, and therefore, the size of the photonic band-gap [20].

Consider the standing wave associated with the air band, forced to be orthogonal
to the lowest energy standing wave state of the dielectric band. The energy densities of electric field within a high permittivity medium, $U_1$, and a lower permittivity medium, $U_2$, can be expressed as

$$U_1 = \epsilon_{\text{high}} |E_1|^2,$$  

(3.38)

$$U_2 = \epsilon_{\text{low}} |E_2|^2.$$  

(3.39)

The polarisation of electric field crossing a boundary from the high permittivity region (1), to a region of lower permittivity (2) determines the change in energy density across that boundary. When an electric field impinges on this boundary perpendicularly, the conservation of $D$ across the boundary, explicitly $\epsilon_{\text{high}} E_1 = \epsilon_{\text{low}} E_2$, results in the following energy relationship

$$U_2 = \frac{\epsilon_{\text{high}}}{\epsilon_{\text{low}}} U_1.$$  

(3.40)

Namely, the electric field energy density within the low permittivity region (2) will be larger than that within the high permittivity region (1). Qualitatively, this suggests that the fields are mainly contained within the low permittivity region and so a low concentration factor results [20].

When an electric field impinges on a boundary tangentially from a high permittivity medium to a low permittivity medium, $E_\parallel$ is conserved, explicitly, $E_1 = E_2$ and the following energy relationship is observed

$$U_2 = \frac{\epsilon_{\text{low}}}{\epsilon_{\text{high}}} U_1.$$  

(3.41)

Namely, the electric field energy density within the high permittivity region (1) is very high, and so a high concentration factor results [20]. These distinct differences in concentration factor for the field profile of the standing wave of the air band have been brought about purely by changing the polarisation state of electromagnetic radiation within the same geometry. This will result in a distinct difference in band-gap width for the two polarisation states.

### 3.3.4 The scalability of Maxwell’s equations

Let us again consider an ideal multilayer, figure 3.9. The width of a photonic band-gap is dictated by many factors as discussed in previous sections, 3.3.3.2-3.3.3.4. The frequency at which the resonance occurs is dictated by how standing waves arrange within periodic media at the Brillouin zone boundary. It is, therefore, dependent on
Figure 3.9: An example of a scaled photonic system. This example shows a specific case of \( s = 0.5 \), i.e. the system has been reduced in size by half. The relationship between the variable \( r \) and \( r' \) is also depicted.

The incident wavevector and the lattice constant of the structure. For media which have a non frequency-dependent dispersion, changing the periodicity of the structure will alter the resonant condition, and a different incident wavevector will be required to produce the necessary harmonic resonances.

In order to examine how the master equation scales with length, two systems are analysed and are presented in figure 3.9. The first possesses a periodicity defined by \( \epsilon(r) \), and the resultant master equation is simply that of equation 3.22. The second has been scaled in size by a scaling factor, \( s \). The scaling transformation \( r' = sr \) has been applied to the original system to produce the scaled system with a resulting periodicity of \( \epsilon'(r') \) [20]. Applying this change of variable, and the consequent change in \( \nabla \), namely \( \nabla = s\nabla' \), to the original master equation, equation 3.22, results in the following:

\[
s\nabla' \times \left( \frac{1}{\epsilon'(r'/s)} \right) s\nabla' \times \mathbf{H}(r'/s) = \left( \frac{\omega}{c} \right)^2 \mathbf{H}(r'/s).
\]  

(3.42)

Dividing both sides by \( s^2 \) obtains

\[
\nabla' \times \left( \frac{1}{\epsilon(r'/s)} \right) \nabla' \times \mathbf{H}(r'/s) = \left( \frac{\omega}{cs} \right)^2 \mathbf{H}(r'/s).
\]

(3.43)
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As the permittivities of the system have remained constant under the transformation, \( \epsilon'(r') = \epsilon(r) \). Equation 3.43 can now be expressed as

\[
\nabla' \times \left( \frac{1}{\epsilon'(r')} \nabla' \times H(r'/s) \right) = \left( \frac{\omega}{c_s} \right)^2 H(r'/s).
\]

(3.44)

This is the corresponding master equation for the scaled system [20]. We note that the field profile of the new scaled system is \( H(r'/s) \). Explicitly, \( H'(r') = H(r'/s) = H(r) \) and so the field profiles within the new scaled system, \( H'(r') \), have simply been scaled with the system [20]. This has consequently resulted in the scaled change in the eigenfrequency of the system as \( \omega' = \omega/s \). This result defines the master equation as being scale invariant.

3.3.5 Rotational symmetry, complete band-gaps and quasi-order

Ordered, periodic photonic crystals possess an inherent degree of rotational symmetry associated with their geometry: a square lattice will have 4-fold symmetry, a hexagonal lattice will have 6-fold symmetry and so on. There exists a geometric crystallographic restriction, whereby periodic, ordered, tessellated systems may only possess one of five possible orders of rotational symmetry in a particular spatial plane. These are rotational orders of 1, 2, 3, 4 and 6 [103]. The order of rotational symmetry that a photonic crystal geometry possesses directly determines the shape of its associated Brillouin zone and therefore how isotropic the structure is. The high symmetry points of a structure’s Brillouin zone dictate the directions within the photonic crystal geometry that will produce a different band-gap response. If the Brillouin zone of the structure is perfectly spherical the structure is completely isotropic and a full-and-complete band-gap will result, even when comprised of low refractive index contrast media.

Face-centred cubic Bravais lattices have the most spherical Brillouin zone of all periodic, ordered 3D photonic crystal geometries. As a consequence of this, they have the capability to produce a complete photonic band-gap with a refractive index contrast as low as 2, determined for the diamond structure [70]. This is the lowest possible refractive index contrast that will produce a complete photonic band-gap for a periodic, ordered 3D photonic crystal structure. Photonic crystal structures with a completely spherical Brillouin zone can not possess an ordered, periodic crystalline structure, due to the constraints set by the geometric crystallographic restriction. However, higher orders of rotational symmetry are possible to achieve through ‘quasi-periodic’ order. This occurs when the rotational and translational order of a structure’s geometry is no longer conserved over short- and long-ranges. In quasi-ordered crystal geometries,
there generally exists a short-range, but no distinct long-range, translational order and a long-range, yet a lack of short-range, orientational order [16]. Such systems may be comprised of tessellations of irregular shapes such as in the case of 2D quasi-periodic Penrose tiling [16].

3.4 Summary

Photonic crystal structures are comprised of alternating materials with different refractive indices. They are generally periodic and ordered in nature and possess an associated Brillouin zone. When light is incident on such a structure, with a wavevector corresponding to the Brillouin zone boundary, standing wave resonances are set up within the system. The two possible standing waves states, with the same wavevector, that are set up in the system arrange with antinodes in either the high or low permittivity regions in accordance with the symmetry of the unit cell of the structure. This is defined mathematically through the orthogonality relation, equation 3.29. The standing wave mode with antinodes in the high permittivity regions will be a lower energy, and therefore lower frequency, mode. When antinodes are present in the low permittivity region, a higher frequency mode will result. The frequency of each mode is defined by equation 3.35 and is dependent on the proportion of electric field present in each permittivity region. The frequency splitting produced by a single incident wavevector invokes the presence of a photonic band-gap. Present within this band-gap are states that are not eigenmodes of the system and so are not allowed to exist within the crystal geometry and are consequently reflected from the system. When non-normal incident light impinges on the structure, the wavevector in the direction of periodicity must be conserved. The wavevector required to produce an off-angle resonance must increase, resulting in a smaller wavelength, larger frequency, reflection. This phenomenon is called iridescence and is a property that is unique to structural colour. The local energy densities of the field profiles of the modes just above and below the photonic band-gap are distinctly different; this is the origin of the photonic band-gap. When the refractive index contrast of the system is increased, the field profiles change drastically, particularly that of the air band, and so a larger photonic band-gap results. Properties such as polarisation and crystal geometry may also change the band-gap width. In general, it is the concentration factor of electric fields within the high permittivity region for each standing wave field profile that determines the energy density of each mode above and below the photonic band-gap. Consequently, this directly determines the width of the photonic band-gap.
Chapter 4

Experimental and theoretical methods

The electromagnetic response of naturally occurring optical structures can be characterised by using many different methods. For instance, it is useful to use both optical imaging and optical spectroscopy techniques on a photonic sample, as important and distinct information can be gained by using each method. In conjunction with these optical methods, high-resolution imaging microscopy can be employed in order to identify the micro-structures that induce the observable optical effects. Detailed high-resolution images of the photonic systems provide information that allows theoretical modelling to be undertaken on analogous systems. Theoretical modelling can be used in conjunction with the experimental procedures in order to determine how electric fields are arranged within the probed structures, something that is unobtainable through experimental characterisation alone. This aids the determination, or confirmation, of the origin of electromagnetic features observed in the experimental data. A wide range of experimental and theoretical techniques have been implemented in order to conduct the experiments described in this thesis; some for the optical regime and some for the microwave regime. In some instances samples are naturally occurring and can be probed directly with a small amount of sample preparation; in others, millimetre-scale fabrication techniques are necessary. This chapter outlines the main methods and principles behind experimental and theoretical techniques and also the fabrication methods used to perform experiments described in later chapters.

4.1 Optical microscopy

A Carl Zeiss Axioskop 2 polarising microscope was employed in order to obtain optical images of individual scales, or groups of scales, obtained from beetle/butterfly sam-
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This allows imaging of a sample in both reflection and transmission and with the option of using bright-field or dark-field illumination. Many natural samples are not flat and most possess some curvature, particularly those present on the elytra of beetles. Individual photonic crystal containing scales can be removed from the wing of a butterfly or the curved elytron of a beetle, however, most wing/elytral scales also possess a curved morphology. If the curvature of the scale is large enough, the microscope imaging procedure can not obtain a clear, in-focus image over the whole sample. In order to overcome this, a series of images is taken from the depth of the sample by altering the focus of the microscope, consequently changing the z-position of the focal plane of the microscope. The microscope employed possesses a ‘z-stacking’ function, where an average image at user-defined z-heights may be obtained, and a clear image of a curved sample can be captured. Figure 2.11, presented in chapter 2, shows images of weevil scales captured using this method.

4.2 Spectroscopy

An average human with 20/20 vision is able to optically resolve independent pixels separated by 1 arcminute, or 1/60 of a degree [104]. Individual scales that are present on a beetle or butterfly are generally tens-of-microns in diameter, well below an observer’s resolvable limit. In most cases, elytral/wing scales comprise many intra-scale coloured domains, sometimes as small as 2 µm in diameter, that are certainly unresolvable by an observer at any distance. The optical microscopy method outlined in section 4.1 can resolve these scales by use of magnifying lenses. However, it is the accumulation of optical reflections from a large area of wing or elytra, containing a collection of many scales, that is generally visible to an observer. The reflectance profile produced from large, millimetre-size sites of whole sections of wing/elytra can be measured using a bifurcated fibre-optic probe connected to a CCD detector array spectrometer (AvaSpec-2048, Avantes, Eerbeek, The Netherlands), using a deuterium/halogen light as a source (AvaLight-D(H)-S). This method was employed when measuring the cumulative effect of colour reflections from domained samples and other large-area reflectance spectra. For normalisation, a white diffuse reference tile (Avantes WS-2) served as a reference standard. In order to measure the angular dependence of reflected wavelengths from a millimetre-sized region of a sample, a two-arm set-up was employed comprising an emitting and a receiving fibre-optic probe alongside independent angular vernier scales that can be rotated to a desired incident angle and associated reflected angle.

The colour-producing scales of the measured samples are generally attached to a wing or elytral surface which are commonly dark in appearance. They act as optical absorbing substrates. This allows light that is transmitted though the photonic crystal. 
structure to be absorbed, thereby not inducing any unwanted additional scattering effects to the light reflected from the photonic crystal. Consequently, this preserves a saturated colour reflection produced by the intra-scale structure alone.

4.3 Microspectrophotometry

Reflectance spectra of areas as small as $2 \times 2 \mu m^2$ from within individual scales were acquired with a microspectrophotometer (MSP). This method comprised a xenon light source, a Leitz Ortholux microscope and an S2000 fibre optic spectrometer (Ocean Optics). The microscope objective was an Olympus 20x, NA 0.46. All collected data are normalised against a white, diffuse reflection standard. The micron-sized collection aperture area of the MSP allows the reflectance spectra from within single intra-scale reflecting domains to be obtained.

When performing MSP in natural samples, it is possible to perform the MSP measurements on scales that are still present on the dark absorbing wing/elytral substrate in most cases. However, in some cases it is necessary to isolate single scales which are individually mounted onto an adhesive-tipped glass micro-pipette. The micro-pipette can then be positioned in a micro-manipulator that is free to rotate over a $360^\circ$ polar angle. Angular data may then be obtained from an individual scale with no interference from neighbouring scales or, in the case of Coleoptera, the curved nature of elytra upon which the scales are positioned. In these cases, any light that is transmitted through the scales generally propagates into the surrounding space and is not reflected from an underlying substrate if mounted onto the micro-pipette correctly. Consequently, this method also preserves the colour reflections from within individual scales without any undesirable back-reflections from an underlying substrate. In addition to gaining angular reflection data from individual scales, mounting a single scale onto a micro-pipette also allows both the top- and under-side of individual scales to be investigated with the MSP method.

The limited numerical aperture of the microscope objective allows scattered light from a sample to be collected over a finite region of the whole scattered hemisphere. Performing MSP on a sample under rotation may result in the reduction in reflected intensity as the angle of incidence upon the sample is increased. The white standard that is used as a reference in the MSP method is highly scattering and so the intensity of scattered light collected from the sample is always arbitrary, regardless of illumination angle. Consequently, individual wing/elytral scales that scatter diffusely may be analysed under angular rotation using the MSP method in order to examine wavelength changes, as opposed to intensity changes, up to a total rotation angle of approximately $45^\circ$ with the numerical aperture in use.
4. Experimental and theoretical methods

4.4 Imaging scatterometry

The imaging scatterometer is a novel method for directly imaging the full scattered hemisphere of an illuminated sample in the far-field. The equipment was inspired by the set-up of Kinoshita et al. [48] but developed by Stavenga et al. at the University of Groningen [105]. The great experimental advantage that it offers is the capability to capture the entire $-90^\circ \leq \theta \leq 90^\circ$ hemisphere of scattered light from a sample as the set-up is not limited by a numerical aperture. From the full hemispherical scattering patterns obtained by probing optical samples in the scatterometer, it is possible to acquire valuable information regarding the scattering mechanisms of photonic structures. Optical effects produced by structural attributes such as periodic order, quasi-order, disorder and surface structure details present in a system may be observed and imaged with this method. In addition to this, the change in scattering profile and scattered wavelength upon rotation of a sample can be imaged with the scatterometer. Imaging scatterometry can be performed using both narrow- and wide-angle illumination.

4.4.1 Narrow-angle illumination

The scatterometer comprises two xenon light sources: the primary beam ($S_1$) and the secondary beam ($S_2$), as depicted in figure 4.1. Generally narrow-angle illumination is performed using the primary beam as an incident source. The light from the primary beam passes a diaphragm ($D_1$) which is then focused by lenses $L_1$ and $L_2$ to the focal point $F_1$ of $L_2$, where a sample is positioned. This focal point is concurrently one of the two focal points of the ellipsoidal mirror $E$, the heart of the scatterometer. The light that follows this path is limited in size by $D_2$ and is then incident upon the second lens, $L_2$. Light that passes $L_2$ is permitted to pass through the ellipsoidal mirror by means of a small, central axial hole. The, approximately, axially back-scattered light is then focused by lenses $L_3$ and $L_4$ via a half-mirror onto a camera, $C_1$, which is connected to a binocular viewer. Viewing and imaging the sample through this route allows for the precise adjustment of the incident primary beam spot upon the sample. Any non-axially scattered light from the sample is then incident upon the ellipsoidal mirror, $E$, where it is reflected and then focused onto the second focal point of the mirror, $F_2$. It then passes lenses $L_6$ and $L_7$ to be focused onto a second camera $C_2$ where the scattered pattern is then imaged. A spatial filter is placed at position I in order to block first order, axially propagating, transmitted light [105]. This narrow-angle illumination method produces a beam spot diameter of 8.5 $\mu$m.

In order to image the scattering patterns produced by a sample with the scatterometer, single elytral/wing scales were mounted onto an adhesive-tipped glass micropipette and precisely positioned at the focus of the incident beam at $F_1$ using a micro-
4. Experimental and theoretical methods

Figure 4.1: The imaging scatterometer [105]: the primary beam ($S_1$) and the secondary beam ($S_2$) act as incident sources. The light from the primary beam passes a diaphragm ($D_1$) which is then focused by lenses $L_1$ and $L_2$ to the focal point $F_1$ of $L_2$, onto a sample. This is aided by the positioning of an aperture at $D_2$ and a small, central hole in the ellipsoidal mirror, $E$. The back-scattered light from a sample is then focused by lenses $L_2$ and $L_3$ via a half-mirror onto a camera, $C_1$. This is also connected to a binocular viewer which allows for the positioning of the sample with respect to the incident beam-spot. Light that is scattered from the sample is reflected from the ellipsoidal mirror, $E$, onto the second focal point of the mirror, $F_2$. Scattered light then propagates through two lenses, $L_6$ and $L_7$, but axially propagating light is blocked by a spatial filter, positioned at $I$. The scattering pattern produced by the sample is then imaged by a second camera, $C_2$. This method produces scattering patterns from a beam spot that is approximately $8.5 \mu m$ in diameter and is referred to as narrow-angle illumination. Light from the secondary beam can be used in wide-angle scatterometry with a beam spot size of approximately $50 \mu m$ in diameter when aperture $D_4$ is removed.
manipulator. The micro-manipulator allows the incident beam to be positioned at the desired location on a sample by means of three-dimensional translations or angular rotations. When the sample is rotated, the angle at which light from the primary beam is incident changes. Consequently, angle-dependent data can be measured. When a sample is rotated by $\theta$, the resulting angle of a specularly reflected beam will be $\alpha = 2\theta$ when captured by the detecting camera.

Once imaged by the scatterometer, the captured image of the total scattered hemisphere from a sample is processed and represented as a full hemispherical polar plot. Figure 4.2 shows an example of such a hemispherical polar plot, taken using the primary beam as a source and camera $C_2$ as the detector. Figure 4.2 was captured by probing a single scale from the weevil *Eupholus loriae*, presented in figures 2.9(c) and 2.4.2(c) in section 2.4.2, at normal incidence. From the centre of the polar plot presented in figure 4.2, the red rings represent scattered angles of $5^\circ$, $30^\circ$, $60^\circ$ and $90^\circ$. The inner $5^\circ$ ring represents the region of the scattering profile that is blocked by the spatial filter at $I$ in figure 4.1. The dark strip that appears on the left-hand side of each polar plot results from the shadow of the micro-pipette, used to hold the sample. It is clearly identifiable from figure 4.2 that this sample produces diffraction effects, likely to originate from a surface structure present on the top of each scale, alongside the characteristic blue scattered hue produced from the weevil’s intra-scale photonic crystal structure.

**4.4.2 Wide-angle illumination scatterometry**

Light produced from the secondary beam, $S_2$ on figure 4.1, is incident upon diaphragm $D_3$ and focused by lenses $L_4$ and $L_5$ onto diaphragm $D_5$, which is placed in the focal plane of lens $L_5$. The transmitted light is then incident upon a beam splitter, $H_1$, then onto the ellipsoidal mirror, $E$, which focuses this light onto a sample. The sample then scatters the light back onto the ellipsoidal mirror, from which it is reflected and focused onto the second focal plane of the mirror. From here it passes through lenses $L_6$ and $L_7$ where it is imaged onto a second camera, $C_2$ as with the narrow-angle method.

When using the secondary light source, the aperture of the diaphragm $D_4$ can be moved laterally in order to vary the angle of incidence of the secondary beam onto the sample [105]. If $D_4$ is completely removed from the scatterometer, the secondary beam will illuminate the sample from all angles. This process is named wide-angle scatterometry.

Figure 4.3(a) presents an example of an image taken when probing a single scale of the butterfly *Parides sesostris* using the wide-angle scatterometry method. In this instance, the polar plot includes the total scattering produced from the sample when light is incident upon it at all angles. Consequently, by probing a sample using this method, the entire iridescent spectrum of the underlying photonic structure is imaged.
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Figure 4.2: A full hemispherical polar plot showing the scattering pattern produced by a photonic-crystal containing scale from the elytra of the weevil *Eupholus loriae*. The red rings represent scattered angles of $5^\circ$ (inner ring), $30^\circ$, $60^\circ$ and $90^\circ$ (outer ring). In addition to the blue scattered hues, a region of diffracted light is also observable in this image, obtained by scatterometry.

Figure 4.3: Hemispherical polar plots imaged from a photonic-crystal containing scale present on the wing of the butterfly *Parides sesostris* using the wide-angle scatterometry method. (a) The polar plot includes the scattering produced from the sample when light is incident upon it at all angles. When probing a sample using this method, the entire iridescent spectrum of the underlying photonic structure is imaged on a single hemispherical polar plot. (b) A linear polariser has been inserted before $L_5$ on the scatterometer and the iridescent spectrum has been imaged. Only data along the white horizontal line contains the correct polarisation data due to the change in incident plane when scattering is incurred from the sample. The red rings on each image represent scattered angles of $5^\circ$, $30^\circ$, $60^\circ$ and $90^\circ$ from the centre of the image.
on a single hemispherical polar plot. The scattered light therefore covers the majority of the polar plot. The wide-angle scatterometry procedure results in an approximately 50 µm diameter beam spot that is incident on the sample over all possible illumination angles. It is also possible to probe the sample with linearly polarised light with this method. By inserting a linear polariser before $L_5$, linearly polarised wide-angle illumination scatterometry can be performed on a sample. However, the scattering process that occurs from the sample will result in the change in polarisation of non-axially-scattered light due to the change in the plane of incidence of the light. Therefore, only a vertical line through the centre of the hemispherical polar plot will contain data scattered with the required linear polarisation. This vertical line that contains the correct polarisation-dependent data is represented by the white dashed line in figure 4.3(b).

4.5 Scanning electron microscopy and the focused ion beam

Generally, imaging of cross-sections through 3D photonic crystal arrays contained within beetle or butterfly scales is performed using transmission electron microscopy, as it has the capability to image a plane parallel to a cross-section made to the sample. However, the transmission electron microscopy preparation process requires the sectioning of thin segments of a sample and is not always a viable option for natural samples. In some cases, particularly concerning weevil scales, the structures are very brittle and the thin sections required for this imaging procedure can not be obtained without fracturing the structure and consequently removing the geometric structural form of the sample. Use of a scanning electron microscope is an alternative method for imaging naturally occurring photonic micro-structures, particularly weevil scales, with a high resolution. The preparation involved in creating cross-sections of natural samples for imaging with a scanning electron microscope does not require thin sectioning or the immersion in preparation chemicals that could cause shrinkage to a sample. Cross-sectioning of weevil scales can be obtained via manual fracturing using a blade or by freeze fracturing with the use of liquid nitrogen. Although effective, these methods do not allow accurate control over cross-section orientation or straight-edge sectioning that is possible to achieve by milling the sample with the use of a focused ion beam. The following sections outline how the concurrent use of the focused ion beam and scanning electron microscope can be used to section and image a sample that contains a photonic micro-structure.
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4.5.1 Scanning electron microscopy

In order to probe the unique micro-structures responsible for producing the observable optical effects measured by optical microscopy or spectroscopy, it is necessary to use a probe that is capable of resolving well below the resolution limit obtainable by an optical beam. The scanning electron microscope (SEM) images the photonic micro-structures by using high-energy incident electrons that interact with the sample via scattering processes [106]. The very small wavelengths of electrons enable extremely high resolution imaging of optical micro-structures, which for natural samples are often hundreds of nanometres in size. The electron microscope employed for imaging the underlying photonic structure within weevil scales was an FEI Nova 600 dual-beam system. An electron beam voltage of 10 $kV$ and current of 0.13 $nA$ were used to obtain magnifications of up to $60,000 \times$. This was suitable for the acquisition of extremely detailed images of naturally occurring photonic structures. Geometric parameters of the underlying photonic structure were subsequently identified using image analysis.

In order to probe a sample with this method, it was affixed to an aluminium stub via strips of conducting carbon tape and then subsequently locked in place onto the sample mount inside the SEM. For the case of a beetle or a butterfly, the sample may consist of a section of elytra/wing from the insect or, if present, individual scales which are scraped from the sample directly onto the conducting tape. In most cases of 3D photonic crystal structures on Lepidoptera and Coleoptera, the structures are encased within scales, and so can be individually isolated. To obtain a clear image with the electron beam, the sample must be conductive: a conductive sample minimises charge build-up on the surface of the sample which can occur for insulating samples that lack the ability to ground accumulated charge. Therefore any natural dielectric samples must be coated with a conductive medium in order to obtain a clear image using the SEM. Each naturally occurring sample was prepared for imaging with the SEM by coating it in layers of gold palladium with the use of a ‘sputter coater’. A thickness of 4 $nm$ of gold palladium was sputtered onto each sample as this proved appropriate for obtaining a clear, stable image of the naturally occurring micro-structures from the SEM for individual curved weevil scales.

4.5.2 The focused ion beam

In many cases, the photonic micro-structures under investigation may not be immediately visible and additional preparation must be made to the sample before the structures can be imaged. For instance, in some natural systems, photonic structures are encased within scales by a chitin shell, such as with weevil scales, that entirely cover the internal micro-structures. Alternatively, the photonic structures may be obscured
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by other materials which may require manual removal. If the structures are already exposed, the sample may be fractured in a non-uniform way that requires an additional straight-edge cut in order to obtain a clearly visible image of the micro-structures for analysis. The focused ion beam (FIB) can be used in each of these cases to obtain a clear cross-section image of the underlying photonic micro-structures. FIB milling is a precise cutting procedure for application on the micro-scale. In contrast to an electron beam, the ion beam uses heavier gallium ions for sample etching. The gallium ion beam was set at a voltage of 30kV and current of 10pA in order to mill cross-sections through individual scales isolated from various weevil samples, so that their inner photonic crystal structure was exposed. Figure 4.4(a) shows an image of a typical single scale from the weevil *Eupholus magnificus*, taken using detailed high resolution scanning electron microscopy. The photonic crystal structure is contained within the scale, enclosed by a cuticular shell. Once the FIB has cut through the scale, a cross-section through it reveals the internal photonic crystal structure. In this case a small square section has been removed from the weevil scale and the resulting cross-section can be viewed in figures 4.4(b) and (c). A similar approach has also been used successfully in a study of other weevil species [107].

The FEI Nova 600 dual-beam system contains both the ion beam used to mill the sample and the electron beam used to image the sample. The electron beam column and the ion beam column are oriented at 52° to each other. The stage holding a sample in the dual-beam system rotates to a maximum angle of 52° in order for the ion beam to be directed orthogonally to the surface of a sample. A perpendicular cross-section can then be obtained from the sample and the revealed section can be probed with the electron beam. The resulting SEM image of the cross-section will be a projection of the true image in the vertical direction through the depth of a cross-sectioned scale. When analysing the acquired SEM image, a correction must be made to the distances measured throughout the depth of the scale in order to account for this projected image capture. The required correction can be determined by a simple trigonometric calculation and the resulting scaling factor can then be applied to the necessary distances to obtain an approximate true length-scale. This scaling procedure is defined by

\[ d_{\text{real}} = \frac{d_{\text{imaged}}}{\sin(52^\circ)}, \]  

(4.1)

where \(d_{\text{real}}\) is the true distance and \(d_{\text{imaged}}\) is the imaged projected distance.
Figure 4.4: A typical single scale taken from the yellow coloured band of an elytron of the weevil *Eupholus magnificus*. (a) The chitinous envelope encases the photonic structure responsible for the yellow coloured hue it produces. (b) A square section has been removed from an individual scale via ion beam milling, revealing the internal photonic crystal structure, also shown in (c). Scale bars: (a) 10 µm, (b) 5 µm (c) 2.5 µm.
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4.6 Microwave experiments

Replication of the optical structures present on the elytra of Coleoptera or the wings of Lepidoptera is sometimes unfeasible at similar length scales due to the complex nature of the structures and the resolution limitations inherent in current fabrication methods. Advances in processes such as direct laser writing are producing increasingly improved resolution limits that provide the prospect for future sample fabrication of such intricate structures at near infrared [108] and optical length scales [109]. Other fabrication methods for the production of optical photonic structures that are currently progressing the field, include stacking processes [110], self-assembly [111], novel methods of bio-templating naturally occurring optical photonic structures [112] and lithography techniques [113]. However, Maxwell’s equations are scalable and so structures that are fabricated with larger lattice constants can be probed with longer wavelengths in order to characterise the optical responses that occur in analogous optical structures [20] [13].

4.6.1 Sample fabrication

Three-dimensional printing using stereolithography techniques allows the fabrication of large-scale complex three-dimensional photonic structures. It has been previously used for fabricating large-scale replicas of simple butterfly photonic structures in the microwave regime [17] [114] and other synthetic structures [115]. With this fabrication technique, even very complex physical structures can be fabricated that possess resonant transmission/reflection frequencies positioned within an experimentally accessible microwave frequency range [13]. The stereolithography machine employed for sample fabrication was a Pro Jet HD 3000. The sample fabrication resolution, of approximately 50 \( \mu m \), is ideal for fabricating structures with lattice constants on the millimetre scale. The majority of the 3D structures fabricated for electromagnetic characterisation and presented in this thesis were designed with a lattice constant of 7 mm. This lattice constant was selected as it was found to induce resonant transmission/reflection features located between the best working frequency of the broadband emitting and receiving horns used to conduct the microwave experiments (10-43 GHz). The overall sample sizes of the 3D printed arrays are selected to adhere to two main constraints: the sample had an incident surface area that was larger than the width of the incident beam ‘spot’ whilst remaining at a size that was within the memory capacity of the stereolithography machine. Complicated structures require more memory per unit cell and so a smaller sample array size may result for these structures. In addition to this, as the transmission response is being experimentally measured, the reflection and transmission band-widths must be comparable. In order for this phenomenon to occur a relatively low number of unit cells was used in the depth of the array, along the line of
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transmitted light at normal incidence.

The material deposited by the stereolithography machine is a solid polymer with refractive index that can range from \( n = 1.656 \) to \( n = 1.71 \). The chosen model geometry for all fabricated photonic crystals comprised a dielectric polymer as the high refractive index medium and air as the low refractive index medium. The stereolithography machine prints wax in place of air, which is subsequently removed after fabrication. The wax support material is removed by immersing the finished sample in just-molten wax which consequently melts the support wax, removing it from the structure. This leaves the finished structure comprising air and the selected polymer. In order to manufacture complex 3D photonic crystal structures with this method, the 3D computer-aided design (CAD) software Solidworks [116] was used to design the structures. The 3D surface-creating software K3DSurf [117] was employed to initially create digital constant mean curvature surfaces which could be subsequently made into the desired array by use of the Solidworks package. The finished designs can be exported as ACIS (sat) files and imported into theoretical modelling software as exact replicas of the experimental samples.

Figure 4.5: The experimental set-up for the microwave experiments comprised two duel-polarised broadband horns, one emitting and one receiving, connected to a vector network analyser (VNA), as presented in figure 4.5. The sample is placed in the centre of aligned horns and surrounded by microwave absorbing foam. The orientations of the electric fields that define TE and TM polarisations have been defined. The sample was probed at various polar angles, \( \theta \), and azimuthal angles, \( \phi \) as defined in this image.
4.6.2 Vector network analyser and broadband horn set-up

The experimental apparatus used to probe the fabricated bicontinuous cubic structures consisted of an emitting and a receiving broadband horn (Flann Model DP241-AB; Dual Polarized Horn (option 10-50 GHz)) attached to a two-port Anritsu Vector Star 70 kHz to 70 GHz vector network analyser (VNA). The broadband horns have an optimum working frequency range of 10-43 GHz. The VNA is able to measure amplitudes and phases of reflected and transmitted microwave radiation. However, in characterising the transmission response of the fabricated samples, only the amplitudes are required. In this respect, the VNA is used as a scalar network analyser. In order to measure the transmission response through a structure, the scattering parameters, or ‘S-parameters’, of the two-port network are measured. The scattering processes that are measured in a two-port network can be defined as:

\[ S_{11} = \frac{M_1}{E_1}, \]  \hspace{1cm} (4.2a)

\[ S_{21} = \frac{M_2}{E_1}, \]  \hspace{1cm} (4.2b)

\[ S_{12} = \frac{M_1}{E_2}, \]  \hspace{1cm} (4.2c)

\[ S_{22} = \frac{M_2}{E_2}, \]  \hspace{1cm} (4.2d)

where \( E \) represents the emitted electric field amplitude and \( M \) represents the measured amplitude. The subscripts identify the port from which a signal is measured or emitted. Before the S-parameters are calculated, the cables that connect the emitting and receiving ports to the broadband horns are calibrated by connecting them to short, open, load and through (SOLT) standards, supplied with the analyser. These standards remove any unwanted reflections incurred within the attached cables.

Figure 4.5 shows the employed microwave experimental set-up. The sample was centred between aligned source and detector horns. The samples were surrounded with carbon-loaded foam, where possible. This acts as a microwave absorber to ensure only the radiation transmitted through the structure was collected by the receiving horn. Each sample was interrogated with both transverse magnetic (TM) and transverse electric (TE) polarised incident radiation, defined in figure 4.5. The structure was characterised electromagnetically at two azimuthal angles as defined by figure 4.5. These angles were \( \phi = 0^\circ \) and \( \phi = 45^\circ \). In each case the sample was rotated through a polar angle range \(-45^\circ \leq \theta \leq 45^\circ \), as defined in figure 4.5.
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Figure 4.6: The Gaussian response of the broadband horns used to conduct the microwave transmission experiments. The $x$– axis represents the lateral position of the detecting horn with respect to the emitting horn. A larger distance from source to detector increases the beam spread, and consequently the size of the emitted ‘beam spot’ of maximum intensity. In the experiments performed in this thesis, the sample was placed 22 cm away from the source to reduce the spread of this Gaussian beam.

The broadband horns used as a source and a receiver are not collimated in the experiments due to the large beam spot area that a collimated source produces. This beam-spot size, relative to the area of the sample interface, produces a very small intensity transmission response with a small signal-to-noise ratio. Consequently, the stop-band features expected to be induced by the sample were not observed when a collimated beam was used as an incident source. Even narrowing the collimated beam size with the use of an aperture did not improve this. The broadband horns emit microwave radiation as a Gaussian beam when uncollimated. The Gaussian nature of the beam was characterised by moving a receiving horn laterally across the emitting horn and averaging the detected intensity at each lateral point. This was undertaken with the source and detector separated by three different distances of 22 cm, 32 cm and 42 cm. The results are presented in figure 4.6. It is possible to determine that the full-width half-maximum of a beam incident on a sample positioned at 22 cm from the source is approximately 5 cm. This indicates that the incident beam diverges by 12.8° from the central axis. In the experiments performed in this thesis, the sample was placed 22 cm away from the source to reduce the spread of this Gaussian beam whilst also remaining in the far-field of the sample. As the incident beam is not an exact ideal
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4.7 Fast Fourier transform analysis

Fourier transforms (FTs) are used in a wide range of applications and are a particularly useful tool for undertaking image analysis. By applying the relevant mathematical FT to an image, the initial spatial image is decomposed into sine and cosine components [120]. As digital images comprise a number of discrete pixels, they can be Fourier transformed using a discrete summing method, the mathematics of which are not described here. In this case, the number of pixels in the image correspond to the number of frequencies in the FT image. In other words the real and Fourier-space images are the same size. On applying the Fourier transform to the original image, the output is returned in frequency, or Fourier, space. In the Fourier-space image, each point is de-
scribed by a spatial frequency. If that frequency is present in the real-space image it is represented on the Fourier-space image as a high intensity peak. Due to the mathematical representation of a discrete Fourier transform method, in the form of a summation, it can be decomposed to a simpler form resulting in a faster computation time. This is known as a fast Fourier transform (FFT). Some examples of FFT images are shown in figure 4.7. Figure 4.7(a) shows an FFT calculated from an image of a disordered structure, found in the white *Cyphochilus* beetle [73]. The resulting FFT image shows no evidence of distinct spatial regularity as only the lowest frequency, or ‘DC component’, shows a bright high frequency response. Figure 4.7(b) shows the FFT obtained from an SEM image of the structure within the elytral scales of the weevil *Eupholus magnificus*. The 2D SEM image was obtained through a cross-section of the 3D structure and revealed a square symmetry through the selected cross-sectioned plane. The resultant FFT image clearly identifies this square symmetry. The radial distance from the centre of the image increases linearly in inverse spatial units but corresponds to a decrease in direct spatial distance, as a reciprocal response. The separation between the periodic features can be measured in Fourier-space and converted into direct spatial units to determine the periodicity of the structure. In addition to this, the rotational symmetry of a system can be determined from the Fourier-space image. It is clear from figure 4.7(b) that the rotational symmetry of the original image is of order 4. Figure 4.7(c) shows the FFT taken from an approximation of a quasi-ordered array designed by Zoorob et al. [118]. The FFT image shows an isotropic rotational symmetry, indicated by the ring formation of identical spatial frequencies that forms radially within the Fourier image. This is one of the key properties of quasi-ordered arrays and FFT image analysis is a tool that can accurately highlight the order of rotational symmetry present in such structures that are sometimes difficult to identify and calculate by real-space interpretations.

4.8 Theoretical modelling

Theoretical modelling is an invaluable aid to experimental science. In particular, modelling the interaction of light with optical structures allows the electromagnetic response of the structure to be determined. By calculating the way in which electric fields configure within a probed photonic system it is possible to determine its transmission/reflection response. Consequently, theoretical modelling offers the ability to obtain a visual representation or a graphical plot of electric field configurations within the analysed system. This is unobtainable from experimentation alone. The theoretical modelling performed and presented in this thesis includes the finite element method (FEM) using the commercially available software HFSS [121] that has been designed
for use in the microwave regime. In addition to this, the iterative eigensolver method provided by the MIT photonic bands package \[122\] was also used. Both modelling processes are performed in the frequency domain and provide numerical results. The FEM involves subdividing the model geometry into many finite elements, or ‘tetrahedra’. At the boundaries of each tetrahedron Maxwell’s equations are solved and boundary conditions are implemented in order to calculate the fields that are present in neighbouring elements. In this thesis, all 3D FEM models are designed and constructed to closely replicate a corresponding experimental set-up. The models used are all ‘driven models’, meaning the excitation method is user-defined and the exact nature of the incident wave source used to illuminate the structure can be selected. For the FEM theoretical modelling performed for this thesis, a plane wave was always used as an incident source. A typical FEM model with a simple cubic geometry, comprising air spheres in a material matrix with refractive index of \( n = 1.71 \), is presented in figure 4.8. The structure is surrounded with air. With the case of periodic, ordered photonic crystal structures, it is possible to create and replicate a unit cell of the structure in order to form an array with the required number of unit cells throughout each dimension of the array. In figure 4.8, the depth of the array has been selected to comprise 4 unit cells. This 4 unit cell geometry can then be repeated in the remaining dimensions as an infinite array by surrounding it with boundaries termed ‘master/slave’ boundaries in HFSS \[121\]. The master/slave boundaries in the model presented in figure 4.8 are represented as infinitesimally thin planes that cover the four sides of the array in the \( \hat{x} - \hat{z} \) and \( \hat{y} - \hat{z} \) planes. Each master and corresponding slave boundary are intrinsically interlinked to their predefined counterpart. They often lie on opposing planes of the model geometry, creating a direction across the unit cell in which to replicate. In order for the structure to successfully repeat as an array, the planes of the model containing master/slave boundaries must possess the same electric field profiles. Therefore the unit cell of the structure used must be selected so that it possesses the same geometry in each of the respective master/slave boundary planes. In using this type of boundary, it is possible to minimise the processing time and power required to solve the model. As, experimentally, an incident beam spot on the structure is generally smaller than the area of the incident interface of the sample, the infinite array does not diverge from the experimental set-up, providing the depth of the structure remains constant in both cases.

By measuring electric field values at planes positioned in the back-scattered and the forward-scattered directions from the analysed structure it is possible to calculate transmitted/reflected Fresnel coefficients, defined in section 3.2. These geometric planes are labelled as plane 1 and plane 2, respectively, in figure 4.8. The boxes at the top and bottom of the model, shown in figure 4.8, are perfectly matched layers (PMLs).
PMLs are comprised of a unique theoretical material that is perfectly absorbing. They are added to a finite model in order to eliminate any reflections that may occur from any termination interfaces present in the model. They are the most efficient absorbing termination points achievable with this FEM modelling procedure as they efficiently absorb radiation that is incident upon it at oblique angles in addition to specular reflections [121]. This is particularly useful when illuminating a structure at a non-normal incident angle and also when probing diffracting structures. This type of boundary is normally placed at a distance greater than \( \lambda \) away from the structure in order to ensure no near-field interference occurs. Another type of termination boundary that may be used in place of a PML when analysing periodic structures are Floquet port boundaries. They are placed in the incident and transmitted planes of the model and concurrently act as an incident source. In this case no PMLs are used and they replace plane 1 and plane 2 in the model presented in figure 4.8. In this instance, radiation is incident upon the structure as a set of plane wave Floquet modes. These Floquet modes are calculated as the diffracted orders of the structure under analysis [121]. The advantages of using Floquet ports are two fold: not only can each diffracted mode from the structure be individually determined and the transmission/reflection properties of each plotted, but the incident and detected linear polarisations can be defined to be opposing. This allows polarisation conversion from a chiral sample to be calculated. In this thesis, the theoretical work involving polarisation conversion in chiral structures was analysed using Floquet port models, all other theoretical FEM models used were designed as PML models.

When analysing the origin of a stop-band produced by a photonic crystal structure, it is useful to plot the electric field profiles from within the array. Electric field profiles can be extracted and plotted, either as an image or graphically using the FEM modelling software HFSS [121]. If the exact frequencies at which standing waves are set up in a system are known, it is possible to directly plot their time-averaged electric field profiles. Standing waves are set up at frequencies of high transmission, that occur either side of a photonic band-gap, that can be identified from the modelled or experimentally determined reflection or transmission data. Figure 4.9(a) displays the model geometry of a gyroid photonic crystal structure comprised of a solid material \((n = 1.656)\) and air in the \( \hat{y} - \hat{z} \) plane. There are 12 unit cells in the depth of the array which are surrounded by master/slave boundaries. Figure 4.9(b) displays the time-averaged electric fields of the upper band-edge frequency of a [0\(\overline{1}\)\(\overline{1}\)] standing wave mode present within this structure. The regions of high (red) field are present inside the air regions as expected from an upper band-edge standing wave resonance. From figure 4.9(b) the planes in the [\(\overline{1}\)0\(\overline{1}\)] direction that induce this resonance are clearly visible. In addition to plotting a map of electric fields within the structure, it is possible
Figure 4.8: A typical 3D FEM model set-up using the theoretical modelling software HFSS [121]. The structure to be interrogated is a simple cubic arrangement of air spheres in a material matrix of refractive index $n = 1.71$. The unit cell has been replicated 4 times throughout the depth ($\hat{z}$) of the array. The 4 exposed sides of the array in the $\hat{x} - \hat{z}$ and $\hat{y} - \hat{z}$ planes are covered by master or slave boundaries. Each opposing master/slave boundary is connected and allows the structure to be repeated as an infinitely repeating array in these directions. Air surrounds the structure.
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Figure 4.9: (a) The $\hat{y} - \hat{z}$ plane view of a 12 unit cell-deep gyroid photonic crystal model. The dark blue regions define the mesh that represents the solid part of the structure, the remaining parts of the system are air. Floquet port planes are positioned at the top and bottom of the system as an incident plane wave source. (b) The time-averaged electric field profile within the system has been plotted at a frequency corresponding to the upper edge of the [011] photonic band-gap. The electric field strength is clearly periodic in the [011] direction of the structure’s geometry can be visualised using theoretical modelling.
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to calculate numerical electric field values over various volumes within the structure. Using FEM modelling, physical quantities such as field strength in specific pre-defined volumes, physical energy and concentration factors can be calculated from these values. In this thesis theoretical modelling was used in conjunction with experimental techniques and theoretical geometric analysis in order to identify, and confirm the origins of, stop-bands produced from triply periodic bicontinuous cubic photonic crystal structures.

4.9 Conclusion

Many different experimental and theoretical methods have been used in order to carry out the work presented in this thesis. Some of this work has taken place in the optical regime and some in the microwave regime. The work carried out in the microwave regime was performed on photonic crystal structures that are naturally occurring and exhibit a complex geometry that can not currently be synthetically fabricated in the optical regime with a high level detail. The naturally occurring bicontinuous cubic structures were fabricated with the use of a stereolithography machine with a resolution of approximately 50 \( \mu m \), which is ideal for fabricating structures with lattice constants on the millimetre scale. The complex nature of the structures and the memory capacity of the employed stereolithography machine results in the limitation of sample size. A sample that possesses an interface with a small surface to which radiation is incident usually provides an obstacle for experimental characterisations due to the relative size of the incident ‘beam-spot’. In order to overcome this issue, a reduced ‘beam-spot’ size was used in the experiments used to probe these structures. This was achieved by using an incident microwave beam that possesses a Gaussian profile. The full-width half-maximum of the Gaussian beam profile, which contains the majority of its incident power, was measured at various distances away from the broadband source. The sample was then placed at an appropriate distance where the full-width half-maximum of the Gaussian beam was smaller than the sample interface. In addition to this, when the sample is positioned closer to the incident beam, the degree of beam-spread produced by the Gaussian beam is reduced. This results in the ability to accurately electromagnetically characterise the bicontinuous cubic structures fabricated for the microwave regime, overcoming the problem of sample size limitations brought about by stereolithography fabrication techniques.

For the work presented in this thesis, a wide variety of experimental techniques have been used in order to probe and characterise many naturally occurring photonic crystal structures. For the work carried out in the optical regime, these methods include optical imaging and spectroscopy, imaging scatterometry and electron microscopy of optical
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micro-structures. Alongside these methods, image analysis was used to determine and quantify various structural parameters including the degree of rotational symmetry and the level of disorder present in various optical structures, discussed in later chapters. In addition to this, theoretical modelling has also been employed. The concurrent use of these methods, outlined in this section, allows for the full characterisation of a photonic system, by gathering extensive data from both the structural and optical perspectives. In particular, the scatterometer has proved to be a useful tool for identifying the spatial scattering consequences of the underlying photonic structures. These include the specular or diffuse nature of the scattering structures and the level of iridescence produced by a photonic system. This device is a relatively new development by Stavenga et al. [105] and is continually being updated in order to obtain new information from the scattering profiles of photonic systems. Generally, few published investigations into naturally occurring photonic crystal structures use such a vast array of techniques to enable a full and extensive characterisation of the structures and optical responses of naturally occurring structures.

The results obtained experimentally can be compared to analogous theoretical modelling. The theoretical model designs used for each system under analysis and presented in this thesis have been selected to closely mimic the experimental set-ups used to probe the physical, organic system whilst simultaneously minimising processing power and time. In most cases, such as the work carried out in chapter 5, the same CAD files are used to create the models used both in the experimental and theoretical interrogation. However, in some cases small approximations to the experimental configurations must be employed in the theoretical models, such as the work presented in chapter 8 of this thesis, in order to reduce the model size and processing time. Theoretical modelling is an extremely valuable tool for confirming the origin of reflection and transmission features observed in experimental data but also provides an additional benefit. Numerical electric field values determined from pre-defined volumes in a theoretical model can be calculated and, from this, various physical quantities can be calculated. If the experimental and theoretical electromagnetic responses of a structure provide a good match, then quantities such as electric field strength in specific volumes, physical energy and the concentration factor of photonic systems can be calculated, something that is only obtainable by theoretical modelling. The combination of the experimental methods outlined in this chapter alongside theoretical modelling of identified photonic geometries, often deduced from SEM image analysis, allows for the full and complete characterisation of the systems under investigation.
Chapter 5

The characterisation of natural photonic crystal replicas in the microwave regime

5.1 Introduction

Self-assembling periodic structures form readily in nature. In section 2.6.1 of chapter 2 a variety of self-assembling structures that form from minimal surfaces or constant mean curvature (CMC) surfaces were discussed. If formed on the correct length scales, their periodic and self-assembling nature makes minimal surface and CMC surface structures appropriate for use as photonic crystals. Such photonic structures have recently been discovered to be present on the elytra and wings of several beetles and butterflies as the source of structural colour [107] [9] [11] [10]. The self-assembly mechanisms behind naturally occurring optical 3D photonic crystals is currently largely unknown. However, the process that leads to the production of the gyroid photonic crystal structure on butterfly wings is beginning to be understood and some theories regarding its production are under development [68] [123] [8] [89] [124] [11].

Generally, the self-assembly mechanism that generates minimal surface structures requires the production of a surface of minimum energy, which ultimately separates two media comprising different refractive indices. Although natural processes are able to self-assemble organic materials to create these structures on optical length-scales, traditional technological fabrication methods have suffered from resolution limitations that prevent the fabrication of extremely intricate structures on a similar length-scale to the naturally occurring systems. Current technologies are being expanded to facilitate the production of self-assembling CMC surface photonic crystal structures. Currently only
structures much smaller than the wavelength of light can be fabricated by self-assembly methods [79] [84] [80] [87] [125] [126]. Advances in non-self-assembly processes such as direct laser writing are producing increasingly improved resolution limits that provide the prospect for future sample fabrication of extremely intricate structures at near infrared [127] [128] [108] [129] and optical length scales [109]. Other fabrication methods for the production of optical photonic structures that are currently progressing the field include stacking processes [110], colloidal self-assembly [130] [111] [131], novel methods of bio-templating naturally occurring optical photonic structures [112] and lithography techniques [132] [133] [113]. Although the desired optical fabrication length-scales are obtainable for some simple structures with these methods, highly intricate and complex 3D optical structures would require a smaller resolution limit than is currently available. In particular the more complex structures associated with the intricate curves of minimal surface and CMC structures are limited to non-optical regimes for current synthetic fabrication methods. In section 3.3.4 of chapter 3 the scalability of Maxwell’s equations was discussed. Due to the scalable properties of Maxwell’s equations, it is possible to probe larger photonic structures, in longer wavelength regimes, in order to facilitate the experimental determination of the electromagnetic response of analogous smaller optical structures. Three-dimensional printing using stereolithography principles, outlined in section 4.6.1, is a fabrication technique suitable for creating complex three-dimensional photonic structures on millimetre length scales suitable for analysis in the microwave regime. This method has previously been successfully used for fabricating synthetic quasi-ordered photonic crystals [115] and large-scale replicas of simpler butterfly photonic structures in order to measure their electromagnetic responses in longer wavelength regimes [114] [17]. With this fabrication technique, even very complex physical structures, comprising elaborate geometries, can be manufactured to possess resonant transmission/reflection frequencies that lie comfortably within an experimentally accessible microwave frequency range. In this instance, the sample fabrication resolution, of approximately 50 $\mu$m, does not limit the use of millimetre-scale lattice constants and interrogation wavelengths used in the experiments [13].

In this chapter the electromagnetic characteristics of the three fundamental triply periodic bicontinuous cubic photonic structures are investigated using both experimental and theoretical methods. The structures were fabricated on the millimetre length-scale and probed in the microwave regime. The photonic structures were all found to possess a linear polarisation-dependent response. In order to assess the origin of this polarisation dependence, the origin of each stop-band was determined and the concept of concentration factors, introduced in section 3.3.3.4, was used to describe the energy difference in each case.
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Figure 5.1: Examples of the three basic constant mean curvature surfaces; the (a) P, (b) D and (c) G surfaces, based on simple cubic, face-centred cubic and body-centred cubic Bravais lattice symmetries, respectively. The dark and light sides of each surface represent the two different interconnecting labyrinths that form the crystal structure. Underneath each image is a set of images taken from each surface at different perspectives. From left to right the images are rotated to a view approximately along the [001], [011] and [111] directions for each surface geometry.

5.2 Fabrication and characterisation procedure

The three-dimensional computer-aided design (CAD) software Solidworks [116] was used alongside the three-dimensional surface-creating software K3DSURF [117] to fabricate three synthetic three-dimensional CMC surface structures. These three structures are produced from the P-, D- and G-surfaces and are based on the simple cubic (SC), face-centred cubic (FCC) and body-centred cubic (BCC) Bravais lattice symmetries, respectively. The unit cells of the three CMC surfaces that form each of these structures are presented in figure 5.1(a), (b) and (c) respectively. The dark and light coloured sides of each surface in the figure represent the two opposing sides of the surface that form two independent labyrinths. Each of the, completely connected, labyrinths are intertwined with the other in order to form the complete crystal structure. In this study, each structure comprises a solid labyrinth made of a dielectric polymer and an air labyrinth. Each resultant unit cell is repeated as an array, forming the photonic crystal. Each sample was fabricated with a unit cell lattice constant of 7 mm. The 7 mm lattice constant was chosen so that the first order electromagnetic transmission features associated with each structure were located in the frequency range of 10-43 GHz. This frequency range coincided with the best working frequency range of the broadband
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source and detector that were used to conduct the experimental characterisation of each structure, as outlined in section 4.6 in chapter 4. Although all three structures vary with structural parameters such as pore size diameter, the lattice constant was chosen to be constant between samples so that the analysis and characterisation of stop-band positions could be conducted with a direct comparison between the three structures. Due to the memory capacity of the stereolithography machine used to fabricate the structures, each sample was designed with a total of four unit cells in the depth of the array in order to maximise the possible number of unit cells that form the surface area upon which microwaves were incident. Allocating four unit cells to the depth of each array allows the transmission experiments to be performed with a reduced level of absorption, that may occur for larger depths. This results in a more comparable analogy to the reflectance produced by the structure. All fabricated samples were designed so that the interface on which microwaves were incident was parallel to the (001) plane of the structural geometry.

The experimental apparatus consisted of an emitting and a receiving broadband horn attached to an Anritsu Vector Star 70 kHz to 70GHz vector network analyser as described in section 4.6 in chapter 4. The sample was centred between aligned source and detector horns and each sample was surrounded with microwave absorber, consisting of carbon-loaded foam, to ensure that only the radiation transmitted through the structure was collected by the receiving horn. The experiments were performed in transmission, using both transverse magnetic (TM) and transverse electric (TE) linear polarizations at two azimuthal angles, defined by figure 4.5 in section 4.6.2. These two angles were $\phi = 0^\circ$ and $\phi = 45^\circ$. Each sample was mounted upon a rotating table and measurements taken every 1° over a polar angle range of $-45^\circ \leq \theta \leq 45^\circ$, as defined by figure 4.5 in section 4.6.2. As the three structures under investigation are based on cubic symmetries, this range of experimental angles includes interrogation of the sample through the high-symmetry directions present in their geometries and allows for the electromagnetic characterisation of each structure over an extensive angle range. Their responses have been characterised, both experimentally and theoretically in the microwave regime. The CAD models that were designed and used in the fabrication of the microwave replicas were the same digital models that were used in the comparative theoretical FEM modelling that was employed to assess the electric field behaviour within each system.

5.3 Analysis of effective plane geometry

Section 3.2.2 outlined a method for determining the frequency shift of reflected light from a multilayer, where periodic effective geometric planes are parallel to the interface
upon which radiation is incident. This resulted in a blue shift, or increase in reflected frequency, when incident angle was increased. By adapting equation 3.16, presented in section 3.2.2, it is possible to determine that the wavevector response of a multilayered configuration of effective planes, such as that presented in figure 3.3, roughly follows the response of a $tan^2(\theta_1)$ function over the polar angle range of $-90^\circ \leq \theta_1 \leq 90^\circ$. This derivation is presented below:

$$k_0^2 = k_x^2 + k_z^2 = (k_z tan(\theta_1))^2 + k_z^2 = k_z^2 (1 + tan(\theta_1)^2),$$

where $\theta_1$ is the angle between the incident beam and the normal to the effective structural planes and $k_x$ and $k_z$ are the component incident wavevectors in the $\hat{x}$ and $\hat{z}$ directions, as shown in figure 3.16 presented in section 3.2.2. Consider a set of effective geometric planes arranged at an angle 45° to the incident surface. When increasing the incident polar angle, from the normal to the incident surface, the incident beam may move in a direction away from or towards the normal to the set of effective planes. If the incident angle moves towards the surface normal of the set of periodic effective planes, a red-shift in reflected frequencies results. If moving away from the normal to the set of effective planes, the resonant frequency is blue-shifted, in accordance with the approximation of the response outlined by the derivation in equation 5.1. Therefore, the reflected frequency shift that occurs by changing the incident polar angle upon the surface of a structure is determined by the orientation of effective planes in relation to the incident surface.

A 3D photonic crystal contains many different orientations of effective structural planes. As a result, the frequency response from a 3D photonic crystal will include many resonances that either red- or blue-shift at different rates, approximated by equation 5.1, when the incident angle is changed according to the crystal lattice geometry. Explicitly, when a wavevector is incident upon a 3D photonic crystal, a standing wave resonance will be induced if it has a component part along a direction of periodicity within the crystal geometry and if it possesses an appropriate wavelength. A broadband incident beam, such as that used in the microwave experiments outlined in section 5.2, comprises many different incident wavelengths. As a result, at a particular incident angle, many of the orientations of periodic effective planes present within the 3D crystal geometry can induce a standing wave resonance, and consequently a photonic band-gap, providing the incident beam has a component of the appropriate incident wavevector along that direction. The required wavevectors necessary to induce each standing wave is determined, predominantly, by the effective plane spacings along each of the various periodic directions throughout the crystal. Alongside this, the dispersion of each stop-band adheres approximately to the description given above.
Each of the structures characterised in this chapter were designed so that the interface to which radiation was incident was parallel to their (001) geometric planes. The dispersion properties relating to a set of periodic effective planes is determined by the angle between the surface normal to that set of planes and the incident beam. As a result, for example, the periodic effective planes arranged in the [001] direction will produce a dispersion given by the approximation of equation 5.1 where the incident angle is also equal to $\theta_1$. Consider the same 3D photonic crystal geometry with the incident interface selected to be parallel to another set of planes, or with the selection of an arbitrary interface orientation. In this case the values of $\theta_1$, namely the angles between the incident beam and the normal to each effective structural plane, have changed for each set of effective periodic planes within the geometry. As an example, the incident angle is no longer equal to $\theta_1$ for the set of (001) planes. As a result, the dispersion associated with each set of planes still approximately follows the $1 + \tan(\theta_1)^2$ function but each band-gap will have a different $\theta_1$ value at normal incidence, and at all other angles when compared to another interface clipping orientation. Explicitly, clipping or changing the orientation of the interface of a specific photonic crystal geometry will change the value of $\theta_1$ for all effective plane geometries. Consequently, the dispersion of each associated band-gap will still follow the same general trend, but the change of value $\theta_1$ will change the appearance of the new dispersion graph accordingly.

### 5.4 The P-surface

The P-surface, presented in figure 5.1(a), belongs to the $Pm\bar{3}m$ crystal space group [134]. A surface equation that can describe the minimal P-surface by a nodal surface approximation is

$$\cos(X) + \cos(Y) + \cos(Z) = t,$$

where

$$X = \frac{2\pi x}{a},$$

$$Y = \frac{2\pi y}{a},$$

$$Z = \frac{2\pi z}{a},$$

$x$, $y$ and $z$ represent the Cartesian spatial co-ordinates and $a$ is the lattice constant of a unit cell. The value of ‘$t$’ in equation 5.2 determines the relative volumes of each interconnecting labyrinth of the P-surface, consequently determining the filling fraction of the resulting structure. The value of ‘$t$’ was chosen to be $t = 0$ for the fabrication of
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Figure 5.2: The resulting photonic crystal array based on the minimal P-surface. The lattice constant of the structure is 7 \text{ mm} which produces a resonant stop-band response in the microwave regime. The array has dimensions of 20 \times 20 \times 4 unit cells. The structure has a material volume fraction of \( \phi_s = 0.5 \) comprising 50\% dielectric polymer with refractive index \( n = 1.710 + 0.014i \) and 50\% air. Scale bar: 10 \text{ mm}.

the P-surface photonic crystal replica, which corresponds to a material volume filling fraction of \( \phi_s = 0.5 \). The photonic crystal array was fabricated as a 20 \times 20 \times 4 \text{ unit cell} model using the stereolithography technique. The structure comprised one dielectric polymer labyrinth, with a refractive index of \( n = 1.710 + 0.014i \), and one air labyrinth and is presented in figure 5.2.

5.4.1 Microwave vector network analyser experimental measurements

Figures 5.3(a)-(d) show the experimental transmission data obtained from the P-surface structure over the polar and azimuthal angle ranges discussed in section 5.2. Each plot is represented in the reduced frequency regime where \( c \) is the speed of light and \( a \) is the lattice constant. The data are represented by grey-scale plots which display, from dark to light, low to high transmitted intensity. The dark bands therefore represent, primarily, the stop-bands produced by the photonic crystal. Each stop-band arises from the interaction of microwaves with the effective structural planes that exist within the structure’s geometry. The corresponding spacings of these planes and their interaction with an incident wavevector were considered in order to determine the origin and relative frequencies of each transmission stop-band observed in figures 5.3(a)-(d), as outlined in section 5.3. The Miller indices of the directions within the crystal structure
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that possess the set of periodic planes that give rise to each stop-band has been labelled on figures 5.3(a)-(d). There is a very distinct difference in the width of the stop-bands, particularly for the [011] band, between the TE and TM data. This difference is explained in the following section by the use of theoretical modelling. In addition to this, the confirmation of the directions through the crystal and the sets of periodic effective planes that are responsible for each stop-band can be obtained by theoretical modelling and analysis of the resulting electric field configurations present within the structure.

5.4.2 Theoretical modelling

Theoretical FEM modelling was undertaken on a P-surface structure designed to replicate the experimental model and set-up exactly. Identical CAD models were used in the theoretical models and in the fabrication of the physical models used in the experiment. The results, presented in figure 5.4, display an extremely good correlation with the corresponding experimental data, presented in figure 5.3. The strong agreement between theoretical and experimental data allows subsequent theoretical field analysis to be undertaken in order to determine the structural origin of each stop-band. Figures 5.4(a)-(d) have been labelled with the Miller indices of the associated directions at which effective planes give rise to stop-bands within the structure, confirmed by electric field plots extracted from the theoretical models. The example field plots presented in figure 5.5 display the time-averaged electric field profiles obtained at the lower frequency edge of the (a) [001] stop-band and the (b) [111] band, using TE polarised incident radiation. Figure 5.5(a) displays a standing wave-type resonance with a clear periodicity, or ‘quantisation’, in the z-direction, explicitly, the standing wave resonance is clearly visible in the structure and occurs due to the set of (001) planes present within the structure. However, figure 5.5(b) displays a quantisation in a diagonal direction with resonances occurring due to the (111) set of planes present within the structure.

There exists a slight difference in the band-width of some of the transmission stop-bands between the two incident polarisations used, as observed in figure 5.4. This difference was quantified by the calculation and analysis of the associated concentration factors at the stop-band edges for each incident polarisation from the theoretical models. A description of the concentration factor and its role in determining bandwidths is presented in section 3.3.3.4 of chapter 3. In this chapter all concentration factors are quoted to 2 decimal places as this was found to be sufficient when making the relevant comparisons. The largest difference in the width of the stop-band between the two polarisations occurs with the [011] and [011] bands, at \( \theta = 45^\circ \), for each polarisation were calculated to be \( CF_{\text{lower} \ TM} = 75.80\% \),
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Figure 5.3: The experimentally determined transmission bands associated with the P-surface photonic crystal replica. Each plot is represented in the reduced frequency regime where \( c \) is the speed of light and \( a \) is the lattice constant. The sample was analysed over a polar angle range of \(-45^\circ \leq \theta \leq 45^\circ\) at azimuthal angles of (a) and (b) \( \phi = 0^\circ \) or (c) and (d) \( \phi = 45^\circ \), defined in figure 4.5. The incident radiation used was linearly polarised TM, (a) and (c), or TE, (b) and (d), radiation. The origin of each stop-band has been identified using the notation of Miller indices, as described in section 5.3.
Figure 5.4: The theoretically determined transmission stop-bands associated with the P-surface photonic crystal. Each plot is represented in the reduced frequency regime where \( c \) is the speed of light and \( a \) is the lattice constant. The sample was analysed over a polar angle range of \(-45^\circ \leq \theta \leq 45^\circ\) at azimuthal angles of (a) and (b) \( \phi = 0^\circ \) or (c) and (d) \( \phi = 45^\circ \), defined in figure 4.5. The incident radiation defined in the models were linearly polarised TM, (a) and (c), or TE, (b) and (d), radiation. The origin of each stop-band has been identified using the notation of Miller indices, as described in section 5.3.
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Figure 5.5: The theoretically determined time-averaged electric fields present in the P-surface photonic crystal at (a) the lower edge of the [00\bar{1}] band and (b) at the lower edge of the [\bar{1}\bar{1}\bar{1}] band in the dielectric medium. The data was obtained with TE linearly polarised incident radiation at an azimuthal angle of $\phi = 45^\circ$ and polar angle of $\theta = 30^\circ$.

$CF_{upper\ TM} = 56.80\%$ and $CF_{lower\ TE} = 68.45\%$, $CF_{upper\ TE} = 68.02\%$, respectively. Each concentration factor corresponds to a band-edge frequency of $f_{lower\ TM} = 0.511$, $f_{upper\ TM} = 0.558$ and $f_{lower\ TE} = 0.513$, $f_{upper\ TE} = 0.518$, respectively, in reduced units. The band widths of the TM and TE [00\bar{1}] bands at $\theta = 45^\circ$ also differs. The concentration factors at the lower and upper edge of the TM and TE [00\bar{1}] bands, at $\theta = 45^\circ$, were calculated to be $CF_{lower\ TM} = 69.07\%$, $CF_{upper\ TM} = 62.82\%$ and $CF_{lower\ TE} = 73.33\%$, $CF_{upper\ TE} = 59.99\%$, respectively. Each concentration factor corresponds to a band-edge frequency of $f_{lower\ TM} = 0.343$, $f_{upper\ TM} = 0.429$ and $f_{lower\ TE} = 0.338$, $f_{upper\ TE} = 0.439$, respectively, in reduced units. It is the differences in the concentration factors at the edges of each band that gives rise to different band-widths associated with each incident polarisation. Namely, the difference in the concentration factors at the edges of the TE [0\bar{1}\bar{1}] band is much smaller than for that of the TM [0\bar{1}\bar{1}] band and so the TE [0\bar{1}\bar{1}] band-width is smaller. The origin of the difference in concentration factor for each polarisation at each band-edge can be described by studying the orientation of electric field with respect to the dielectric struts that form the photonic crystal geometry. This can be demonstrated for the [00\bar{1}] band when TE and TM light is incident upon the P-surface structure at $\theta = 45^\circ$. The P-surface photonic crystal structure can be approximated by a cubic arrangement of dielectric
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struts. Such a structure is presented in figure 5.6. At normal incidence, the electric field vectors of both TE and TM incident radiation experience the same arrangements of dielectric struts. Consequently, the cube appears the same to both polarisations, as shown by figure 5.6(a). Explicitly, for within a single unit cell, for both polarisation cases the electric field vectors run parallel to the length of 4 struts and perpendicular to the length of 8 struts when travelling through the crystal geometry. For this reason, at normal incidence the transmission response of the TE and TM data are identical, as shown in figures 5.3 and 5.4. When the incident beam moves away from normal incidence, as displayed in figure 5.6(b), the electric fields in the TE polarised case experience similar proportions of the dielectric struts to the normal incident case. However, this is not the case when TM polarised light is considered. When polar angle, \(\theta\), is larger than zero the electric field in the TM polarised case will no longer be parallel to the length of any rod, as shown in figure 5.6(c). Where previously the electric field, \(E\), of the TM beam ran parallel to 4 of the possible 12 struts at normal incidence, the electric field, \(E\), now has an \(E \cos \theta\) component running parallel to these struts. In addition to this, TM polarised light now has components of electric field in the direction parallel to 4 of the struts to which electric fields were previously perpendicular. Subsequently, there is an additional \(E \sin \theta\) component of electric field, \(E\), that now runs parallel to these extra 4 struts. Therefore, away from normal incidence, there is an absence of symmetry relating to the two opposing polarisation states. When light is incident on the structure at \(\theta = 45^\circ\) and standing wave resonances are occurring along the [00\overline{1}] direction, this difference in electric field configuration relative to dielectric struts may account for the difference in concentration factors between the two incident polarisations. Consider the TM case purely along the [00\overline{1}] direction, where at normal incidence the electric field ran parallel to 4 of the dielectric struts. When incident angle is increased, only an \(E \cos \theta\) component of the incident electric field runs parallel to each of these struts in the [00\overline{1}] direction. Consequently this will reduce the electric field concentration factor for the lower [00\overline{1}] TM band edge. As a result, the TE electric fields will experience a higher concentration factor compared to the TM case for the [00\overline{1}] lower band edge at \(\theta = 45^\circ\). In turn, a higher concentration factor at the lower band-edge will result in the reduction of its frequency and alter the band-width. For all other symmetry directions the proportion of electric fields running parallel or perpendicular to dielectric struts has a great effect on the concentration factor of each polarisation case, as also highlighted in section 3.3.3.4 [20]. This may contribute to the difference in concentration factors for the two polarisation cases when field profiles along the [01\overline{1}] direction, where \(\theta = 45^\circ\), are considered. A publication by Poladian et al. [135] also calculated, by theoretical modelling, that a sizable band-gap difference was expected to occur in the [0\overline{1}1] direction between TE and TM polarisation cases for the P-surface structure.
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Figure 5.6: (a) The P-surface photonic crystal structure can be approximated by a series of dielectric struts arranged as a cube. The electric fields of TE and TM polarised light experience the same geometry when light is incident upon the structure at normal incidence. (b) When polar angle $\theta$ is increased, the electric fields of TE and TM polarised light experience very different proportions of the dielectric struts. Consequently the cube does not appear the same to both linear polarisation states away from normal incidence. (c) Purely along the [001] direction the electric field of TM polarised light will experience less of the dielectric rods compared to TE polarised light per unit cell. This results in a difference in concentration factor and consequently a different bang-gap width for the two polarisation cases.

The publication stated an analysis on the P-surface structure using group theory may also predict this polarisation-dependent response. The work presented in this section explicitly identifies a possible reason behind this sizable difference in band-gap width along this high-symmetry direction and the behaviour of linearly polarised light away from normal incidence, including the quantitative analysis using concentration factors.

5.5 The D-surface

The structure that forms from the D-surface, presented in figure 5.1(b), belongs to the $Fd\bar{3}m$ crystal space group [136] and is based on face-centred cubic (FCC) Bravais lattice symmetry. A surface equation that can describe the minimal D-surface by a
The nodal surface approximation is
\[
\sin(X)\sin(Y)\sin(Z) + \sin(X)\cos(Y)\cos(Z) \\
+ \cos(X)\sin(Y)\cos(Z) + \cos(X)\cos(Y)\sin(Z) = t,
\]
where \(X, Y\) and \(Z\) are defined by equations 5.3. For the fabrication of the D-surface photonic crystal replica, the value of ‘\(t\)’ in equation 5.4 was also chosen to be \(t = 0\), corresponding to a material volume fraction of \(\phi_s = 0.5\). The dimensions of the D-surface photonic crystal array were chosen to be \(18 \times 18 \times 4\) unit cells and the fabricated sample is presented in figure 5.7. The polymer that makes up the solid labyrinth of this structure has a refractive index of \(n = 1.680 + 0.014i\).

5.5.1 Microwave vector network analyser experimental measurements

Figures 5.8(a)-(d) show the experimental transmission data obtained from the D-surface structure obtained over the angle ranges discussed in section 5.2. The geometric analysis discussed in section 5.3 was also performed on the D-surface structure, in order to ascertain the structural origin of each band. The directions through the crystal struc-
ture that provide the periodic effective structural planes that give rise to each stop-band have been labelled on figures 5.8(a)-(d) with their associated Miller indices. The spacing of certain geometric planes in the D-surface structure are identical to those within the P-surface structure, such as the set of $\{\bar{1}\bar{1}\bar{1}\}$ planes. Consequently these planes invoke stop-bands at approximately the same frequency and exhibit similar dispersion behaviour over the experimentally and theoretically analysed polar angle range. This can be observed in the comparison of the $\{\bar{1}\bar{1}\bar{1}\}$ bands in figure 5.8(c) and (d) and the $\{\bar{1}\bar{1}\bar{1}\}$ bands in figures 5.3 and 5.4(c) and (d). However, in comparison with the P-surface structure, every unit cell of the D-surface structure possesses an additional periodic plane in the $[00\bar{1}]$ direction. Consequently, the $[00\bar{1}]$ stop-bands in figures 5.8(a)-(d) occur at a higher frequency than that in figure 5.3(a)-(d). The directional Miller indices associated with periodic planes that give rise to each resonance, labelled on figure 5.8, have also been verified by the theoretical modelling and field analysis, presented in the following section.

5.5.2 Theoretical modelling

Theoretical FEM modelling was undertaken on the D-surface structure using both TM and TE polarisations over the same polar and azimuthal angles as were investigated in the experiment, using the identical CAD model that was used to fabricate the physical model. These theoretical results, presented in figures 5.9(a)-(d), also display a strong agreement with the experimental data. Consequently, electric field analysis was conducted in order to confirm the effective structural planes responsible for each transmission stop-band. Figures 5.10(a) and (b) present the arrangement of the time-averaged electric field profiles at two of the frequencies where standing waves are set up along directions of high-symmetry within the D-surface structure. The electric field plots were obtained with TE linearly polarised incident radiation at an azimuthal angle of $\phi = 45^\circ$ and polar angle of $\theta = 10^\circ$, where each stop-band is clearly identifiable and does not overlap with another. Figure 5.10(a) presents the time-averaged electric field arrangement in the dielectric medium at the lower edge of the TE $[00\bar{1}]$ band in figure 5.9(d). The regions of high electric field are present in the dielectric medium and quantisation occurs in the $\hat{z}$-direction. The arrangement of the time-averaged electric field profiles in air at the upper edge of the TE $[\bar{1}\bar{1}\bar{1}]$ band in figure 5.9(d) is presented in figure 5.10(b). For this case, the structure has been rotated to a view that is close to the $[\bar{1}\bar{1}\bar{1}]$ direction, for clarity. The regions of high electric field are present in the air labyrinth and quantisation occurs along the $[\bar{1}\bar{1}\bar{1}]$ direction. Each stop-band in figure 5.9 has also been labelled with the Miller indices of the associated directions at which effective planes give rise to stop bands within the D-surface structure, verified
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Figure 5.8: The experimentally determined transmission bands associated with the D-surface photonic crystal replica. Each plot is represented in the reduced frequency regime. The sample was analysed over a polar angle range of $-45^\circ \leq \theta \leq 45^\circ$ at azimuthal angles of $\phi = 0^\circ$, (a) and (b), or $\phi = 45^\circ$, (c) and (d), defined in figure 4.5. The incident radiation used was linearly polarised TM, (a) and (c), or TE, (b) and (d), radiation. The origin of each stop-band has been identified using the notation of Miller indices, as described in section 5.3.
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Figure 5.9: The theoretically determined transmission stop-bands associated with the D-surface photonic crystal. Each plot is represented in the reduced frequency regime. The sample was analysed over a polar angle range of $-45^\circ \leq \theta \leq 45^\circ$ at azimuthal angles of $\phi = 0^\circ$, (a) and (b), or $\phi = 45^\circ$, (c) and (d), defined in figure 4.5. The incident radiation defined in the models were linearly polarised TM, (a) and (c), or TE, (b) and (d), radiation. The origin of each stop-band has been identified using the notation of Miller indices, as described in section 5.3.
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Figure 5.10: The theoretically determined time averaged electric fields present in the D-surface photonic crystal at (a) the lower edge of the [00\bar{1}] band in the dielectric medium and (b) at the upper edge of the [\bar{1}\bar{1}\bar{1}] band in air. The data was obtained with TE linearly polarised incident radiation at an azimuthal angle of $\phi = 45^\circ$ and polar angle of $\theta = 10^\circ$. The value of $\theta = 10^\circ$ was chosen as, at this angle, each stop-band is clearly identifiable and does not overlap with another.

by electric field analysis.

The experimental and theoretical data presented in figures 5.8 and 5.9 show that the TE and TM responses are extremely similar. In particular, the widths of the experimentally and theoretically determined stop-bands do not vary drastically when the incident polarisation is changed. This structure has the most isotropic Brillouin zones of all three structures under investigation here, however, there is a clear difference in stop-band widths induced by different incident polarisations for the [\bar{1}\bar{1}\bar{1}] and [11\bar{1}] bands. This has also been quantified by the electric field results obtained from the theoretical modelling. The concentration factors at the upper and lower edges of the [\bar{1}\bar{1}\bar{1}] band were calculated for each polarisation at an incident polar angle of $\theta = 10^\circ$ and an azimuthal angle of $\phi = 45^\circ$. The concentration factors at the lower and upper edge of the TM and TE bands at this angle were calculated to be $CF_{\text{lower, TM}} = 76.17\%$, $CF_{\text{lower, TE}} = 91.7\%$, $CF_{\text{upper, TM}} = 79.0\%$, and $CF_{\text{upper, TE}} = 84.8\%$. The concentration factors for the [11\bar{1}] band at this angle were calculated to be $CF_{\text{lower, TM}} = 75.3\%$, $CF_{\text{lower, TE}} = 94.8\%$, $CF_{\text{upper, TM}} = 81.8\%$, and $CF_{\text{upper, TE}} = 86.7\%$.
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\[ CF_{\text{upper TM}} = 76.06\% \quad \text{and} \quad CF_{\text{lower TE}} = 73.28\%, \quad CF_{\text{upper TE}} = 69.22\%, \] respectively.

The extremely small difference in concentration factors for the TM $[\bar{1}\bar{1}\bar{1}]$ band results in the small stop-band width associated with it. Although the most isotropic of 3D photonic crystal structures, the D-surface structure is also dependent on incident linear polarisation in its stop-band response. This is particularly visible for the case of the TE and TM $[\bar{1}\bar{1}\bar{1}]$ stop-band, present in figures 5.8(c) and (d) and 5.9(c) and (d). As with the polarisation dependence of the P-surface structure, the arrangement of dielectric struts of the D-surface structure is likely to be responsible for this effect.

5.5.3 P- and D- surface summary

Both the P- and D- surface photonic crystal structures have been electromagnetically characterised, both by experimental and theoretical analysis in the previous sections. The structural origin of each associated stop-band has been identified and common/contrasting structural attributes between the two structures have been determined. In some cases the effective structural planes responsible for a particular stop-band in the P-surface structure have the same spacing as the equivalent set of planes in the D-surface structure. Consequently, the frequencies at which they occur are comparable and each respective stop-band exhibits similar behaviour over the analysed polar angle range. The experimental and theoretical data have shown an extremely good agreement which has allowed the electric field analysis at band-edge frequencies to be conducted. The electric field profiles obtained theoretically at band-edge frequencies have allowed the identification of the structural origin of each stop-band resonance. In addition to this, theoretical modelling allows the calculation of concentration factors to be performed in order to determine the differences in response between polarisations. The arrangement of dielectric struts within the P- and D- surface structures are a possible reason for the presence of linear polarisation-dependent stop-bands. The origin of this phenomenon was described for the P-surface structure alongside a quantitative analysis using concentration factor values. In this geometric analysis, the orientation of the incident electric field interacts with horizontal and vertical struts in a different manner at various geometric orientations. When band-edge standing waves are set up in the photonic crystal, the arrangement of dielectric struts may produce polarisation-dependent concentration factors, consequently increasing or reducing the respective band-edge frequencies. This would create polarisation-dependent bandwidths for certain stop-bands. In the next section the electromagnetic characterisation of the G-surface structure, or ‘gyroid’, is presented.
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5.6 The G-surface

Figure 5.11: The resulting photonic crystal array based on the G-surface. The lattice constant is 7 mm which produces a resonant electromagnetic response in the microwave regime. The array has dimensions of $15 \times 15 \times 4$ unit cells. The materials used in the structure are a dielectric polymer with refractive index $n = 1.656 + 0.014i$ and air. The material volume fraction of the structure is $\phi_s = 0.4$ and was chosen in order to mimic the electromagnetic response of the gyroid photonic crystal found in the wing scales of the butterfly $P. sesostris$. Scale bar: 10 mm. [13]

The G-surface that forms the gyroid structure is the most abundantly occurring of all minimal surfaces in nature: forming in mixtures of oil and water, human skin and butterfly scales [83] [84] [9]. The gyroid belongs to the generic crystal space group $I4_132$ [137]. The G-surface can be described by a nodal surface approximation defined by the equation

$$\sin(X)\cos(Y) + \sin(Y)\cos(Z) + \sin(Z)\cos(X) = t, \quad (5.5)$$

where $X$, $Y$ and $Z$ are defined by equations 5.3 presented in section 5.4 [138]. The gyroid is based on the body-centred cubic (BCC) Bravais lattice symmetry. The gyroid structure differs from the previously investigated P- and D-surface structures, not only in Bravais lattice symmetry but also, as it contains two chiral axes. The chiral axes present in the structure occur along the [100] direction of the crystal structure as a four-fold screw axis which projects squares and in the [111] direction as a three-fold
screw axis which projects triangles \([12][69]\). The precise rotation of these chiral axes are described as a right-handed 4_1 rotation along the [100] direction and a left-handed three-fold rotation along the [111] direction. The value of ‘\(t\)’ in equation 5.5 was chosen to be \(t = -0.3\) which corresponds to a material volume filling fraction of \(\phi_s = 0.4\). This value was chosen in order to mimic the response of the optical CMC gyroid photonic crystal found in the structurally coloured wing scales of the butterfly \textit{Parides sesostris} [9]. The structure comprised one polymer labyrinth, with a refractive index of \(n = 1.656 + 0.014i\), and one air labyrinth. The photonic crystal array was fabricated as a \(15 \times 15 \times 4\) unit cell model. The depth of the fabricated gyroid array comprises four unit cells whereas a \textit{P. sesostris} wing scale has approximately ten unit cells throughout its depth [47]. However, using fewer unit cells in the depth of the array minimises absorption effects when performing transmission experiments. This results in the comparable widths of the transmission stop-bands and corresponding electromagnetic band-gaps. When the number of unit cells in the depth of the photonic crystal is increased, the absorption present in the dielectric medium results in the transmitted band-widths being obscured by low intensity transmission band-edges. This is shown explicitly in a later chapter.

5.6.1 Microwave vector network analyser experimental measurements

Figure 5.12 shows the experimental transmission data taken from the enlarged replica of the optical gyroid photonic structure found within the wing scales of the butterfly \textit{P. sesostris}. The analysis was performed over the angle ranges discussed in section 5.2. Geometric analysis of the effective structural planes present within the gyroid structure was performed in order to ascertain the structural origin of each transmission stop-band as discussed in section 5.3. Consequently, the Miller indices that define the directions through the gyroid that give rise to each stop-band have been labelled on figure 5.12. The geometry of the gyroid structure dictates that the position of the [001] band should be similar to that of the D-surface structure and the [0\(\bar{1}\)\(\bar{1}\)] and [01\(\bar{1}\)] bands will be similar in position to that of the P-surface structure. The [10\(\bar{1}\)] and [10\(\bar{1}\)] bands cross the [0\(\bar{1}\)\(\bar{1}\)] and [01\(\bar{1}\)] bands in the same manner as was observed in the data obtained from the P-surface. Consequently, in the gyroid data the [10\(\bar{1}\)] and [10\(\bar{1}\)] stop-bands appear to overlap the [001] band. The combination of these two periodicities produce the band structure observed at an azimuthal angle of \(\phi = 0^\circ\), shown in figure 5.12(a) and (b). The [001] band is present in the \(\phi = 45^\circ\) data, however it is very weakly occurring in comparison to the other stop-bands originating from the gyroid [13].

When the sample is oriented at an azimuthal angle of \(\phi = 45^\circ\) there exist two differing sets of periodic planes along the [1\(\bar{1}\)\(\bar{1}\)] direction, and equivalent, within the gyroid geometry. The first originates from the set of (1\(\bar{1}\)\(\bar{1}\)) planes present within the
gyroid geometry which possess a very small plane spacing. Consequently, this results in the formation of a stop-band at very high frequencies, out of the analysed frequency range. The second originates from the alternative set of structural planes present in the gyroid structure when rotated azimuthally by 45°. Namely, when a BCC structure is rotated to an azimuthal angle of 45° it may be considered as a face-centred structure. The resonance occurs along the [01̅1] direction of this face-centred arrangement. The spacing between planes in this case results in the [1̅11] band, labelled on figures 5.12(c) and (d) occurring at a higher frequency than that of the [01̅1] band in figures 5.13(a) and (b). This set of resonant planes, identified through geometric analysis was confirmed by electric field analysis from theoretically modelled data.

5.6.2 Theoretical modelling

Theoretical FEM modelling was undertaken on the gyroid replica structure using both TM and TE polarisations over the same polar and azimuthal angles as were investigated in the experiment. The CAD model used to theoretically model the gyroid structure was identical to that used to fabricate the physical model. The results presented in figures 5.13(a)-(d) also display a very strong agreement with the corresponding experimental data, presented in figures 5.12(a)-(d). Figures 5.13(a)-(d) have also been labelled with the Miller indices of the associated directions at which effective planes give rise to stop-bands within the structure, confirmed by time-averaged electric field analysis. Examples of the electric field profiles that were obtained through theoretical modelling that confirmed the structural origin of each stop-band are presented in figure 5.14. Figure 5.14(a) and (b) were obtained at an azimuthal angle of φ = 0° and incident polar angle of θ = 30°. Figure 5.14(a) displays the theoretically determined time-averaged electric fields present at the lower edge of the TE [01̅1] band and figure 5.14(b) at the lower edge of the TM [00̅1] band, both within the dielectric medium. Figure 5.14(a) displays electric fields arranged as a standing wave mode that is quantised in a diagonal direction in the plane, namely the [01̅1] direction due to the (01̅1) set of structural planes within the gyroid. Figure 5.14(b) displays a standing wave that is quantised purely in the ẑ-direction, namely the [001] direction.

There also exists a difference in the widths of the stop-bands between the TE and TM polarised gyroid data sets. This difference was quantified by the calculation and analysis of the concentration factors at the stop-band edges for each incident polarisation. The [001] bands in figures 5.12(a) and (b) exhibit a large difference in stop-band width. The concentration factors at the lower and upper edge of the TM and TE [001] bands were calculated, at a polar angle of θ = 30° to be $CF_{\text{lower TM}} = 70.10\%$, $CF_{\text{upper TM}} = 57.81\%$ and $CF_{\text{lower TE}} = 61.41\%$, $CF_{\text{upper TE}} = 56.07\%$, respectively.
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Figure 5.12: The experimentally determined transmission bands associated with the CMC G-surface photonic crystal replica based on the photonic crystal structure found within the wing scales of the butterfly *P. sesostris*. The structure has a material volume fraction of $\phi_s = 0.4$. Each plot is represented in the reduced frequency regime. The sample was analysed over a polar angle range of $-45^\circ \leq \theta \leq 45^\circ$ at azimuthal angles of (a) and (b) $\phi = 0^\circ$ or (c) and (d) $\phi = 45^\circ$, defined in figure 4.5. The incident radiation used was linearly polarised (a) and (c) TM or (b) and (d) TE radiation. The origin of each stop-band has been identified using the notation of Miller indices, as described in section 5.3. [13]
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Figure 5.13: The theoretically determined transmission bands associated with the CMC G-surface photonic crystal that mimics the optical structure found within wing scales of the butterfly *P. sesostris*. Each plot is represented in the reduced frequency regime. The sample was analysed over a polar angle range of $-45^\circ \leq \theta \leq 45^\circ$ at azimuthal angles of (a) and (b) $\phi = 0^\circ$ or (c) and (d) $\phi = 45^\circ$, defined in figure 4.5. The incident radiation defined in the models were linearly polarised (a) and (c) TM or (b) and (d) TE radiation. The origin of each stop-band has been identified using the notation of Miller indices, as described in section 5.3. [13]
5. The characterisation of natural photonic crystal replicas in the microwave regime

Figure 5.14: The theoretically determined time-averaged electric fields present in the CMC G-surface photonic crystal at (a) the lower edge of the [01\bar{1}] band and (b) at the lower edge of the [00\bar{1}] band, in the dielectric medium. The data was obtained with (a) TE and (b) TM linearly polarised incident radiation at an azimuthal angle of $\phi = 0^\circ$ and polar angle of $\theta = 30^\circ$. 
This results in a 12.29% difference in concentration factors for the TM [00\bar{1}] band and only a 5.34% difference in concentration factors for the TE [00\bar{1}] band. Similarly, the concentration factors of the lower and upper edge of the [\bar{1}\bar{1}\bar{1}] bands in figures 5.12(c) and (d) were calculated, at a polar angle of \(\theta = 45^\circ\), to be \(CF_{\text{lower}TM} = 75.45\%\), \(CF_{\text{upper}TM} = 45.41\%\) and \(CF_{\text{lower}TE} = 71.651\%\), \(CF_{\text{upper}TE} = 63.88\%\), respectively. Each concentration factor corresponds to a band-edge frequency of \(f_{\text{lower}TM} = 0.569\), \(f_{\text{upper}TM} = 0.684\) and \(f_{\text{lower}TE} = 0.588\), \(f_{\text{upper}TE} = 0.653\), respectively, in reduced units.

This results in a 30.04% difference in concentration factors for the TM [\bar{1}\bar{1}\bar{1}] band and a 21.23% difference in concentration factors for the TE [\bar{1}\bar{1}\bar{1}] band. Such relative differences in concentration factors give rise to the different band-widths produced by the two polarisations of incident light [20]. The origin of this difference may also be attributed to the arrangement of dielectric stubs of the gyroid photonic crystal geometry with respect to each incident polarisation. Again, along certain directions within the geometry, this would result in a difference in concentration factor at each of the stop-band edges produced by each incident polarisation. The concentration of electric field of an allowed standing wave mode within the dielectric medium will directly affect its energy and therefore associated frequency and consequently its associated band-width [20].

5.6.3 Experimental and theoretical investigation into polarisation conversion

The chiral axes of the gyroid lie in the [00\bar{1}] and [\bar{1}\bar{1}\bar{1}] directions through the structure. The gyroid has recently been discovered to produce circular dichroism when circularly polarised light is incident upon the structure [69] [129]. The results presented in section 5.6 were obtained using linearly polarised microwave radiation, namely, the emission and collection of a single linear polarisation of radiation. The employed experimental set-up is such that it is possible to facilitate the experimental determination of linear polarisation conversion through the chiral gyroid. The experimental and theoretical data presented in figures 5.12 and 5.13, respectively, indicate the stop-band response from the [\bar{1}\bar{1}\bar{1}] direction can be determined when the sample is oriented at an azimuthal angle of \(\phi = 45^\circ\). The [00\bar{1}] response is present both when the sample is oriented at azimuthal angles of \(\phi = 0^\circ\) and \(\phi = 45^\circ\), but is strongest when the sample is oriented at an azimuthal angle of \(\phi = 0^\circ\). Due to the polarisation conversion that occurs within the structure, it is impractical to normalise against a reference measurement. Consequently, the presented experimental data in this section are unnormalised. The polarisation conversion data taken experimentally, presented in figure 5.15, and theoretically, presented in figure 5.16, at an azimuthal angle of \(\phi = 0^\circ\) show a strong
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correlation. The polarisation converted transmission response from TM (p) polarised incident light to TE (s) polarised light is labelled as $T_{ps}$ and from TE (s) polarised incident light to TM (p) polarised light is labelled as $T_{sp}$. Figures 5.15 and 5.16 show no clear evidence of polarisation conversion in transmission along the [00̅1] direction. The absence of polarisation conversion in the chiral [00̅1] direction may be due to the four-fold, 4₁, chiral nature of this axis. Such a structure possesses strong chirality along this direction due to the nature of the $I4_{1}32$ space group to which it belongs. However, the symmetry of a 4₁ screw axis will result in the same incident and exit polarisation having undergone a rotation within the structure. It is the three-fold axis that may provide the strongest conversion in transmission.

The polarisation conversion data taken experimentally, figure 5.17, and theoretically, figure 5.18, at an azimuthal angle of $\phi = 45^\circ$ shows stronger evidence of polarisation conversion in transmission along the [̅1̅1̅1] direction, yet still there is no evidence of polarisation conversion along the [00̅1] direction. The transmitted polarisation conversion that occurs along the [̅1̅1̅1] direction appears along the upper and lower edges of the gyroid [̅1̅1̅1] stop-band. The edges of the stop-band represent the frequencies that set up standing waves inside the structure, causing the resonant transmission response. The experimental data and the modelling data agree well, although the experimental data is unnormalised and so figure 5.17 exhibits lower intensities than observed in the modelling data, figure 5.18. Individual line plots of $T_{sp}$ transmitted radiation are displayed in figure 5.19. Each line plot was extracted from the experimental and theoretical data at an azimuthal angle of $\phi = 45^\circ$ and polar angles of (a) $\theta = 0^\circ$, (b) $\theta = 5^\circ$ and (c) $\theta = 10^\circ$. The plots show that most features are observed in both the experimental and theoretical data with a lower intensity, particularly at smaller polar angles. The correlation between the theoretically modelled and experimentally taken data deviates as the polar angle is increased due to the unnormalised nature of the experimental data.

5.7 Conclusion

The transmission response of the P-, D- and G-surface photonic crystal structures have been electromagnetically characterised with linearly incident polarisations over comprehensive polar and azimuthal angle ranges, both experimentally and theoretically. The experimental data and theoretical data showed excellent agreement and so electric field analysis was performed from theoretical models in order to identify the origin of each resonant feature produced by each structure. Consequently, the periodic effective planes from which transmission stop-bands originate have been identified. The behaviour of each stop-band upon change of incident angle can be characterised by the
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Figure 5.15: The polarisation conversion of linearly polarised incident radiation from (a) TM to TE, or ‘\(T_{ps}\)’, and from (b) TE to TM, or ‘\(T_{sp}\)’, obtained experimentally at an azimuthal angle of \(\phi = 0^\circ\) defined in figure 4.5. The [00\ overline{1}] direction possesses a 4\(\bar{1}\) chiral screw axis, yet no polarisation conversion occurs for this band. The data are presented in unnormalised transmitted intensity units.

Figure 5.16: The polarisation conversion of linearly polarised incident radiation from (a) TM to TE, or ‘\(T_{ps}\)’, and from (b) TE to TM, or ‘\(T_{sp}\)’, obtained theoretically at an azimuthal angle of \(\phi = 0^\circ\) defined in figure 4.5. The theoretical data match that obtained experimentally, shown in figure 5.15.
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Figure 5.17: The polarisation conversion of linearly polarised incident radiation from (a) TM to TE, or ‘$T_{ps}$’, and from (b) TE to TM, or ‘$T_{sp}$’, obtained experimentally at an azimuthal angle of $\phi = 45^\circ$ defined in figure 4.5. The [111] direction possesses a three-fold chiral screw axis and strong polarisation conversion occurs for this band. The data are presented in unnormalised transmitted intensity units.

Figure 5.18: The polarisation conversion of linearly polarised incident radiation from (a) TM to TE, or ‘$T_{ps}$’, and from (b) TE to TM, or ‘$T_{sp}$’, obtained theoretically at an azimuthal angle of $\phi = 45^\circ$ defined in figure 4.5. The theoretical data match that obtained experimentally, shown in figure 5.17.
5. The characterisation of natural photonic crystal replicas in the microwave regime

Figure 5.19: Line plots showing the polarisation converted experimental and theoretical transmitted intensity of TE to TM, $T_{sp}$, linearly polarised radiation. The data was extracted at an azimuthal angle of $\phi = 45^\circ$ and polar angles of (a) $\theta = 0^\circ$, (b) $\theta = 5^\circ$ and (c) $\theta = 10^\circ$. The experimental data is unnormalised. The deviation of theoretically modelled and experimentally taken data increases as the polar angle increases due to the unnormalised nature of the experimental data.
5. The characterisation of natural photonic crystal replicas in the microwave regime

analysis of structural plane orientation within the 3D structure.

In some cases, a difference in stop-band width was observed between the responses of linear TM and TE polarisations that were used as incident sources. It was found that for each structure there exists one or more periodic directions through the crystal geometry that produces stop-bands of different widths, depending on the incident linear polarisation. The origin of this difference has been attributed to the arrangement of dielectric struts of each photonic crystal geometry. This is directly observable for the geometry of the P-surface structure and was described in this chapter. The dielectric strut arrangement associated with the geometry of each structure may result in different electric field configurations at the Brillouin zone boundaries when two different linear polarisations are incident. Consequently, for certain geometries, this results in a difference in concentration factor at each of the stop-band edges produced by each incident polarisation. The concentration of electric field of an allowed mode within the dielectric medium will directly affect its energy and therefore associated frequency. As a result, the polarisation-dependent concentration factors that arise at each stop-band-edge directly determines its associated band-width. The difference in concentration factors for each polarisation originates from the dielectric strut arrangement of the structures with respect to the incident polarisation alongside the boundary conditions that must be observed across an interface, as discussed in section 3.3.3.4. The results in this section also agree with the theoretical band-diagrams produced by Poladian et al. [135].

The G-surface structure, or ‘gyroid’, was fabricated with the material volume fraction of \( \phi_s = 0.4 \), which closely mimicked that of the gyroid present within the wing scales of the butterfly *Parides sesostris* [9]. The experimentally and theoretically determined stop-band response produced from this structure agreed well. These data show frequencies that are always present in some stop-bands over the analysed azimuthal and polar angles, within the analysed frequency range. In addition to this, the chiral nature of the gyroid structure was explored by means of polarisation conversion. The polarisation conversion of TE to TM linear polarisations, and *vice versa*, was investigated experimentally and theoretically in transmission. The transmitted polarisation conversion that occurred resulted purely from the chiral three-screw axis present along the [111], and equivalent, direction of the gyroid and not from the four-fold axis present along the [001] direction. Consequently, in section 5.6 the [111] direction through the gyroid was found to produce both linear polarisation-dependent stop-bands when TE and TM polarised light is incident on the structure and also strong linear polarisation conversion. However, the widths of the linear polarisation-dependent stop-bands were found to be more contrasting along the [001] direction of the gyroid. Conversely, no polarisation conversion was measured along this direction possibly due to the symmetry
5. The characterisation of natural photonic crystal replicas in the microwave regime

of its associated chiral axis. As a result, the [001] direction of the gyroid has been shown to produce strong linear polarisation-dependent stop-bands when TE and TM polarised light is incident on the structure and yet an absence of linear polarisation conversion along this direction. In addition to this, the chiral axes of the gyroid structure and the polarisation effects they produce have recently been investigated with circularly polarised incident light by Saba et al. [69]. The structure was found to produce strong circular dichroism when probed along the [001] direction [69].

This chapter has compared and contrasted the electromagnetic responses of the P-, D- and G-surface photonic crystal structures. The multi-stop-band response of each structure has been identified and their structural origins discussed. The difference in electromagnetic response between incident linear polarisations have been identified and attributed to the arrangement of dielectric struts within each structure with respect to incident polarisation. In addition to this the polarisation-dependent stop-band widths have been quantified by the analysis of concentration factor. This in-depth analysis and characterisation of the three structures under investigation also aids the understanding of the optical responses produced by analogous naturally occurring photonic crystals in beetle and butterfly samples.
Chapter 6

Detailed investigation into the weevil *Eupholus magnificus*

6.1 Introduction

There exists a vast array of structurally coloured Coleoptera, which often display vivid jewel-like visual patterns including intense, vibrant colour and specular shine [30] [55] [139] [31] [140]. Due to the substantial diversity of stunning coloured appearances adorned on the outer wing casing (elytra) of beetles, Coleoptera are often regarded as one of the most a visually diverse orders of animals on Earth [141]. Research into such structural colour on Coleoptera has uncovered a wide range of photonic structures that are responsible for the variety of observable optical effects. The vast array of coloured appearances and underlying photonic structures present on Coleoptera has often been described as one of the reasons for their evolutionary success; forming the group of organisms with the largest number of known species on Earth [30]. The range of photonic structures discovered on Coleoptera is large and varies from the simple and regular to the disordered. For instance, the regular multilayer of the *Calloodes grayanus* beetle creates a green appearance by alternating high- and low-density chitin layers covering the entire elytra [30], whereas the elytra of the *Cyphochilus* beetle is covered in extremely thin scales that contain a highly optimised, disordered, 3D structure, consequently creating a very bright, white appearance [142][73]. The differences in these mechanisms lead to differences in, not only the broadband nature of the scattering induced by each structure but also, the contrasting angle-dependence of reflected wavelengths from each structure. The photonic band-gap effects produced by ordered photonic structures vary according to their crystal geometry, including the order of dimensionality held by the photonic structure [20]. Many structurally coloured weevils have a covering of scales over their elytra which contain a 3D photonic crystal structure
comprising air and chitin as the constituent materials. The refractive index of chitin is $n = 1.56$ \cite{35} \cite{36} and air is approximately $n = 1$, resulting in the refractive index contrast of such a photonic structure being very low at 1.56. As discussed in section 3.3.5 of chapter 3, the lowest possible refractive index contrast that an ordered photonic crystal structure can possess to produce a full and complete photonic band-gap is approximately 2 and occurs with the geometric structure of diamond \cite{70}. This is much higher than the refractive index contrast achievable from a chitin-air system. Therefore, if an angle-independent response is required by a beetle it is necessary for it to adapt a traditional ordered chitin-air system in novel ways.

The majority of structural colour in beetles is produced by one-dimensional multi-layer systems \cite{31}. However, weevils, a Coleoptera sub-group, are renowned for possessing photonic crystal structures that are three-dimensional in nature. *Eupholus* is a genus of weevil from the Curculionidae family, which is one of the largest families of any animal on Earth with over forty thousand different recognised species within the group \cite{143}. Within the *Eupholus* genus of weevil there exist a wide range of species with varying elytral coloured appearances and patterns; some pigmentary and some structurally coloured. *Eupholus magnificus* originates from the tropical rainforest region of Yapen, Indonesia. It displays coloured bands of two different hues on its elytra; one yellow, one blue. Each coloured band of *E. magnificus* maintains its coloured hue when viewed over all angles and so appears to produce an angle-independent photonic response.

This chapter discusses a detailed investigation into the mechanisms of structural colour production by the weevil *E. magnificus*. Through the use of microspectrophotometry, imaging scatterometry, scanning electron microscopy and Fourier transform analysis, the structural forms responsible for the coloured appearances of the two coloured bands have been identified and are described in this chapter. These two contrasting forms were found to be intra-scale structures of an ordered and a quasi-ordered form. Such a co-existence of differing 3D structural forms on a single species is extremely uncommon.

### 6.2 Anatomy and physiology

Figure 6.1 presents an image of the weevil *Eupholus magnificus*. The elytra of *E. magnificus* are clearly marked by distinct yellow and blue coloured bands. As with all animals, there exists a slight variation of the appearance *E. magnificus* within the species group, in this case the patterning and coloured hue of the striped bands varies slightly between samples: generally, the coloured bands appear blue and yellow or green, covering the elytra in varying proportions, always retaining the coloured hue of
6. Detailed investigation into the weevil *Eupholus magnificus*

Figure 6.1: The weevil *E. magnificus*: the distinct yellow and blue coloured bands are produced by photonic structures contained within scales on top of the weevil’s exoskeleton. Scale bar: 4 mm. [14].

Figure 6.2: An alternative *E. magnificus* weevil sample showing the slight variation in colour between species. In this case, the weevil has green and blue coloured elytral bands. Scale bar: 4 mm.
each elytral band when the viewing angle is changed. Figure 6.2 shows such a variation of the *E. magnificus* weevil, presenting a blue and a metallic green band. The intense, bright colour of each coloured elytral band of *E. magnificus* is produced by photonic crystal structures contained within scales that are distributed over the weevil’s exoskeleton. The alternating coloured bands are separated by dark bands where there are no scales present on the weevil’s elytra. The dark, melanin-rich nature of the weevil’s exoskeleton acts as an optically absorbing substrate: when a scale containing a photonic crystal structure is placed on top of such an absorbing substrate, any wavelengths that are transmitted through the photonic crystal-containing scales are absorbed [144]. This results in an observation of only the wavelengths reflected by the photonic structures within the scales, and so aids the purity of the observed colour from the weevil. Optical microscopy was performed on each coloured band in order to image the scale arrangement over the weevil’s elytra and follows in the next section.

### 6.3 Optical microscopy

The examination of the near-field optical effects produced by individual scales from each coloured band of *E. magnificus* was undertaken using the optical epi-illumination microscopy imaging method outlined in section 4.1. The bright-field reflection images obtained from a yellow band and from a blue band of the *E. magnificus* sample presented in figure 6.1 are shown in figure 6.3(a)(b) and 6.3(c)(d) respectively. The images reveal that the scales that form each coloured band are closely packed, covering most of the black, absorbing substrate of this weevil’s elytra. The typical diameter of an individual scale is approximately 50 µm. Figures 6.3(a) and (c) reveal that both the sizes and the packing arrangement of whole scales over the elytra of *E. magnificus* remain constant between the different coloured bands. Individual scales from each coloured band, however, show a distinct difference in intra-scale optical pattern. Figure 6.3(b) presents the scales of the yellow region and figure 6.3(d) of the blue region of *E. magnificus*. The scales from the yellow band contain small, micron-sized intra-scale coloured domains arranged over the entirety of each scale. The coloured domains are observed throughout the scale with no distinct preferential intra-scale positional order. Similar intra-scale domain based arrangements have been observed in other Coleoptera types [107] and also Lepidoptera [47]. When a collection of such scales is viewed macroscopically, the summation of the reflected wavelengths from each domain produces a consistent, average reflectance response over the entire coloured band. Each individual coloured domain within such scales generally possesses the same 3D, ordered, photonic crystal structure arranged at a different orientation with respect to a neighbouring domain [47] [107] [66] [135] [10]. The iridescent nature of ordered, periodic, 3D photonic
6. Detailed investigation into the weevil *Eupholus magnificus*

Crystal structures results in a distinct change in reflected wavelength when an individual domain is viewed over different angles and, consequently, results in the colour difference between adjacent domains. Whilst iridescence is observed on an *intra-domain* level, when the viewing angle over a collection of domained scales is altered, the change in overall wavelength of each domain collectively produces a negligible change in the macroscopic colour, observed over many domains. This macroscopic ensemble effect results in angle-independent colour reflections from the elytra of this weevil. Photonic crystal domaining is therefore one method of overcoming the dispersive nature of periodic, ordered photonic crystal structures comprising low refractive index contrast media in order to achieve an angle-independent colour appearance.

The blue scales (figures 6.3(c, d)) do not demonstrate such domaining effects, but possess a uniform, homogeneous, blue coloured hue over the entirety of each scale and, consequently, over the whole of each blue elytral band. These distinctly different intra-scale compositions generate the same overall macroscopic optical effect. Namely, each coloured band of *E. magnificus* maintains its coloured hue when viewed over a large angle range, resulting in non-iridescent patterning on the outer wing casing of this weevil. This observation was quantified using optical spectroscopy over millimetre-size regions of each elytral band.
6. Detailed investigation into the weevil *Eupholus magnificus*

Figure 6.4: The reflectance spectra obtained from a millimetre sized area of the yellow (red curve) and blue (black curve) band of the elytra of *E. magnificus* (inset), measured with a bifurcated-probe spectrometer. [14].

6.4 Optical spectroscopy

Optical spectroscopy using the bifurcated probe method outlined in section 4.2 was conducted on each of the coloured bands of *E. magnificus* using a millimetre-radius incident beam-spot. Experimental interrogation over such a millimetre-sized region subsequently examines the spectral response of each coloured band over many elytral scales. The results presented in figure 6.4 reveal very contrasting characteristic reflectance curves for each coloured band at normal incidence. The red curve in figure 6.4 represents the reflectance spectrum of the yellow band at normal incidence and displays a broad reflection peak, centred predominantly about the yellow wavelengths with a maximum reflectance wavelength of approximately 600 nm. The contribution of many different reflected wavelengths from the various intra-scale crystal domains results in the broadening of the overall width of the reflectance curve. The black curve in figure 6.4 represents the spectrum taken from the blue elytral band at normal incidence using the same experimental method. It reveals a broad-band reflection curve, when compared to that produced by the yellow band, with a peak at blue wavelengths of 400 nm. Typically, spectrally flat broadband reflections originate from disordered structures that can concurrently scatter many different wavelengths, such as those possessed by white beetles and butterflies [77] [142] [145] [73]. In addition to a relatively flat-band response, however, the spectrum taken from the blue elytral band has a small reflection peak centred around approximately 400 nm, consequently providing this coloured elytral band with a primarily blue coloured hue.
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The angular reflection response of each band was also quantified using this technique with a millimetre-radius incident beam-spot. Figure 6.5 shows the specular reflectance responses of the (a) yellow and (b) blue bands over incident illumination angles that were systematically varied between normal incidence and 45°. The curved nature of the weevil’s elytra does not allow accurate reflection measurements to be obtained from it beyond this angle due to projection size of the impinging beam spot on the apex of such a curved sample. The colour-scale of both plots in figure 6.5, from blue to red, defines low- to high-reflected intensities in normalised units. The suppression of iridescence from each elytral band is clearly visible over the analysed angle range. Explicitly, the data taken from the yellow band, presented in figure 6.5(a), clearly displays a non-dispersive response, with the reflected mid-peak maximum shifting by only 20 nm over the 45° angle range. This extremely small change in reflected wavelength is far too small to result in a noticeable colour change by an observer. Over the analysed angle range, the reflection maxima always contain wavelengths around 520 nm, an attribute usually associated with a full and complete photonic band-gap response. The angular specular reflection response of the blue band, presented in figure 6.5(b), also displays an angle-independence, in this case the wavelength shift of the mid-peak maximum over the same angle range is only 10 nm, and will also not result in a noticeable colour change by an observer. From the two graphs presented in figure 6.5, it is apparent that each coloured band is non-dispersive over macroscopic areas that contain many scales.

The analysis of the spectra obtained over millimetre-sized regions of each coloured elytral band were combined with microspectrophotometry measurements taken over micron-sized areas of individual scales. This experimental method, outlined in section 4.3, allowed the two colour-producing mechanisms, of the yellow and blue elytral bands, to be probed on an intra-scale level. The microspectrophotometry technique consequently allows for the inspection of intra-scale domain regions, thereby removing the colour averaging effect seen over multiple domains.

### 6.4.1 Microspectrophotometry

Using the method of microspectrophotometry within single scales, outlined in section 4.3, the intra-scale reflectance of each scale-type was investigated. Each of the observable coloured domains within the scales from the yellow band, figure 6.3(b), was probed with this method and the results are presented in figure 6.6(a). It is clear that each domain reflects a distinctly different wavelength, which varies from 400 to 700 nm. It is the collective reflectance spectra from many domains similar to these that contribute to the overall reflectance spectrum represented by the red curve in figure 6.4, obtained over multiple domains. This range of reflected wavelengths represents the to-
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![Figure 6.5](image.png)

**Figure 6.5:** The specular reflectance of (a) the yellow and (b) the blue elytral bands of *E. magnificus* over the incident angle range of 0° to 45° using a millimetre-radius incident beam-spot. The distinct non-dispersive nature of each coloured elytral band is shown by each figure.
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![Figure 6.6](image)

Figure 6.6: The reflectance spectra obtained from intra-scale regions of each elytral band of *E. magnificus*: (a) From a scale from the yellow-band, taken within individual coloured domains (inset) and (b) reflectance spectra taken from the same intra-scale region of a blue elytral scale under rotation over 48° in 2° steps. [14].

The optical iridescent range of the single structure present in all domains. Consequently, each domain can reflect wavelengths only within this range when under rotation. The resulting summation of reflectance produced over many domains, at any single incident angle, provides the scales with the appearance of angle-independent colour, as previously discussed.

Figure 6.6(b) shows reflectance spectra obtained from an individual, isolated scale taken from the blue band of *E. magnificus*. This scale was mounted onto the tip of a glass micropipette which was, in turn, mounted onto a sample holder that was free to rotate alongside an angular vernier scale. The spectra were taken from the same relative intra-scale position whilst under rotation over 48° in steps of 2°. Figure 6.6(b) reveals the angle-independent nature of an individual intra-scale site of a blue scale. The peak reflectance wavelength changes by only 10 nm after 48° of rotation. This 10 nm change in wavelength was also observed in the analogous experiment taken using a larger, millimetre-radius beam-spot, over many scales, presented in figure 6.5(b). This direct correlation indicates that the angle-independent nature of the blue coloured elytral band originates primarily from the intra-scale photonic structure and not from an ensemble, averaging effect as observed from the yellow scales.

Both types of scales produce angle-independent colour reflections over each coloured band when viewed macroscopically. The nature of the characteristic reflectance spectra obtained from each coloured band and from each scale indicates that the two mecha-
nisms that produce this angle-independence are clearly contrasting. The presence of different scattering mechanisms within each scale is indicated by the differences in the reflection spectra of the blue scales, presented in figure 6.6(b), which is more broadband in nature when compared to the reflectance spectra obtained from the domains within the scales from the yellow band (figure 6.6(a)). Such scattering effects can be captured using imaging scatterometry, where the entire scattered hemisphere from a sample can be imaged.

6.4.2 Imaging scatterometry

The imaging scatterometry method outlined in section 4.4 was performed on individual scales taken from each coloured band of *E. magnificus* in order to investigate the spatial dependence of the light scattered by the intra-scale photonic structures. Imaging scatterometry was also performed on regions from each coloured band of the weevil’s elytra where a collection of scales are present.

6.4.2.1 Imaging scatterometry via narrow-angle illumination

Individual scales from both the yellow and blue bands of *E. magnificus* were illuminated with a narrow aperture (5°) light beam, via a small, axial hole in the ellipsoidal mirror (point E in figure 4.1) of the scatterometer. The small, 8.5 µm diameter beam spot produced by the primary beam is comparable to the size of an individual intra-scale domain within the yellow scales. An isolated, individual yellow scale was mounted onto a micro-pipette and rotated in 10° steps, keeping the illumination constant. Each single domain within the yellow scales exhibited some directionality as displayed in figure 6.7(a). The directionality associated with the photonic structure is highlighted in figure 6.7(a) by the change in scattered angle when under rotation. Over the three angles that are presented, it is evident that the rotation of the sample resulted not only in the changing angles of the specularly reflected light, but also in a shift of peak reflectance wavelength. Iridescent behaviour that manifests as a decrease in reflected wavelength was described in section 3.2.2. Explicitly, as the sample is rotated, the incident wavevector moves away from the surface normal to the set of effective periodic planes within the photonic crystal geometry that gives rise to the reflection. This optical feature is characteristic of a highly ordered photonic crystal structure. As the small beam spot, of diameter 8.5 µm, is on the order of the diameter of individual intra-scale domains, the incident beam occasionally impinges on a neighbouring domain and the scattering from the two domains are imaged. This is the origin of the two separate coloured scattering patterns observed in figure 6.7(a). The difference in the scattered angles of the two main regions of reflections within a single hemispherical plot in figure
6. Detailed investigation into the weevil *Eupholus magnificus*

Figure 6.7: Scattering patterns produced by the yellow (a) and blue (b) scales of *E. magnificus*. From left to right the scales were rotated in steps of 10°. The red rings on each polar plot represent scattering angles of 5°, 30°, 60° and 90°. [14].

6.7(a) originates from the curved nature of the scale. Namely, the incident light beam is impinging on two domain regions that exist underneath a curved exterior and the respective surface orientations of each reflect light at different angles.

The illumination of blue scales was performed over many different sites and showed no distinct intra-scale difference in scattering pattern; scattered hue or scattered direction. An individual blue scale was also rotated in 10° steps with illumination remaining constant and the same site on the scale was illuminated at each rotation angle. The resulting scattering patterns presented in figure 6.7(b) are in distinct contrast to the scattering observed from the scales from the yellow elytral band as the scattering from the blue scales exhibits limited/no directionality. Figure 6.7(b) displays highly diffuse scattering patterns that cover the whole hemispherical, polar plot. The scattering from the blue scales does show the predominance of blue scattered wavelengths, however, there are significant scattering contributions from longer wavelengths. Such diffuse scattering implies the blue scales contain a fairly isotropic photonic structure with no distinct preferential scattering direction for particular wavelengths. This broadband scattering effect supports the features present in the reflectance spectra of figures 6.4 and 6.6(b), as discussed in previous sections. Diffuse scattering patterns that appear
due to completely amorphous structures appear white due to the random nature of scattering centres which can consequently scatter all wavelengths equally. The presence of coloured patches in the scattering patterns from the blue scales and an overall preference to scatter blue wavelengths implies this structure is not a completely amorphous optical structure. This is an important feature that will be shown to coincide with the structural characterisation performed using electron microscopy presented later in this chapter.

In addition to the characteristic scattering patterns produced by the intra-scale photonic structures, there exists specular surface reflections that appear as bright, saturated regions on the hemispherical plots taken from the blue scales, shown in figure 6.7(b). The surface reflections change position upon rotation of the scale and also contain evidence of diffraction. The intra-domain scattering pattern from a yellow scale (figure 6.7(a)) shows almost specular red and yellow reflections which appear in a diffracted band pattern. This indicates a surface diffracting structure is also present on the surface of both types of scales.

### 6.4.2.2 Wide-angle scatterometry

On removal of the diaphragm, D3 in figure 4.1 presented in section 4.4, a sample can be illuminated with wide-angle illumination from the secondary beam of the imaging scatterometer, as outlined in section 4.4.2. The resultant polar plot showing the scattering exhibited by illumination of this manner will display the reflected wavelengths over all angles of incidence from a sample over an illuminated region with a diameter of approximately 50 µm. Figure 6.8 presents the wide-angle scatterometry polar plots taken from a yellow scale (a) and a blue scale (b) from *E. magnificus*. As the 50 µm diameter beam spot of incident light is comparable to the size of a single *E. magnificus* scale, the full hemispherical angle-dependence of a single scale can be probed with this method. The polar plot presented in figure 6.8(a) shows very limited evidence of iridescence over an area comparable to the size of a whole, single scale, with the predominance of yellow wavelengths being reflected over all angles. This confirms the angle-independent nature of the domain configuration of a single scale from the yellow band of *E. magnificus*. The ensemble effect of many similar scales within this coloured band will act to further suppress the iridescence of the native 3D photonic crystal structure, resulting in the non-iridescent reflection properties observed from figure 6.5(a). Figure 6.8(b) presents the wide-angle scatterometry polar plots obtained from the blue band of *E. magnificus* using the same 50 µm beam spot diameter. The non-iridescent nature of these scales is also clearly highlighted, with a constant blue colouration over the entirety of the hemispherical polar plot.
6. Detailed investigation into the weevil *Eupholus magnificus*

6.5 Scanning electron microscopy and focused ion beam milling

The optical effects described in sections 6.3 - 6.4.2 result from the interaction of light with photonic structures present within each scale. Transmission electron microscopy (TEM) is often used in order to image cross-sections through beetle scales. Both thin (80 nm) and thick (500 nm) sections of *E. magnificus* scales were prepared in order to be imaged with TEM, however, the brittle nature of these samples meant the photonic structures within the scales fractured and imaging from the sections was inaccessible. Therefore, in order to probe each coloured scale to determine the photonic structures responsible for each effect, scanning electron microscopy (SEM) was employed due to its ability to resolve structures on the nano-scale, as discussed in section 4.5.1. Figure 6.9 presents images of a typical single scale isolated from the yellow band of *E. magnificus* taken using detailed high-resolution scanning electron microscopy. The photonic crystal structure is contained within the scale, enclosed in a chitin shell with surface ridges on the upper surface. The focused ion beam (FIB) milling method described in section 4.5.2 was employed to cut through the scale in order to expose the inner photonic structure. On removing a substantial part of the scale with this method, the internal photonic crystal structure is exposed as a transverse cross-section. This revealed an arrangement of juxtaposed domains of a highly ordered photonic crystal with clearly identifiable boundaries between them as presented in figure 6.10. The horizontally arranged intra-scale photonic crystal domains create the individual neighbouring yellow, green and blue colour centres observable in the optical image.

Figure 6.8: Wide-angle scatterometry obtained from a scale from (a) the yellow elytral band and (b) the blue elytral band of *E. magnificus*. 
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Figure 6.9: (a) A typical single scale from the yellow elytral band of *E. magnificus* displayed as a bird’s-eye view and also (b) showing the tip of that scale that will be removed by FIB milling to expose the inner photonic structure. Scale bars: (a) 30 µm, (b) 10 µm.
shown in figure 6.3(b) and also the inset of figure 6.6(a). The domains are arranged both horizontally throughout the scale and will also, occasionally, arrange vertically across the depth of the scale (figure 6.10(b, c)). The ensemble effect arising from the horizontally arranged domains is the production of a single, constant, average colour appearance over the whole of the yellow bands when viewing angle is changed (as discussed earlier in the chapter). Although the horizontal arrangement of intra-scale domains has been observed in some naturally occurring systems including beetles [107] [31] and butterflies [47] [9] [11], the presence of a vertical juxtaposition of domains is certainly very uncommon. This arrangement of domains through the depth of the scale will result in an additive colour mixing process from within a single observed intra-scale domain region: the resulting spectrum from such an observed domain will generally appear as a double-peak reflection. This may be similar to the data presented in figure 6.6(a) as the violet dashed curve, showing reflection maxima at 430 nm and 485 nm.

Figure 6.11 presents SEM images of a typical single scale from the blue elytral band of *E. magnificus*. The scale exhibits a similar surface structure to that observed from the surface of a yellow scale, figures 6.9(a, b), and also possesses a closed scale anatomy that requires FIB milling. Cross-sections of the scales from the blue band of *E. magnificus* were exposed in the same way as for those from the yellow band, and high resolution SEMs were taken of the internal photonic structure. Figure 6.12 presents a cross-section of the internal photonic structure exposed by FIB milling. It is apparent from figure 6.12 that the mechanism behind the homogeneously blue-coloured appearance observed in optical microscopy images, figure 6.3(c, d), is again a photonic structure as opposed to pigmentary colour. The structure is comprised of insect cuticle and air, just like the structure within the yellow scales. However, the structure responsible for the blue-coloured elytral band on *E. magnificus* differs significantly from the ordered, domained structure discovered within scales from the yellow band. The photonic structure within the blue scales does not possess the distinct and well-defined structural periodicity that is observed within the scales from the yellow bands. The apparent introduction of slight disorder within the photonic crystal structure of the blue scales consequently removes the clear presence of domaining. Figure 6.13 presents SEM images taken from a broken blue scale of *E. magnificus*. Here the scale has fractured causing the top section of the scale to be removed, revealing the internal quasi-ordered structure which, again, highlights the absence of domains and structural order. The introduction of disorder in this structure acts to scatter light in a more diffuse, less specular manner than would be the case for a perfectly ordered photonic crystal. This is the mechanism responsible for the diffuse scattering patterns observed in the hemispherical polar plots presented in figure 6.7(b). The broadband wavelength reflection present in figures 6.4 and 6.6(b)
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Figure 6.10: SEM images of a scale from the yellow elytral band of *E. magnificus*, cross-sectioned using FIB milling. Below the ridged surface (a), a highly ordered periodic 3D-lattice exists (b), (c). Scale bars: (a) 10 µm, (b) and (c) 2 µm. [14].

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Figure 6.11: (a) A typical single scale from the blue elytral band of *E. magnificus* displayed as a bird’s-eye view and also (b) showing a side view of the scale. Scale bars: (a) 20 µm, (b) 20 µm.

is also attributed to the addition of slight disorder to the structure. Consequently, the structures within the blue scales are not scattering all wavelengths equally to produce a white colour, neither are they selectively reflecting a narrow-band of wavelengths as photonic crystal theory suggests would occur for a highly ordered structure. The structural order must fall between an ordered and a completely disordered structure.

The two coloured elytral bands of *E. magnificus* therefore possess two contrasting photonic structural forms. They differ primarily by the level of structural order present in their geometry. The co-existence of differing levels of structural order on the same species is extremely rare in nature. In addition to this, the different structures present in these scales produce the same overall optical effect, namely, an angle-independent coloured appearance. The structural analysis that follows identifies and quantifies the level of order and disorder present in both scale types. It also outlines how two *different* types of structure, from the yellow elytral band and from the blue elytral band, can
Figure 6.12: SEM images of a blue scale from *Eupholus magnificus*, cross-sectioned using FIB milling. Below the ridged surfaces (a), of the blue scale the lattice is quasi-ordered (b),(c). Scale bars: (a) 10 µm, (b) 5 µm, (c) 2 µm. [14].
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Figure 6.13: SEM images of a broken blue scale of *E. magnificus*. Here the scale has fractured and the top section has come away, revealing the quasi-ordered intra-scale photonic structure with no domains. Scale bars: 5 $\mu$m.
both produce an observable angle-independent colour from photonic structures that are comprised of low refractive index contrast materials with differing structural order.

6.6 Structural analysis

The SEMs displayed in figures 6.10 and 6.12 present the elytral scales and underlying photonic crystal structures of the yellow and blue scales respectively. There are many attributes of each scale that can be examined by structural analysis including features from both their internal structures and surface structures. On first inspection, it is apparent that the scales presented in figures 6.10 and 6.12 have a varied depth across the scale, with the edges having a smaller depth than the centre. The arrangement of the scales on the elytra of the weevil is such that each scale incurs some overlap with neighbouring scales, as displayed in figures 6.3(a) and (c). This creates a complete covering of the absorbing elytral substrate. A typical scale from each coloured band must have an appropriate shape in order to assemble in this way. Figures 6.9 and 6.11 present a single scale from each coloured band and the difference in shape is clear, with the edges and the base of each scale remaining flat and thin. This results in a variation of the reflected intensity across the scale due to a difference in number of effective layers of the crystal within an individual scale. The scales from the yellow band have a photonic crystal depth that varies between 1.2 - 4.6 µm inside the chitin enclosed envelope. Within these regions there appears to be 3 - 15 effective layers of photonic crystal geometry in the depth of the scale. Due to the additional disorder present in the scales from the blue elytral bands, the number of effective layers is not discernible, however, the scale depth in the centre is approximately 4.4 µm, and so is comparable to that of the yellow scales.

The level of positional order and disorder possessed by the photonic structures from the yellow and the blue band of E. magnificus was quantified by Voronoi analysis [146] [147] performed on SEM images obtained from each scale-type. The exact structural form of the ordered photonic crystal structure from the yellow elytral band was determined by an iterative image analysis. The iterative image analysis entailed cutting cross-sections through various basic Bravais lattice symmetries consisting of air spheres in a material matrix at planes of high-symmetry using the Solidworks CAD package [116]. The image cross-sections obtained from the image analysis were compared to each intra-scale domain present in the SEM images of the scales from the yellow band. The most suitable crystal class was then assigned to it as a first order approximation. Other 3D lattice geometries with the same Bravais lattice basis were then analysed and compared with a similar image analysis process. An alternative fast Fourier transform (FFT) method was used to analyse the quasi-ordered photonic structure present within
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6.6.1 Voronoi analysis and entropy calculations

In order to analyse and quantify the level of order and disorder present in each type of scale, Voronoi analysis [146][147] was used in conjunction with a calculation of configurational (positional) entropy. Voronoi analysis is a method used to analyse the geometry of a structure. A Voronoi diagram is comprised of individual Voronoi cells which are created by the connection of perpendicular bisectors to nearest neighbour sites in a given periodic array. Each Voronoi cell is defined as the region in space that is closest to an individual site than any other [146]. Consequently, each Voronoi cell region will be bounded by an \( n \)-sided shape, where \( n \) identifies the number of nearest neighbours held by each individual site. A Voronoi diagram will therefore consist of an array of many different-sided shapes, tessellated together to produce the overarching structure. Voronoi diagrams were created from high contrast, binary images of original SEM images obtained from the cross-sections of the scales from the yellow and blue elytral bands of *E. magnificus*. The image analysis was conducted using MATLAB software. The MATLAB ‘centroids’ command was used to generate an array of points that approximate the periodicity of the original structure. This was done by identifying the central points within the air gaps between the solid network that define the structure. These central points were then used to approximate the lattice sites of the array from which the Voronoi image was then created, also within MATLAB. Figure 6.14, below, presents the Voronoi diagram obtained from a single domain in the SEM image of figure 6.10(c), that possesses a hexagonal symmetry. The Voronoi diagram presented in figure 6.14 clearly displays a highly ordered structure, with each Voronoi cell being bound by a hexagon. This reveals that all Voronoi cell regions consequently have the same number of nearest neighbours.

The Voronoi process was performed on the quasi-ordered photonic structure discovered within the blue scales of *E. magnificus* from the broken scale presented in figure 6.13(b). This Voronoi diagram, presented in figure 6.15, displays a highly contrasting array of Voronoi cells to that obtained from the ordered structure. The element of disorder present in the photonic structure found within the blue scales has subsequently altered the regions of space closest to individual sites, and therefore the number of nearest neighbours that each site possesses. This creates a Voronoi array of many different-sided polygons.

In order to quantify the level of order or disorder present in each Voronoi diagram, an equation to determine the configurational entropy of each system was employed.
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Figure 6.14: A Voronoi diagram obtained from a cross-section of a domain within a scale taken from the yellow coloured band of *E. magnificus*.

Figure 6.15: A Voronoi diagram obtained from a large intra-scale region taken from the blue coloured band of *E. magnificus*. 
The configurational entropy of a system is defined as:

$$S = -\sum P_n \ln(P_n), \quad (6.1)$$

where $P_n$ is the fraction of $n$ sided shapes present in an individual Voronoi diagram [148] [149]. This equation can be scaled in order to produce scaled entropy values between $0 \leq S \leq 1$ as follows

$$S = -\frac{\sum P_n \ln(P_n)}{\ln(N)}, \quad (6.2)$$

where $N$ is the number of different $n$ sided shapes in an individual Voronoi diagram [150]. When applied to the Voronoi diagram produced from the domain from a yellow scale in figure 6.14, $P_n = 1$ and $N = 1$, where $n = 6$ and a value for the scaled configurational entropy results as $S_y = 0$. This defines a high level of positional order and the absence of positional disorder within this system. When the same equation, 6.2, is applied to the Voronoi diagram obtained from the quasi-ordered photonic structure within the blue scale, figure 6.15, the presence of many different polygons produces a highly contrasting value of configurational entropy of $S_b = 0.66$. The structure within the blue scales possesses a scaled configurational entropy value in between that of complete order, $S = 0$ and the disorder limit [148] [149] [150]. This, again, infers the presence of quasi-order as opposed to complete disorder. Ideally, such quantitative analysis of disorder and order may prove to establish a benchmark for an optimal level of order and disorder necessary to produce an angle-independent quasi-ordered photonic crystal system. However, such a benchmark can only be established by evaluating a large sample size of quasi-ordered systems, both experimentally and through quantitative configurational entropy analysis. In order to characterise further the level of quasi-order present in the quasi-ordered system, fast Fourier transform analysis was performed.

**6.6.2 Fast Fourier transforms**

The fast Fourier transform (FFT) method, outlined in section 4.7, was employed to investigate the spatial frequencies possessed by both the ordered and the quasi-ordered photonic crystal structures. The 2D FFT image obtained from the domain with hexagonal symmetry within figure 6.10(c) from a yellow elytral band is presented in figure 6.16(a). It displays the characteristic periodicities associated with such a hexagonal geometric plane; it displays characteristic long- and short-range translational periodic order and a long- and short-range rotational symmetry of order 6. The FFT obtained from the SEM of a scale from the blue band shows a contrasting configuration of spatial frequencies. The FFT presented in figure 6.16(b) displays two principal components:
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6.6.3 Ordered photonic crystal characterisation

Figure 6.17(a) shows a domain cross-section obtained from a scale from the yellow elytral band of *E. magnificus* with a hexagonal symmetry and figure 6.17(b) from a...
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domain with square symmetry. Both images were taken from the SEM presented in figure 6.10(c). The basic Bravais lattice responsible for these two identifiable geometries was investigated using an iterative image analysis approach. Hexagonal and square symmetries similar to those presented in figures 6.17(a) and (b) are present in the (111) and (100) plane of a structure with face-centred cubic (FCC) Bravais lattice symmetry (figures 6.17(c, d)). These geometric symmetry cross-sections are the best match with the SEM images from all three basic cubic Bravais lattices. The corresponding relative lattice vectors associated with such a configuration are also consistent with an FCC arrangement and are shown by the scale bars associated with each figure displayed on figures 6.17(a-d). From SEM analysis, an FCC cubic supercell lattice vector of \( a = 414(\pm 46) \) nm was determined to be present within *E. magnificus* scales from the yellow elytral bands. This value was calculated from the mean and standard deviation of 51 measurements taken throughout the depth of a scale from two different intra-scale domains. Such an FCC supercell structure is presented in figure 6.18 for clarity. As with all natural samples, perfect pore shapes and sizes are rarely observed. However, by including the correction described in section 4.5.2, an average radius of spheres was calculated to be \( r = 100(\pm 30) \) nm. The radius of pore sizes varied not only with position across the depth scale but more noticeably between differing geometric domains. This is likely to originate from the difference in depth through the geometry from which a cross-section was taken. In turn this also produced an apparent difference in the lattice constant across and throughout the scale. This determination of the basic Bravais lattice symmetry allows for theoretical modelling to be undertaken. A description of the results of this modelling follows in section 6.6.3.1.

A further investigation using a similar iterative image analysis technique was performed with other FCC structures including a typical diamond structure comprised of air spheres in a cuticle matrix. This diamond structure did not provide a match with the SEM images. However, the D-minimal surface photonic crystal structure, also based on the FCC Bravais lattice symmetry [136][9], revealed a stronger match with the SEM images. The (111) and (100) plane cross-sections obtained from a D-surface structure have been displayed in figures 6.19(c) and (d), respectively, along with the corresponding domain structures taken from figure 6.10(c), displayed explicitly in 6.19(a) and (b). Other cross-sectional geometries obtained from the SEM image presented in figures 6.10(b) and (c) were also compatible with cross-sections obtained from the D-surface structure along non-high symmetry planes. These SEM images and corresponding planes obtained from the iterative analysis of the D-surface structure are presented in figures 6.20(a-d).
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![Figure 6.17](image)

Figure 6.17: SEM images of a scale cross-section showing a domain with (a) hexagonal symmetry and (b) square symmetry obtained from a yellow elytral band of *E. magnificus*. These cross-sections correspond to the (111) (c) and (100) (d) plane of an FCC lattice geometry comprised of air spheres in a material matrix. Scale bars: (a) and (c) $a$, (b) and (d) $a/\sqrt{2}$, where $a =$ supercell lattice constant.

### 6.6.3.1 Theoretical modelling of the ordered structure

Initial modelling of a simple FCC structure with a cubic supercell lattice vector of $a = 368 \text{ nm}$ comprising air spheres of a radius $r = 100 \text{ nm}$ in a cuticle matrix ($n = 1.56$) was undertaken using the MIT photonic bands package [122]. The band diagram of this structure is presented in figure 6.21. The reflectance peaks obtained from microspectrophotometry of various coloured domains in figure 6.6(a) correspond to partial photonic band-gaps created by the structural orientation of each intra-scale domain. Therefore the photonic band-gaps present in the band diagram of figure 6.21 can be directly related to mid-peak reflections from the experimental optical data presented in figure 6.6(a). The wavelength gap at the X, L and K points (as labelled in figure 6.21) correspond very closely to the wavelengths of the reflectance maxima shown in 6.6(a) and also presented as an inset in figure 6.21. This photonic band diagram was obtained using a lattice constant that lies within the one standard deviation of the mean calculated value. This is a further indicator that the photonic structure within the yellow scales of *E. magnificus* is based on an FCC Bravais lattice symmetry.
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Figure 6.18: The face centred cubic (FCC) supercell. The basic Bravais lattice symmetry of the photonic crystal structure found in the yellow elytral scales of *E. magnificus* was determined to be based on the FCC geometry. In this schematic image, 'a' represents the supercell lattice constant and the relative distance to a nearest neighbour lattice point is $a/\sqrt{2}$ and has been highlighted.

As the D-surface structure was identified to be a more precise approximation to the structure present within the scales from the yellow elytral band of *E. magnificus*, the band diagrams obtained from the experimental data and theoretical modelling of the D-surface photonic crystal in section 5.5 were analysed with the supercell lattice constant obtained from the iterative image analysis in the preceding section. Photonic bandgaps appear within the reduced frequency range of 0.7 and 1.1667 from the D-surface structure, depending on the incident angle of light. A lattice constant of 448 nm will be required to reflect the wavelength range reflected by the various domains present in a scale from the yellow elytral band presented in figure 6.6(a). As the refractive index contrast and filling fractions present in the D-surface structure analysed in section 5.5 are not based on that possessed by *E. magnificus*, the data is not expected to correlated precisely. However, a 448 nm lattice constant is within one standard deviation of the mean value calculated from image analysis. TEMs were taken on sections of the *E. magnificus* scales, varying in thickness. However, detailed imaging of the intra-scale structures was unobtainable due to their brittle nature. A possible reason for this is the inherent filling fraction and diameter of the solid network that create the structures. Consequently, the exact filling fraction of the structures present in *E. magnificus* scales can not be calculated as TEMs can not be obtained.
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Figure 6.19: SEM images of a cross-section through a scale from a yellow elytral band of *E. magnificus* showing a domain with (a) (111) and (b) (100) planar symmetry of a D-surface photonic crystal structure. The corresponding cross-sections obtained from iterative image analysis of the D-surface photonic crystal structure are presented in (c) and (d).

Figure 6.20: (a), (b) SEM images of a cross-section through a scale from the yellow elytral band of *E. magnificus* showing domains with planar symmetries not pertaining to high-symmetry planes. The corresponding cross-sections obtained from iterative image analysis of the D-surface photonic crystal structure are presented in (c) and (d).
Figure 6.21: Theoretical photonic band diagram of an ideal inverse FCC photonic crystal with cubic supercell length $a = 368$ nm and radius of air spheres $r = 100$ nm. The striped boxes highlight the partial band-gaps at the X, L and K points corresponding to the reflectance maxima shown in figure 6.6(a), presented as an inset above the band diagram. [14].
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6.6.3.2 Diffraction from the scale surface structure

The hemispherical polar plots comprising the scatterometer images, presented in figure 6.7, provide evidence that both yellow and blue scales produce diffraction effects. Close analysis of figure 6.7(a), for the scattered light collected from a single illuminated yellow scale, shows that the angular separation of the diffracted orders of red wavelengths is approximately $12^\circ$. The SEM images presented in figure 6.10 clearly show that the scales from the yellow band have a surface ridge structure on the upper scale, which have a pitch of approximately $3 \, \mu m$. To determine if the pitch of the surface ridge structure upon the yellow scales produces the diffracted orders observed in the scatterometry figures, the grating equation [151], equation 6.3 below, is employed:

$$dsin\theta_m = m\lambda. \quad (6.3)$$

$$3\mu m \cdot \sin(52^\circ) = 623nm. \quad (6.4)$$

where $d$ is the pitch of the grating, $\theta_m$ is the diffracted angle of the $m^{th}$ diffracted order and $\lambda$ is the incident wavelength. The grating equation, 6.3, reveals that a red wavelength of $623 \, nm$ will be the first diffracted order at a diffracted angle of $12^\circ$ produced from a surface ridge structure with a pitch of $3 \, \mu m$. Therefore, this confirms that the surface ridging is directly responsible for the diffraction observable from the imaging scatterometry data. Since this is the diffraction collected from interrogation of a small area encompassing a single domain within a single scale, it will not be resolved or discernible when the incident beam spot encompasses multiple scales over a much larger area. A diffuse coloured appearance is more likely to be observed. Similar photonic crystal diffraction gratings have recently been theoretically analysed for application as a highly efficient diffraction grating [152]. In 2001 Maystre theoretically examined a 2D photonic crystal comprising a hexagonal array of dielectric rods in air and also a hexagonal array of air rods in a dielectric matrix. Directly above each photonic crystal array were periodic dielectric rods or air grooves. They were arranged with a periodicity designed to be a multiple of the lattice constant within the photonic crystal. In this case, the photonic crystal diffraction grating was shown to produce blazing effects, with extreme efficiency for both linear incident polarisations [152].

6.7 Conclusions

The weevil *Eupholus magnificus* is adorned with alternating coloured bands of two different hues on its elytra; a yellow and a blue band. The two bands both produce
angle-independent colour as presented in figures 6.5(a) and (b). The scales that are present over each coloured elytral band contain photonic structures that contain contrasting levels of geometrical order. The scales from the yellow coloured band have a highly ordered photonic crystal structure arranged in domains. Each juxtaposed 3D domain is comprised of the same 3D crystal class, arranged at different orientations with respect to neighbouring domains. Each individual structural domain produces angle-dependent reflection due to the ordered, periodic nature of the photonic crystal. Consequently, each domain has different spectral properties. Over many domains, from many scales, the ensemble additive effect produces an appearance and colour that offers far-field angle-independence. Similar domained arrangements have been documented in other species with 3D photonic crystals [153] [107] [9] [31]. Colour averaging via domaining is a common method for production of large area far-field angle-independent colour reflection in many beetles, which would otherwise not be possible to obtain with the low refractive index contrast of air-cuticle ($n = 1.56$) with an ordered structure alone. In addition to this, the ordered intra-scale structure of the yellow elytral bands has been identified as the bicontinuous interconnecting D-surface structure, thought to be one of the most isotropic 3D periodic geometries in nature. This weevil has also adapted its photonic crystal structure to overcome the low refractive index contrast of air-cuticle by the use of a quasi-ordered photonic structure, rather than highly ordered photonic crystal structures [14]. Since an ordered arrangement of lattice sites is not present in these structures, quasi-ordered photonic structures are not constrained to the periodic crystallographic restrictions [103]. Quasi-ordered photonic crystal geometries therefore have the potential to create more isotropic optical scattering structures due to their relatively spherical Brillouin zones [118]. As a result, the intra-scale photonic structure of the blue elytral band is capable of producing an angle-independent colour appearance directly, without the need for domaining. The co-existence of two different photonic geometries with contrasting structural order on an individual species is very rare in nature. *E. magnificus* is an example of a natural organism that has developed two contrasting mechanisms for producing angle-independent colour using low refractive index media. The quasi-ordered structure also shows evidence of being an interconnected structure. It may, therefore, be the case that the same fabrication processes are involved for its formation as with the D-surface structure found in the yellow scales. If so, this indicates the possibility of producing highly isotropic, 12-fold symmetric quasi-ordered photonic structures by controlling the introduction of disorder into the formation of the self-assembling D-surface structure. The discovery of these contrasting mechanisms on a single species of weevil may inspire the fabrication of such quasi-ordered structures once the formation of intra-weevil-scale photonic crystal assembly is known and further understood.
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Synthetic fabrication of many 3D photonic crystal systems is well advanced [154] [155] [156] [157] [128], however, with few exceptions [5], it is only highly ordered 3D systems that have been fabricated for the visible band. These have exhibited full and complete photonic band-gap (FCPBG) properties due, largely, to the high refractive index contrast of their constituent materials [20]. The cost incurred by fabricating these structures is not only through the expensive fabrication techniques required, the limited available sample size, but, most importantly, the absolute requirement to use high refractive index contrast materials [14]. Quasi-ordered photonic structures offer the possibility to overcome the need for high refractive index contrast media for the production of angle-independent wavelength reflections. Quasi-ordered photonic crystals are beginning to be synthetically fabricated [118][5], with their designs reaching 12-fold rotational symmetry. An exact quantitative point of reference of quasi-order may provide implications for synthetic photonic crystal fabrication in scenarios where high index-contrast materials are inappropriate, incompatible or unavailable. The quantification of the level of quasi-order in this system originated in the detailed measurements describing the extent of quasi-order in the *E. magnificus* photonic crystal system via FFT and Voronoi and entropy analyses [14]. The FFT analysis revealed a highly isotropic 12-fold symmetric quasi-ordered structure was present in these scales. The entropy analyses were performed both on the ordered and the quasi-ordered intra-scale structures from *E. magnificus*. While the scaled entropy value ($S_y$) calculated from the ordered structure was low, the entropy value calculated for the structure forming the quasi-ordered photonic crystal, was $S_y = 0.66$. The structural limit between order, disorder and quasi-order is currently unknown. The quasi-ordered *E. magnificus* system described in this chapter provides a quantified point of reference, via Voronoi and scaled entropy analysis, with which synthetic photonic crystals may be designed to exhibit the visual equivalent of FCPBG properties (namely angle-independent reflected colour) using materials with a relatively low refractive index contrast [14].

The two types of scale in *E. magnificus* produce the same overall non-iridescent effect for the two different coloured regions using alternative forms of photonic crystal. This work outlines contrasting biological methods for production of similar optical effects and offers insight into the costs and benefits of quasi-ordered photonic crystal design from the perspective of bio-inspiration [14].
Chapter 7

The optical properties and structural optimisation of the butterfly *Parides sesostris*

7.1 Introduction

The butterfly *Parides sesostris* is a member of the family Papilionidae [158] and is commonly found in South American rain forest regions. Males are adorned with green coloured patches on the dorsal side of their wings (figure 7.1(a)), yet the ventral side remains dark and brown in appearance. The coloured patterning on the dorsal side of the wing varies according to sex; within both sexes there exists a variation between the amount of red and white patches that are also displayed over the wings. The green colour present on a *P. sesostris* wing is generated by a 3D photonic crystal structure contained within scales that are positioned on top of the dark wing. Figure 7.1(b) displays the scale arrangement and packing that is present on top of the *P. sesostris* wing. As with the weevil discussed in section 6.2 of chapter 6, the colour-producing scales cover a very dark melanin-rich absorbing wing substrate, which aids the saturation of coloured hue reflected from the structurally-coloured scales, creating an enhanced and more highly contrasted observable colour. Although the green coloured appearance of *P. sesostris* is produced structurally, the red coloured hue present on some *P. sesostris* butterflies is produced by a pigment. In general, Lepidoptera and Coleoptera often produce green and blue hues by structural mechanisms, and produce red colourations with pigmentation and rarely by photonic structures [29] [30]. It is thought that butterflies and beetles cannot perform the chemical processes necessary to produce green pigments and so photonic crystal production is employed as a more energetically favor-
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able option [29] [30]. However, the pigment melanin is found in many organic systems [159] [35] [160] [65] including Lepidoptera [161] and absorbs most of the optical and UV wavelengths, with stronger absorption occurring at lower optical wavelengths [162]. The structural form of the photonic crystal responsible for producing the green coloured appearance of *P. sesostris* has been heavily postulated in recent literature. There have been numerous experimental and theoretical examinations of the scales that contain the 3D photonic crystal structure in order to ascertain its exact geometric structural form. Vukusic et al. [153] originally considered the structure to be a tetrahedral structure. Prum et al. later added that the structure is ‘characterized by a complex crystal-like array of spherical air cavities that are interconnected to one another in a tetrahedral nanostructure’ [163]. It was in 2008 when Michielsen et al. [9] determined the exact structural class of the photonic crystal present in *P. sesostris* scales to be a gyroid structure, formed from the constant mean curvature G-surface [137]. The gyroid structure is comprised of two interconnecting labyrinths that form the periodic photonic crystal array, as opposed to an array of spherical air voids, or otherwise. The gyroid photonic crystal structure has also been found to be present within many other Lepidoptera including *Calliphrys rubi* and *Teinopalpus imperialis* as a structural colour producing mechanism [9] [12]. The identification of the gyroid photonic crystal geometry present in many butterfly systems has also motivated studies into the self-assembling processes that produce such photonic crystal structures in butterflies. Theories regarding the exact self-assembling mechanism behind their production in butterfly scales have started to be unveiled, with the hope that synthetic photonic crystal fabrication methods may be inspired by the natural processes [68] [123] [8] [89] [124] [11].

7.2 Anatomy and physiology

The butterfly scales that provide *P. sesostris* with its bright green coloured appearance possess a complex morphology [47] [53]. The image presented in figure 7.2(a) displays a cross-section through a typical scale extracted from the green colour-producing region of *P. sesostris* and was obtained by a transmission electron microscope (TEM) [47] [53]. The image clearly shows that the intra-scale gyroid photonic crystal structure is arranged in a domained configuration, in a similar manner to that observed in the colour-producing scales possessed by the weevil *E. magnificus* in chapter 6 [14]. Each juxtaposed crystal domain possesses the same gyroid photonic crystal structure, arranged at a different orientation with respect to a neighbouring domain. As outlined in sections 6.3 and 6.5, an ordered 3D photonic crystal arranged in domains such as this results in many colour reflections emanating from a single scale. When viewed over many domains, a colour mixing process subsequently results, producing an angle-
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*Parides sesostris*

Figure 7.1: (a) The butterfly *Parides sesostris* [13]: the green coloured regions of its dorsal wings are structurally coloured with a 3D photonic crystal arranged within scales (b) that exist on the butterfly’s dark, absorbing wing substrate. (a) Scale bar: 10 mm (b) scale bar: 200 µm. Images courtesy of P. Vukusic.

independent colour appearance [9]. In addition to this, on the upper side of each *P. sesostris* scale there exists a surface structure. The surface structure consists of a periodic array, extending from a thin membrane that covers the photonic crystal domains and forms a chitinous envelope on top of the scale. The lower surface of each scale is also covered in the chitinous envelope but remains flat and thin. Figure 7.2(b) presents an SEM image displaying how the surface structure is arranged upon the 3D photonic crystal structure within each scale. The periodic nature and the pitch of the surface structure consequently forms an optical diffraction grating on top of each scale. The exact morphology of the surface structure is indicative of a diffraction grating designed to be both an efficient reflection and transmission grating [18]. The light that is transmitted through the diffracting surface structure is subsequently incident upon a photonic crystal domain at a variety of diffracted angles. This results in a larger range of wavelengths being reflected from each individual domain. Due to the intra-domain additive colour mixing process that subsequently results, the reflected band-width from individual domains is broadened. This contributes to the additional colour mixing process that occurs across many domains. Consequently the diffracting surface structure enhances the optical colour mixing process introduced by domaining and acts to improve the angle-independence of the coloured hue observed over the entire green wing region of *P. sesostris*.

The equation that can describe the constant mean curvature gyroid ‘G-surface’ by a nodal surface approximation is defined by equation 5.5, presented in section 5.6.
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Figure 7.2: (a) A TEM image showing a cross-section through a *P. sesostris* green scale. The 3D gyroid photonic crystal structure is arranged in domains within the scale and there exists a diffracting surface structure above the crystal-domained arrangement. (b) An SEM image of a broken *P. sesostris* green scale, clearly displaying the 3D nature of the phonic crystal structure and the arrangement of the surface structure in relation to the photonic crystal regions. (a) Scale bar: 2.5 µm (b) scale bar: 5 µm. Images courtesy of P. Vukusic [47].

Michielsen et al. calculated the material volume fraction that best represents the structure present in the wing scales of *P. sesostris* using an iterative image analysis technique [153] [9]. This was determined to be $\phi_s = 0.4$, comprising 40% chitinous material and 60% air. This filling fraction corresponds to a value of the parameter ‘t’ in equation 5.5 of $t = -0.3$ [9]. The lattice constant was calculated to be $a = 260(\pm 63)$ nm using the same image analysis method [9].

It is apparent from figure 7.2 that the green wing scales present on *P. sesostris* possess a remarkably complex anatomy designed for producing an angle-independent coloured appearance. The need for adapting the morphology of each scale originates from the use of an ordered photonic crystal structure comprised of low refractive index contrast materials to produce this colour. The design of an appropriate underlying photonic crystal structure can also aid the iridescence suppression required by the butterfly. Initially, this may be done by selecting an ideal 3D structural class that suppresses iridescence and subsequently by tuning variable parameters of the photonic crystal to obtain the desired response. As the exact structural form of the ordered 3D photonic crystal responsible for its colour production is now known, it is possible to analyse how the structure itself is optimised in order to aid the coloured appearances the butterfly requires. Presented in the following sections are new optical data obtained from *P. sesostris*. In addition to this, the theoretical modelling and analysis of the electromagnetic responses of a variety of different gyroid photonic crystal structures.
are presented in order to assess how the fundamental structure itself within *P. sesostris* is optimised. Firstly, the comparative analysis of the electromagnetic response of the analogous millimetre gyroid replica, presented in chapter 5, is performed alongside the analysis of the optical response of the gyroid present in *P. sesostris* scales.

### 7.3 The electromagnetic response of the gyroid photonic crystal within *Parides sesostris* scales

The experimental and theoretical characterisation of the gyroid photonic structure presented in section 5.6 of chapter 5 was performed on a gyroid structure that closely mimicked that found within *P. sesostris* wing scales. Due to the scalability of Maxwell’s equations, as described in section 3.3.4 [20], it is possible to directly relate these results to the optical gyroid present in *P. sesostris*, possessing a lattice constant of $a = 260(\pm 63) \text{ nm}$ [9]. The reduced frequency plots presented in figures 5.12 and 5.13 and discussed in section 5.6 have a photonic band structure that spans the reduced frequency range of 0.5 to 1 ($c/a$), where $c$ is the speed of light, within the analysed frequency range. When applied to a gyroid with a lattice constant of $a = 260 \text{ nm}$, this reduced frequency range corresponds to an optical frequency range of 576-1154 THz, or a wavelength range of 520 nm to 260 nm. The lowest frequency band was determined to reach a minimum frequency of 0.5 ($c/a$) in figures 5.12 and 5.13, which corresponds to the highest wavelength produced by this structure of 520 nm - lying mid way through the green band of the visible spectrum. All lower wavelengths of the visible spectrum are also reflected by this structure, and also some UV. As a consequence, it is largely the lower photonic stop-bands of the dispersion diagrams presented in figures 5.12 and 5.13 that contribute to any visible colour produced by this gyroid structure. The transmission stop-bands in figures 5.12 and 5.13 indicate a native optical gyroid with this specified lattice constant and filling fraction will reflect predominantly blue wavelengths with a contribution from the lower green wavelengths. When arranged in the domain arrangement, as observed within *P. sesostris* scales, the additive colour mixing process that incorporates these reflected wavelengths will reduce the saturation of green colour, due to the large range of blue reflected wavelengths present. Wilts et al. [164] recently discovered the presence of a pigment in the surrounding envelope of *P. sesostris* scales that absorbs wavelengths primarily at approximately 395 nm. The presence of such a pigment would act to eliminate the lower blue reflected wavelengths emanating from the gyroid domains. This ‘spectral tuning’ method would act to improve the largely green coloured appearance required by the butterfly and would also aid the angle-independence of the scattered light from the wing scales [164].
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parative theoretical photonic band-structure presented by Wilts et al. was calculated with a larger lattice constant than was established by Michielsen et al.. However, on comparison with the stop-band behaviour, described in this section, produced with the lattice constant value established by Michielsen et al. the introduction of the spectral tuning pigment would greatly aid the saturation of the green coloured hue, beyond that calculated by Wilts et al. [13] [164].

7.4 Scatterometry

Imaging scatterometry was performed on single, isolated scales extracted from the green region of *P. sesostris*, as outlined in section 4.4. Both the top-side and the under-side of individual scales were examined by narrow- and wide-angle illumination in order to assess the differences in spatial scattering brought about by the surface structure present on the top-side of each scale.

7.4.1 Narrow-angle illumination scatterometry

Figures 7.3 and 7.4 present the narrow-angle scatterometry polar plots obtained from the under- and top-side of a single *P. sesostris* scale, respectively. The scale was rotated in 15° steps from 0° to 45° in both instances, with illumination remaining constant. Figure 7.3, obtained from the under-side of the scale where intra-scale domains are not obscured by a surface structure, was obtained from a domain which appeared green at normal incidence. The blue shift in frequency incurred by rotating the sample results from the incident beam moving away from the surface normal to the set of effective periodic planes that give rise to the resonance. The specular nature of the reflection from this domain is clearly identifiable and is demonstrated by the change in angle of reflected light in the hemispherical plot upon rotation.

Figure 7.4 presents the corresponding narrow-angle scatterometry polar plots obtained by illuminating the top-side of the scale. The surface structure present on the top-side of the wing scales consequently obscures the visibility of domains, as displayed in figure 7.1(b). The beam was incident upon the same region of the scale at each rotated angle. All hemispherical polar plots obtained by illuminating the top-side of a scale exhibit a diffuse, green, background scatter. Alongside the diffuse scattering, illumination of the top-side of the scale produces strongly diffracted light and is present in a band perpendicular to the orientation of the surface ridges. The diffraction that is observed on a local area of an individual scale will not be visible by an observer viewing multiple scales. On comparison of the polar plots presented in figures 7.3 and 7.4, the contrasting nature of the scattering patterns between the interrogation of the
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Figure 7.3: Hemispherical polar plots obtained by narrow-angle illumination imaging scatterometry from the under-side of a single *P. sesostris* scale. The scale was rotated from 0° to 45° in 15° steps and the scattering patterns imaged at (a) 0° (b) 15° (c) 30° (d) 45° to the incident beam. The red rings represent scattering angles of 5°, 30°, 60° and 90° from the centre of each plot.

The specular nature of the reflection from an individual gyroid domain is altered drastically purely by the addition of the surface structure on the top-side of the scale in order to produce highly diffuse, green scatter.

Figure 7.4(d) shows the scattering produced by the top-side of a scale when rotated by 45° from the axial incident light beam. It is apparent that a scale oriented at this angle also scatters red light, appearing at the base of the hemispherical polar plot, in addition to the green diffusely scattered light. The exposure time of the imaging camera in the scatterometer was increased in order to obtain a clear image of the red scattering effect produced by the rotated scale. Figures 7.5(a) and (b) display the resulting scattering patterns produced by the scale at 30° and 45° to the incident beam, respectively, imaged with an increased exposure time. The scatterometer is capable of collecting the full scattered hemisphere from a sample when light is incident
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upon it at normal incidence. However, when a sample is rotated, a proportion of the back-scattered hemisphere moves out of the collectible range of the ellipsoidal mirror. Consequently this results in a proportion of the hemispherical polar plot remaining dark where back-scattering is not possible. The contrasting region of red scatter in figure 7.4(d) and 7.5(b) occurs at the scattering angles of the hemispherical polar plot that would generally be absent of back-scattered light from a sample oriented at 45°. As transmission through a sample in the scatterometer generally occurs along the axial direction, it is possible to conclude that the red scatter originates from transmitted, forward-scattered light through the scale oriented at a high angle to the incident beam. Samples previously under investigation in the scatterometer, and also the under-side of this *P. sesostris* scale, have simply shown an absence of forward-scattered light at these angles. The presence of red, forward scattered light present in figures 7.5(a) and (b) further portrays the efficient forward scattering mechanism achieved by the surface structure present on the top surface of *P. sesostris* scales. The complementary red coloured appearance of the forward-scattered light results from the remaining light that is not back-scattered or absorbed from the photonic mechanisms present on/within the scales.

**7.4.2 Wide-angle illumination scatterometry**

Figures 7.6 and 7.7 present the wide-angle scatterometry polar plots obtained from the under- and top-side of a single *P. sesostris* scale, respectively. The scales were illuminated with unpolarised light and also TM and TE polarisations at normal incidence to the secondary beam. Figure 7.6(a) displays the total iridescence produced by the under-side of a single *P. sesostris* scale. Figure 7.6(a) shows that the iridescent nature of the 3D gyroid photonic crystal structure within these scales results in both green and blue reflections occurring. The blue and green reflections produced from the under-side of a single scale, and possible UV reflections at higher angles, concurs with the spectral range identified by the experimental and theoretical characterisation of the gyroid found in these scales outlined in subsection 7.3 of this chapter and also section 5.6 of chapter 5. Figures 7.6(b) and (c) display the wide-angle scatterometry images obtained with TM and TE polarised light. As described in section 4.4.2, only the data present within a vertical line along the centre of the diagram is representative of the respective incident polarisation used. In each case, there appears to be no distinct change in scattering response when wide-angle TE or TM polarisation is incident upon the under-side of the scale, despite the polarisation-dependent response observed from a single gyroid photonic crystal. This is due to the cumulative colour averaging effect observed over the 50 µm diameter interrogation area. The slight discrepancy at approximately 50°
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Figure 7.4: Hemispherical polar plots obtained by narrow-angle illumination imaging scatterometry from the top-side of a single *P. sesostris* scale. The scale was rotated from 0° to 45° in 15° steps and scattering patterns were imaged at (a) 0° (b) 15° (c) 30° (d) 45° to the incident beam.

Figure 7.5: Hemispherical polar plots obtained by narrow-angle illumination imaging scatterometry from the top-side of a single *P. sesostris* scale oriented at (a) 30° and (b) 45° to the incident beam with an increased exposure time. The images display red forward scattered light from the sample, alongside the diffuse green scatter observed at smaller rotation angles.
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Figure 7.6: Hemispherical polar plots obtained by wide-angle illumination imaging scatterometry from the under-side of a single *P. sesostris* scale. The scale was illuminated with unpolarised incident light (a), TE incident light (b) and TM incident light (c).

between TE and TM incident light in figure 7.6 results from Brewster angle effects.

Figure 7.7(a) displays the total iridescence produced by the top-side of a single *P. sesostris* scale. The suppression of iridescence by the introduction of the surface structure upon each scale is highlighted when a comparison of figures 7.7(a) and 7.6(a) is made. The most noticeable differences that occur due to the presence of the surface structure are the absence of blue scattered wavelengths and the dominance of green scattered wavelengths that cover most of the scattered hemisphere. Wide-angle illumination of the top-side of the scale exhibits no difference in response with opposing linear polarisations, with the exception of Brewster angle effects.

### 7.4.3 Summary of *Parides sesostris* scatterometry

The scatterometry data obtained from the top- and under-side of individual *P. sesostris* scales has highlighted the differences between the forward- and backward-scattering responses observed when illuminating each side of a single *P. sesostris* scale. The
narrow-angle scatterometry performed on the under- and top-side of a single wing scale demonstrates how the surface structure present on the top-side diffuses light and reduces iridescence. Narrow-angle scatterometry has also demonstrated a forward scattering process is induced by the surface structure. This was identified from the presence of forward-scattered light in the hemispherical polar plots when the sample is rotated to high angles from the incident beam. This consequently further aids the suppression of iridescence from *P. sesostris* wing scales. The wide-angle scatterometry data obtained from the under-side of a scale presented in figure 7.6(a) reveals how the domaining mechanism alone is not sufficient to fully suppress the iridescence of the underlying gyroid photonic crystal structure. The addition of the highly efficient diffracting surface structure on the top-side of each scale aids the diffusion of scattered light and also the suppression of iridescence in each scale, resulting in an angle-independent green colour appearance, figure 7.7(a). The surface structure and the domaining method combine to form a dual mechanism for producing an angle-independent green colour.
appearance from the gyroid photonic crystal structure. However, this system describes embellishments in addition to the underlying fundamental gyroid photonic structure. The actual photonic crystal itself may also act to suppress iridescence on a more fundamental level, providing correct parameters such as filling fraction and number of unit cells in the depth of the scale are employed. The following section describes how the gyroid photonic crystal structure within \textit{P. sesostris} is optimised.

### 7.5 Optimisation of \textit{Parides sesostris}

As the materials available to Lepidoptera for photonic crystal production are limited, \textit{P. sesostris} utilises the approach of domaining an ordered photonic crystal in order to suppress iridescence from individual scales. The additional surface structure on the top-side of each scale acts to aid the suppression of iridescence brought about by intra-scale domains of photonic crystal. This section outlines how the fundamental gyroid structure itself, present on the wings of \textit{P. sesostris}, aids iridescence suppression alongside these more instantly recognisable photonic embellishments present within \textit{P. sesostris} scales.

In chapter 5.6 the full experimental and theoretical electromagnetic characterisation and analysis of a gyroid with a $\phi_s = 0.4$ material volume fraction was undertaken. Primarily, the transmission stop-bands associated with each polarisation and high-symmetry directions through the structure were identified. This acts as a starting point for comparison of this gyroid structure with others by changing its physical parameters. Although the constituent materials used by \textit{P. sesostris} in its photonic crystal structure are limited, most other variables associated with photonic crystal production are, in theory, changeable. The exact processes that lead to the self-assembly of this gyroid photonic crystal structure are largely unknown. Some theories of butterfly photonic crystal self-assembly processes are currently being developed \[68\] \[123\] \[8\] \[89\] \[124\] \[11\], however, parameters that must remain fixed during these processes are unknown. For instance, the lattice constant may either be pre-defined by the self-assembly fabrication process, or may have evolved to be optimised to reflect specific blue/green wavelengths. Additional geometric and structural parameters may change the electromagnetic response of the structure and may also be optimised for a particular optical function. The effect of changing the filling fraction of the gyroid structure on its optical response was investigated by theoretical modelling. In addition to this, theoretical modelling was performed on gyroid arrays that possessed an increasing number of unit cells in their depth.
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7.5.1 Filling fraction

In order to examine how the filling fraction of the gyroid photonic crystal structure comprised of air and chitin \((n_{\text{chitin}} = 1.56)\) affects the reflected and transmitted photonic band-width, the material volume fraction was systematically varied from \(26\% \leq \phi_s \leq 74\%\). This was done by changing the value of ‘t’ in equation 5.5 in steps of 0.1 over the range of \(-0.7 \leq t \leq 0.7\). Each of these structures was theoretically modelled using the FEM method outlined in section 4.8 and the reflection and transmission responses were then calculated. Our model geometry for each analysed filling fraction consisted of a six unit-cell-deep array that was repeated with master/slave boundaries in the remaining dimensions. The reflection and transmission responses over the analysed material volume fraction range are presented in figure 7.8(a) and (b), respectively, as grey-scale plots from normal incidence calculations. Each graph shows a distinct change in, not only frequency but also, reflected/transmitted band-width over the analysed range. As the structure approaches either 100% air or 100% material the band-width must decrease, due to the weak periodicity this creates within the structure. Explicitly, at large values of \(\phi_s\), high concentration factors result for both standing wave modes that form the edge of the photonic band-gap. Not only does this induce a smaller photonic band-gap, but it also will reduce the eigenfrequency of each standing wave mode, as observed in figures 7.8(a) and (b). At smaller values of \(\phi_s\), the concentration factor is small for both standing wave modes, consequently reducing the width of the photonic band-gap and increasing the eigenfrequency of each standing wave mode, also observed in figures 7.8(a) and (b). The filling fraction that produced the maximum band-width lies somewhere in between these two extremes. The reflected band-width produced from each filling fraction was calculated from the theoretically modelled reflectance spectra. The reflected band-width was measured as the difference in the band-edge frequencies. The frequency of each band-edge was confirmed by inspection of standing wave modes present in electric field plots obtained from the theoretical models. The band-width, in reduced frequency units, was then plotted against volume fraction and is presented in figure 7.8(c). These data show explicitly that, over the analysed filling fractions, smaller band-gaps do occur at the largest and smallest analysed filling fractions. Figure 7.8(c) also reveals that the maximum reflected band-width for a gyroid structure comprised of air and chitin \((n_{\text{chitin}} = 1.56)\) is produced by a structure that has a material volume filling fraction in the range of \(0.37 \leq \phi_s \leq 0.43\), or \(-0.4 \leq t \leq -0.2\). The gyroid photonic crystal structure found within the wing scales of the butterfly *P. sesostris* has a material volume filling fraction of \(\phi_s = 0.4\), \(t = -0.3\) [9] as marked on figures 7.8(a) and (b) by red lines. This material volume filling fraction lies in the centre of the maximised reflected bandwidth range. The filling
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Figure 7.8: Grey-scale plots representing the collective reflection (a) and transmission (b) responses from gyroid photonic crystal structures with material volume fractions that range from $26\% \leq \phi_s \leq 74\%$, corresponding to $-0.7 \leq t \leq 0.7$ [13]. The reflected photonic band-width has been extracted, plotted and presented in (c) against material volume fraction [13]. The gyroid material volume fraction used by *P. sesostris* is $\phi_s = 0.4$, identified by the red lines, and lies in an optimum region for maximising the reflected band-width.
fraction that produces this optimal, maximised reflected band-width can be explained by directly relating it to the optical path lengths of each constituent material present in the structure. For the case of a 1D multilayer, it may be considered to be ideal when the optical path lengths of each component layer are identical. This structural composition creates an optimum quarter-wavelength condition within the structure, consequently producing the largest photonic band-gap width possible for a system comprised of specific media. A multilayer comprised of air and chitin \((n_{\text{chitin}} = 1.56)\) will require a filling fraction that includes 39.06\% chitin and 60.93\% air in order for the optical path lengths to be equal in each medium. This is comparable to the 40\% chitin and 60\% air possessed by the gyroid structure within the wing scales of \textit{P. sesostris}.

Large photonic band-gap widths are often associated with complete band-gaps and are generally achieved by using high refractive index contrast materials in the construction of a photonic crystal. The photonic band structures presented in figures 5.12 and 5.13 in section 5.6 closely mimic the response from the gyroid present within \textit{P. sesostris} scales. The photonic band-structure produced by this gyroid structure exhibits iridescence suppressing behaviour. Namely, within the stop-bands there exist some frequencies which will always be reflected over the analysed angular ranges and polarisations. The TM and TE \([11\bar{1}]\) and \([\bar{1}\bar{1}\bar{1}]\) bands and the TM \([00\bar{1}]\) band in figures 5.12 and 5.13 contain a small range of frequencies that are always present in the stop-band, around the visible frequencies associated with the \textit{P. sesostris} gyroid, over the \(-45^\circ \leq \theta \leq 45^\circ\) angle range. This is a feature that directly originates from the width of the stop-bands and may not be achieved if another filling fraction, that produces a smaller reflected band-width, is used. Therefore, as a direct consequence of using an optimised filling fraction, a local suppression of iridescence is also present within individual domains inside \textit{P. sesostris} wing scales. This is a previously overlooked fundamental mechanism that \textit{P. sesostris} utilises alongside many other mechanisms in order to suppress iridescence [13].

7.5.2 Number of unit cells

The Fresnel equations presented in section 3.2 of chapter 3 indicate that higher intensity reflections result from an interface that separates high refractive index contrast media. \textit{P. sesostris}, and other animals, does not have such materials available to it. Therefore, in order to maximise its colour and brightness, or the intensity of the coloured reflections produced from its wing scales, this butterfly must develop another mechanism to achieve this. In photonic crystal systems, the maximum intensity of reflected light from a system is produced from an array that has a semi-infinite number of unit cells through the depth of the array. \textit{P. sesostris} scales have approximately ten unit cells in the largest
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Figure 7.9: Colour-plots displaying the collective theoretical (a) reflection and (b) transmission responses from gyroid photonic crystal arrays that vary with numbers of unit cells in the depth of the array. The material volume fraction of the gyroid structure used in all models was $\phi_s = 0.4$. The addition of contour lines have been calculated and added to the transmission graph, (b), for clarity.
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Figure 7.10: Line plots displaying the reflectance responses of a gyroid structure with material volume fraction $\phi_s = 0.4$ with varying numbers of unit cells in the depth of the array. The peak intensity of the principal reflection feature increases with number of unit cells, whereas the secondary Fabry-Perot resonances decrease in intensity.

depth of a scale. The minimum number of unit cells that can approximate the reflected intensity from a semi-infinite photonic crystal array was investigated by theoretical FEM modelling. The modelling procedure involved systematically varying the number of gyroid unit cells present in the depth of the, otherwise infinite, array. The reflection and transmission responses of each model, ranging from two to twenty unit cells in the depth of the array, was calculated. The collective reflection and transmission from each model is represented as colour-scale plots in figures 7.9(a) and (b), respectively. The difference between the reflection and transmission band-gap responses arise from the absorption inherent in the chitin volume of the structure. The individual reflectance line plots of each data set are also presented in figure 7.10. Figures 7.9(a) and 7.10 show that the reflected band-width exhibits an observable decrease when the number of unit cells forming the depth of the array is increased from two to four unit cells. The change in reflected band-width from four to twenty unit cells is negligible. Alongside the change in band-width, figure 7.10 also displays how the intensity of the peak reflectance of each spectrum changes. There is an observable increase in reflected intensity when increasing the number of unit cells from two to four. Beyond four unit cells the intensity changes by a negligible amount. This is presented explicitly in figure 7.11(a), where the maximum mid-peak intensity is plotted against number of unit cells. Therefore, in order to maximise only this reflected intensity from a gyroid array, approximately a four unit cell depth is required. Such a four-layered gyroid system is present in another...
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Figure 7.11: Line plots displaying the peak reflectance responses of (a) the principle maximum peak and (b) the secondary Fabry-Perot resonances observed in figure 7.10. The analysed gyroid structure has material volume fraction $\phi_s = 0.4$ in each case.

butterfly, *Callophrys rubi* [10] [69] [12]. An SEM image of this four-layered system is presented in figure 2.8(c) in section 2.4.1. This indicates that other butterflies may utilise the many different optimisation methods in different ways in order to optimise specific optical parameters for a particular optical function. An SEM of the four-unit cell system is presented in figure 2.8(c) in section 2.4.1. However, figures 7.9(a) and 7.10 demonstrate that a four unit-cell-deep array still produces finer optical details that appear as secondary resonances either side of the principle reflection peak. These secondary resonances manifest as Fabry-Perot resonances that occur from the front and back interfaces of the finite sample. The intensity of the Fabry-Perot resonances gradually reduce when the number of unit cells in the depth of the array is increased. The maximum intensity of these secondary fluctuations have been measured for each reflectance spectrum and plotted in figure 7.11(b). At approximately ten unit cells the array approximates an infinite crystal in this sense, with the Fabry-Perot resonances either side of the principle reflection response becoming negligible. This is the same number of unit cells present in the largest depth of *P. sesostris* green scales, as shown in the TEM presented in figures 7.12 and 7.2(a). The optical effect this induces is the purest, or most saturated, and brightest colour reflection possible by using the fewest number of unit cells possible.

7.6 Conclusions

The butterfly *P. sesostris*, presented in figure 7.1(a), produces the green coloured appearance on its dorsal wings by the use of a photonic crystal structure. The 3D gy-
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Figure 7.12: A magnified TEM image displaying the number of gyroid unit cells present in the depth of a *P. sesostris* scale. There exists approximately 10 unit cells throughout the largest depth of the scale. Scale bar: 2.5 µm. Image courtesy of P. Vukusic.

The gyroid photonic crystal structure responsible for this structural colour is contained within scales that are present on the surface of the dark, absorbing wing of the butterfly (figure 7.1(b)). The morphology of the scales comprise an ordered surface structure above a domained photonic crystal arrangement. Imaging scatterometry performed on the under- and top-side of individual *P. sesostris* scales was undertaken and using both narrow- and wide-angle illumination angles. The narrow-angle response from each side of the scale showed contrasting scattering responses: the under-side provides highly specular, angle-dependent reflections whereas the scattering from the top-side of the scale produces highly diffuse, angle-independent scattering including strong diffraction effects. The difference in scattering response originates purely from the surface structure present on the top-side of each scale. The highly diffracting nature of the periodic surface structure enhances the colour averaging and iridescence suppression brought about by domaining due to an induced forward-scattering process. This forward-scattering process is observed clearly in the scatterometry images presented in figure 7.5(a) and (b) where the complementary red scatter appears at scattering angles where back-scatter is normally prevented from a sample under rotation. This phenomenon is not observed when the corresponding scattering profiles are imaged from the under-side of the scale, or with most samples probed by the scatterometry method. Wide-angle scatterometry performed on either side of the scale also shows contrasting results: the underside remains iridescent despite domaining, whereas the iridescence is greatly suppressed on the top-side where the additional surface structure is present. This also confirms the role of the diffusive surface structure.

The surface structure aids the domain configuration in suppressing the iridescence inherent in a 3D ordered, periodic photonic crystal structure comprised of low refrac-
tive index contrast media. However, on a more fundamental level, the photonic crystal structure itself is also optimised, not only in the lattice constant used to enable the required frequencies to be reflected but also, with the parameter of filling fraction. The gyroid material volume fraction used by *P. sesostris* is $\phi_s = 0.4$, comprising 40% chitinous material and 60% air. It is this filling fraction that maximises the reflected band-width from the structure for the specific refractive index contrast used, as shown by the graph presented in figure 7.8(c). This consequently results in certain frequencies always being present in each of the stop-bands, as experimentally and theoretically identified in section 5.6 of chapter 5. The extent of overlap of frequencies in these stop-bands over the analysed angle range will be reduced or may not be present at all if any other filling fraction was used. The use of an optimised filling fraction for producing the widest possible reflected band-width is likely to be an adapted design feature of *P. sesostris* because it aids iridescence suppression on a fundamental structural level. The suppression of iridescence is so highly sought after by the butterfly that additional more elaborate embellishments are also employed, with each mechanism assisting the achievement of a highly developed system for producing angle-independent colour reflection.

In addition to this, the number of unit cells present in the depth of the photonic crystal array also lies within an optimal range for producing high intensity colour reflections with minimal contributions from secondary, Fabry-Perot resonances (figures 7.9, 7.10 and 7.11). The number of unit cells throughout the depth of the scale is therefore optimised to reproduce the physical effects of a semi-infinite photonic crystal, while physically using the minimum number of unit cells necessary to do so. Interestingly *Callophrys rubi* is another butterfly that uses a gyroid photonic crystal structure to produce its wing colouration and uses approximately 4 unit cells in the depth of its array. This is the absolute minimum number of unit cells that can approximate the maximum reflected intensity alone from the gyroid array. This indicates that other butterflies may optimise various parameters in alternative ways to invoke a slightly different optimum optical response using the materials available to them.

Lepidoptera often produce the coloured patterns present on their wings through the use of photonic crystals. Sometimes the effect that is required through the use of structural colour is not achievable through the production of a photonic crystal alone, often due to limitations in available materials. This study has shown that *Parides sesostris* is an example of a butterfly that goes to extraordinary lengths to produce an angle-independent coloured appearance that is unobtainable purely by a native photonic crystal structure. It is highly likely that the optimised filling fraction used by *P. sesostris*, and the many other attributes to its structurally colour producing scales, have developed through many years of evolution, and hence why such features are truly
optimal in order to achieve the desired optical response. In this case the desired optical effect is angle-independent colour, which is generally trivially available through the use of pigmentation. However, the chemical processes necessary to produce green colour appearances are not readily obtainable by many insects [29] [30]. The energetic cost of producing the structural embellishments present within and around a *Parides sesostris* colour producing scales is clearly beneficial to the butterfly, creating efficient and highly intense colour reflections, only available by use of a photonic crystal.
Chapter 8

The tunable gyroid

8.1 Introduction

The ability to control the flow of light with photonic crystals is an extremely desirable electromagnetic property that has led to the use of photonic crystals in many technologically based applications. Fibre optic cables [3] [4], LEDs [5], and even lasers [93] [94] have benefited from the highly efficient narrow-band optical reflections that are achievable by the selection of an appropriate photonic crystal geometry. It is possible to tailor a photonic crystal structure to obtain the exact optical response required by designing the most appropriate structure for its purpose. However, by designing and then fabricating such a photonic system, the resultant electromagnetic response is fixed. By using a dynamic structure it is possible to alter the structural parameters of the photonic crystal and subsequently achieve a tunable response. Such tunable photonic crystal systems are being developed for use in tunable photonic crystal lasers [93] [94], tunable optical fibres [165], and as stretch tunable mirrors [166]. Methods used to alter the geometry of a photonic structure in order to obtain tunable responses include temperature control [167], voltage control [165], applying a direct stress or a strain to the structure [168] [166] and also gas condensation methods used to alter the inherent refractive index properties of the system [169]. The majority of the fabricated tunable structures have predominantly been limited to 1D [170] and 2D structures [171] [172] [173].

The interconnected nature of 3D minimal surface, photonic crystal structures makes them desirable candidates for use as tunable 3D photonic crystal structures due to the structural integrity they hold. Within 3D photonic crystal structures there exist many sets of periodic effective planes that are oriented in multiple directions within the geometry that each give rise to a stop-band response. When a 3D photonic crystal structure is put under compression in a single direction, the rate at which the stop-band fre-
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Figure 8.1: (a) A compressible gyroid comprised of a rubber polymer, with permittivity of $\epsilon = 2.85 + 0.15i$, and air. The gyroid consists of a $10 \times 10 \times 10$ unit cell array with a single unit cell lattice constant of 9 mm. (b) When under compression, the surface area of the exposed faces of the array decreases. A $10 \times 10 \times 10$ array allows the full-width half-maximum of the incident Gaussian microwave beam to fit within the compressed array interface when compressed up to 20 mm. When under compression, all directions perpendicular to the compression direction bow outwards, consequently increasing the dimensions of the array in these directions. In the experiments the microwave beam is incident on the sample perpendicular to the direction of compression.

8.2 Sample fabrication

The fabrication of the stretch tunable gyroid was performed with a stereolithography machine, similar to that described in section 4.6.1, that can deposit a rubber polymer material. The rubber polymer has a permittivity of $\epsilon = 2.85 + 0.15i$, corresponding to a refractive index of $n = 1.69$, calculated by the established Fabry-Perot technique performed on a thin block of the material [18] [174]. The fabricated gyroid consisted of one solid, rubber labyrinth and one air labyrinth. The sample was designed with a lattice constant of 9 mm as a $10 \times 10 \times 10$ unit cell array, with a material volume
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fraction of $\phi_s = 0.4$ and is presented in figure 8.1(a).

When a compression is made to the sample, the interface upon which microwave radiation is incident reduces in size, as shown by figure 8.1(b). The array dimensions were selected so that, when the sample is put under compression, the surface area of the incident interface was large enough to encompass the majority of the power of the incident beam. The size of the beam that comprised the majority of the beam power was calculated from the experimentally determined Gaussian beam profile presented in figure 4.6 in chapter 4. The full-width half-maximum of the beam profile, when the sample is positioned at 22 cm from the source, was calculated to be approximately 5 cm. Consequently, the structure was compressed to a minimum of 70 mm in each experiment. In addition to this, the array size was selected so that the sample was stable under compression as it experiences a bowing effect in directions orthogonal to the compression. All directions perpendicular to the compression direction bow outwards, consequently increasing the dimensions of the array in these directions. This increase in sample size reaches a maximum across a plane in the centre of the sample, between the two compression plates. The surfaces that are directly adjacent to the two compression plates experience a slightly smaller expansion due to friction effects, however, they do still expand. The $10 \times 10 \times 10$ unit cell array provides the sample with stability when under compression and experiences expansions in a symmetric manner within the compression device. Using a sample with fewer unit cells in the line of microwave propagation may induce additional, asymmetric bowing. The stability of the sample under compression and the symmetry of the expansion along the line of incident beam propagation is a major benefit to the experimental set-up and characterisation. However, the cost brought about by this selected array size is an increase in the absorption of propagating radiation through the sample. In section 5.6 of chapter 5, a similar gyroid array consisting of four unit cells in the line of normally incident light was characterised electromagnetically. In section 7.5.2 of chapter 7, the effect of changing the number of unit cells in the depth of the array was analysed. Figures 7.9(a) and (b), presented in section 7.5.2 display the difference in the transmission and reflection response when the number of unit cells is increased. As the number of unit cells in the line of normally incident radiation increases, the transmission response deviates gradually from the expected reflection response due to the inherent absorption present within the compositional materials of the array. Figure 7.9(b) shows that the stop-band width can be identified from each set of transmission data and corresponds to the reflected band-width, but the band edges have a weaker transmitted intensity. This reduction in intensity of stop-band edges obscures the clear presence of individual stop-bands in the transmitted data. This affects the clarity of the stop-bands for the 10 unit cells data presented in figure 7.9(b) in section 7.5.2. This decrease in band-edge
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intensity was also observed in the experimental data obtained in this section and as a result was found to obscure the clarity of stop-band behaviour when the gyroid was compressed, particularly at higher frequencies. However, when the transmitted magnitude is plotted, the band edges become more identifiable and distinguishable, whilst simultaneously preserving the position and width of each stop-band. In order to overcome the obstacle that the combination of absorption and a large number of unit cells provides to the clarity of the experimental data, the data presented in this section are plotted in transmitted magnitude as it provides a clear demonstration of the behaviour of each stop-band when the sample is under compression. The main point of interest of the work presented in this chapter is stop-band movement, as opposed to the general characterisation of the gyroid which has already been performed in an earlier section on an array that used fewer unit cells in the depth of the structure. Previously, investigations into stretch-tunable photonic crystals have been limited to 1- and 2-dimensional structures [175] [168] [96] [166] [176]. In addition to this, previously published work in the field regarding 2-dimensional tunable photonic structures have been limited to structures that are comprised of an array of ‘holes’ or air gaps in a material [175] [168] [166] [176]. The work presented in this chapter differs from the previously published work as it was performed on a 3-dimensional structure that is also bi-continuous and naturally occurring.

8.3 Experimental set-up

The experimental set-up used for the work presented in this chapter was similar to that described in chapter 5. The schematic presented in figure 8.2 depicts the set-up employed to carry out the experimental characterisation of the fabricated tunable gyroid described in section 8.2. The sample was centred between aligned broadband emitting and receiving horns. The same broadband horns and VNA set-up outlined in chapter 5 were used to conduct the experiments. The differences in the experimental set-up for the work carried out in this chapter and in chapter 5 lies within the sample holding method. In the experiments presented in chapter 5 the sample was surrounded by absorbing foam, however, in order to conduct the experiments outlined in this chapter it was necessary to position the compliant gyroid directly between a device manufactured to apply a compression force to it. The red plates in figure 8.2 represent the surfaces of the compression device to which a force was applied in order to compress the sample. A systematic compression was made to the sample so that the total size of the array was reduced by $0 \text{mm} \leq x \leq 20 \text{mm}$, in 5 mm steps. This compression is represented by changing the value of $x$ in figure 8.2 by these discrete amounts. The broadband source was incident upon the sample in a direction perpendicular to the compression
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Figure 8.2: The experimental set-up employed to investigate the photonic effects of compressing a compliant gyroid photonic crystal array. The red plates indicate the surfaces to which a force was applied to make a series of compressions to the structure. The broadband horns that form the source and detector in the experiment are incident upon the sample in a direction perpendicular to the compression direction. The sample was compressed in 5 mm steps so that the total size of the array, indicated by \( x \), was reduced by \( 0 \, \text{mm} \leq x \leq 20 \, \text{mm} \). The sample was rotated over a polar angle range of \( -45^\circ \leq \theta \leq 45^\circ \) according to the definitions in this diagram and both TE and TM linear polarisations were employed at each compression distance.
direction. The compression device comprises no metal components and is made purely of the material tufnol - a plastic-wood composite. Both plastic and wood are low reflectors of microwave radiation, and so this material provides both the strength and durability necessary for the function of the device, whilst minimising reflections from it by remaining as transparent to the incident radiation as possible. The sample was rotated over a polar angle range of $-45^\circ \leq \theta \leq 45^\circ$ and both TE and TM linear polarisations were employed at each compression distance, as depicted in figure 8.2. All data was collected with the sample oriented at an azimuthal angle of $\phi = 0^\circ$, as defined by figures 4.5 and 8.2.

### 8.4 Experimental data

Displayed in figures 8.3 and 8.4 are the experimental data of transmitted magnitude obtained from the compliant gyroid using TM and TE incident polarisation, respectively, with the sample positioned at an azimuthal angle of $\phi = 0^\circ$. The data are represented by grey-scale plots which display, from dark to light, low to high transmitted magnitude. The dark bands consequently represent the stop-bands produced by this gyroid structure under compression. The frequency axes are presented in reduced frequency units, using the original, uncompressed lattice constant of 9 mm for normalisation. The sample was compressed in 5 mm steps across the $[\bar{1}00]$ direction and probed at compression distances of 0 mm, 5 mm, 10 mm, 15 mm and 20 mm, shown in figures (a), (b), (c), (d) and (e), respectively, of figures 8.3 and 8.4. The stop-bands present within each data set observe a clear shift in frequency when a compression is made to the array. The characterisation of the gyroid structure, presented in section 5.6 of chapter 5, identified the directions within the gyroid array that contain the set of periodic effective planes that give rise to each stop-band. The Miller indices associated with these directions have been labelled on figures 8.3 and 8.4. Consequently, the frequency shifts brought about by a compression to the array can be discussed with respect to the deformations that occur along these identified directions. In order to do this the maximum expansions of the sample, occurring across the centre of the sample in the $[00\bar{1}]$ and $[0\bar{1}0]$ directions when a compression in the $[\bar{1}00]$ direction was made, were measured at each compression distance. This expansion was found to be symmetric in nature, namely the increase in sample size is equivalent in the $[00\bar{1}]$ and $[0\bar{1}0]$ directions when the compression is made in the $[\bar{1}00]$ direction. Measurements were taken at the edge of the sample, adjacent to the top and bottom surfaces of the compression plates, and also along the centre of maximum expansion. The results of these measurements are presented in the table displayed in figure 8.5. The array was measured to expand by 103.3%, 104.9%, 107.4% and 109.7% across the plane of maximum expansion in the
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Figure 8.3: The experimentally determined transmitted magnitude data displaying the stop-bands associated with the 3D compliant gyroid photonic crystal structure using TM linearly polarised incident radiation. The structure has an initial material volume fraction of $\phi_s = 0.4$ and lattice constant of 9 mm. The structure was compressed by (a) 0 mm, (b) 5 mm, (c) 10 mm, (d) 15 mm and (e) 20 mm, resulting in an overall final compressed size of 100%, 94.4%, 88.9%, 83.3% and 77.8% of the whole array, respectively, across the [\(\bar{1}00\)] direction. Each plot is represented in the reduced frequency regime, normalised by the initial lattice constant value, namely by 9 mm. The sample was analysed over a polar angle range of $-45^\circ \leq \theta \leq 45^\circ$ at an azimuthal angle of $\phi = 0^\circ$. 

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Figure 8.4: The experimentally determined transmitted magnitude data displaying the stop-bands associated with the compliant gyroid photonic crystal structure using TE linearly polarised incident radiation. The structure has an initial material volume fraction of $\phi_s = 0.4$ and lattice constant of 9 mm. The structure was compressed by (a) 0 mm, (b) 5 mm, (c) 10 mm, (d) 15 mm, and (e) 20 mm, resulting in an overall final compressed size of 100%, 94.4%, 88.9%, 83.3% and 77.8% of the whole array, respectively, across the [100] direction. Each plot is represented in the reduced frequency regime, normalised by the initial lattice constant value. The sample was analysed over a polar angle range of $-45^\circ \leq \theta \leq 45^\circ$ at an azimuthal angle of $\phi = 0^\circ$. 
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<table>
<thead>
<tr>
<th>Expansion</th>
<th>Mid-plane expansion</th>
<th>Edge expansion</th>
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<tbody>
<tr>
<td>[100] (%)</td>
<td>[010], [001] (%)</td>
<td>[010], [001] (%)</td>
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<tr>
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<td>100</td>
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<tr>
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<tr>
<td>77.8</td>
<td>109.7</td>
<td>104.2</td>
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Figure 8.5: The relative expansions that occur in the [010] and [001] directions of the compliant gyroid sample when a compression is made in the [100] direction. The first column represents the compression made to the sample across the [100] direction, represented as an expansion with a value less than 100% for consistency. The sample experiences a bowing effect due to friction at the compression plate boundaries. Consequently the maximum expansion occurs along a plane mid-way between the two plates. Smaller expansions occur across the edges of the structure that are adjacent to the compression plates. The expansions are found to be symmetric in nature across the [010] and [001] directions.

\[ \hat{y} \text{ and } \hat{z} \text{ directions, i.e. across the [010] and [001] directions, when a compression of 5 mm, 10 mm, 15 mm and 20 mm (or 94.4%, 88.9%, 83.3% and 77.8% of the original size) was made to the array in the } \hat{x} \text{ direction, along [100]. The movement of each stop-band, presented in figures 8.3 and 8.4, can be attributed to the relative change in plane spacing from which this concurrent expansion and compression of the array results. Figures 8.3 and 8.4 both display evidence of red- and blue-shifting stop-bands at each compression distance. From these expansion and compression measurements alone, it is clear that the spacing of the set of planes in the [001] direction increases with the compression and simultaneous orthogonal expansions. Explicitly this set of planes have undergone a 109.7% expansion across the region of maximum compression when compressed by 20 mm, or 77.8%, and so the [001] stop-band is expected to decrease in frequency. This frequency shift is clearly identifiable in figures 8.3 and 8.4 as the compression is applied to the structure. In addition to this it is possible to calculate, from trigonometric analysis, that the spacing of planes along the [011] direction is also expected to increase. Explicitly, this set of planes have undergone a 109.7% expansion across the region of maximum compression when compressed by 20 mm, or 77.8%. This also will result in a reduction in frequency of the [01̅1] and [0̅01] stop-bands upon compression of the gyroid. This frequency change is observed in figures 8.3 and 8.4. These stop-bands are all red-shifted. The stop-band that is blue-shifted upon deformation follows similar dispersion behaviour to that of the [001] band. This characteristic dispersion results from an incident beam that moves away from the surface normal to
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![Diagram](image)

Figure 8.6: (a) An example of a \( (10\bar{1}) \) plane within the cubic symmetry of the gyroid structure. In the experimental set-up, the incident beam is moving away from the surface normal to this set of effective planes, (b). This consequently results in a similar dispersion to that produced by the \([00\bar{1}]\) set of planes. The geometry of the gyroid is such that the frequency at which the \([10\bar{1}]\) stop-band occurs is extremely close in frequency to that of the \([00\bar{1}]\) band when no compression is made to the structure. At normal incidence the two stop-bands are completely indistinguishable from each other.

the set of effective planes when incident polar angle is increased. The only possible set of effective planes that can support this type of dispersion and simultaneously incur a frequency increase when the compression is made to the sample are the planes arranged in the \([10\bar{1}]\) and \([\bar{1}0\bar{1}]\) directions. The surface normal to these sets of planes points in the \(\hat{x} - \hat{z}\) direction and the sample is rotated purely in the \(\hat{y} - \hat{z}\) plane, as depicted in figure 8.6. Consequently, as polar angle is increased, the incident beam moves towards the surface normal of the \([01\bar{1}]\) and \([0\bar{1}1]\) set of effective planes within the gyroid, but away from the normal to the \([10\bar{1}]\) and \([\bar{1}0\bar{1}]\) sets of planes. This brings about the dispersion of the \([10\bar{1}]\), and \([\bar{1}0\bar{1}]\), bands observed in figures 8.3 and 8.4. By trigonometric analysis it is possible to calculate the reduction in plane spacing in these directions. Explicitly, a 95.1\% reduction in plane spacing has occurred when the maximum compression is applied to the sample (calculated from the mid-plane expansion values). Consequently, when the sample is under compression, the stop-band resonances that arise from sets of planes in these directions will increase in frequency. This band movement is clearly observable in figures 8.3 and 8.4.

At the maximum compression of 77.8\%, the frequency shifts of each stop-band, in reduced units, were calculated to be approximately 0.072, 0.039 and 0.177 for the \([01\bar{1}]\), \([00\bar{1}]\) and \([10\bar{1}]\) bands, respectively, from the TM and TE polarised data. Although the plane spacings in the \([00\bar{1}]\) and \([01\bar{1}]\) directions expand at the same rates, the difference
in the initial and final spacings within a unit cell of each case is 0.437 mm and 0.617 mm, respectively. The slightly larger expansion of the [01¯1] compared to the [00¯1] band accounts for the relative difference in frequency shift between the two. However, the compression produces a much larger frequency shift of the [10¯1] band.

The difference in response of the TE and TM data is unclear at the higher analysed frequencies, due to the high absorption of the material used and also the presence of stop-bands that appear close together in frequency. The use of theoretical modelling of an approximated analogous set-up will uncover the stop-band behaviour at these high frequencies and follows in the next section.

Not only do the frequencies of each stop-band change upon compression of the gyroid array, but also the stop-band widths become narrower when a compression is made to the array. As the sample is comprised of air and a rubber material that are independently connected, compressing the sample results in the displacement of air within the volume occupied by the array. Consequently the compression of the gyroid structure results in the increase of its material volume fraction. As a direct result of increasing the material volume fraction, the stop-band widths are expected to become narrower, as is observed experimentally. It is possible to approximate the average volume taken up by the array when under the maximum compression of 20 mm by considering the maximum and minimum expansions that occur, presented in figure 8.5, and representing this as an average, uniform expansion. This results in an array volume of 637.5 mm³, with the original volume being 729 mm³. This reduction in volume consequently displaces the air within the system to produce a higher material volume fraction of \( \phi_s = 0.46 \) in comparison to the \( \phi_s = 0.4 \) present in the original, uncompressed array. In the following section, a theoretical analysis of the change in band-width by changing the material volume fraction was also undertaken in a similar manner to that performed in section 7.5.1 of chapter 7. In addition to this, theoretical data obtained from a comparable theoretical set-up is presented. The results in this section can therefore be compared to theoretically determined data and electric field plots in order to verify the origin of the [10¯1] and [10¯1] stop-bands. A clearer stop-band response may also be gained by theoretically analysing a structure with fewer unit cells in the depth of the array, allowing for the determination of higher frequency stop-band behaviour when under compression.

8.5 Theoretical modelling

Theoretical modelling was undertaken on a similar gyroid structure to the physical model, comprising the same initial lattice constant, filling fraction and refractive indices, using the FEM method outlined in section 4.8. The exact compression conditions
Figure 8.7: The theoretically-determined transmitted magnitude data, obtained using TM linearly polarised incident radiation, displaying the stop-bands associated with the compliant gyroid photonic crystal structure when under compression. The structure has an initial material volume fraction of \( \phi_s = 0.4 \) and lattice constant of 9 \( \text{mm} \), just as with the physical model. The structure was compressed to (a) 100%, (b) 94.4%, (c) 88.9%, (d) 83.3% and (e) 77.8% of its original size. The expansion values used in the models were selected to be the maximum expansions measured experimentally and were assumed to be uniform. The theoretical models were designed with 5 unit cells along the normally incident transmission line of the array and were repeated as an infinite array in both other dimensions. Each plot is represented in the reduced frequency regime, normalised by the uncompressed lattice constant.
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Figure 8.8: The theoretically-determined transmitted magnitude data, obtained using TE linearly polarised incident radiation, displaying the stop-bands associated with the compliant gyroid photonic crystal structure. The structure has an initial material volume fraction of $\phi_s = 0.4$ and lattice constant of 9 mm just as with the physical model. The structure was compressed to (a) 100%, (b) 94.4%, (c) 88.9%, (d) 83.3% and (e) 77.8% of its original size. The expansion values used in the models were selected to be the maximum expansions measured experimentally and were assumed to be uniform. The theoretical models were designed with 5 unit cells along the normally incident transmission line of the array and was repeated as an infinite array in both other dimensions. Each plot is represented in the reduced frequency regime, normalised by the uncompressed lattice constant.
that occur in the experiment can not be matched in the theoretical model, therefore an approximation of the experimental set-up was made. Due to the complexity of the gyroid structure, and the consequently large number of elements used in the model’s meshing process, a 10 unit-cell-deep model requires large amounts of processing power. In order to overcome this obstacle, the model geometry was approximated by comprising 5 unit cells in the depth of the array, namely in the direction of normally incident radiation. This 5 unit-cell-deep array was repeated with master-slave boundaries in orthogonal directions. In doing this, the band-widths of each stop-band are likely to differ slightly to that observed in the experimental data, as outlined in section 8.4. However, by reducing the number of unit cells present in the depth of the array, the transmission response becomes more comparable to the corresponding reflection response of the gyroid structure at each compressed distance. This offers a great benefit to the analysis of the stop-band response and movement resulting from the compliant gyroid under compression, particularly when analysing the stop-band response at higher frequencies, previously obscured by absorption in the experimental data.

The use of master-slave boundaries in the model also results in the requirement of fewer mesh elements than would be necessary for explicitly defining the finite array in the model. In order to fully represent the graded expansion in the $\hat{y} - \hat{z}$ plane across the $\hat{x}$ direction, caused by the edge effects from friction at the compression plate boundaries, the whole array would need to be explicitly defined in the model and master-slave boundaries could therefore not be used. This would also require an extremely large amount of processing power. Therefore, the models were assumed to expand uniformly in the $\hat{y} - \hat{z}$ plane along the $\hat{x}$ direction. The extent of expansion was chosen to be the maximum expansion measured in the experiment, as previously described by figure 8.5. This value was chosen as it lies in the centre of the sample, where the majority of the incident beam power is concentrated.

Presented in figures 8.7 and 8.8 are the theoretically calculated transmission magnitude data, displaying the stop-band behaviour of the compressed gyroid array using TM and TE incident radiation, respectively. The data presented in figure (a) of each data set were obtained from the uncompressed array and the data presented in figures (b), (c), (d) and (e) of each data set were obtained from arrays that were compressed to 94.4%, 88.9%, 83.3% and 77.8% of its original size, respectively. The differences between the theoretically modelled and the experimentally collected data can be explained by the approximations that were used in order to construct the theoretical models. The differences in the values of transmitted magnitude between the experimental and theoretical data can be explained by the difference in the number of unit cells present in the depth of the array in each case. Fewer unit cells were used in the models and so any radiation that is permitted to propagate through the array experiences less absorption than for
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the experimental case, which uses double the number of unit cells. Consequently, a
higher percentage of light is transmitted outside of the stop-band frequency ranges in
the theoretical models. The widths of the stop-bands also differ slightly due to the
additional disorder brought about by the graded expansion, or ‘bowing’, that occurs in
the experimental set-up and is not present in the theoretical models. As a result, the
widths of the experimentally determined stop-bands are expected to be slightly larger
than the corresponding theoretically determined stop-band widths. Upon compression,
the change in material volume fraction will also differ slightly between the experimental
and theoretical case, due to the uniform expansion approximation that was applied to
the theoretical models. In order to assess the expected change in stop-band width,
the material volume fraction of a gyroid comprised of air and a material with a permittivity of \( \epsilon = 2.85 + 0.15i \) was systematically varied from \( 0.26 \leq \phi_s \leq 0.74 \) and
theoretically modelled. Figure 8.9 presents the calculated transmitted magnitude from
this theoretical modelling at normal incidence. Figure 8.9(a) shows that the stop-band
width changes in a similar manner to that observed in section 7.5.1 of chapter 7, due
to the similar refractive indices used in both cases. Figure 8.9(b) shows the line plots
obtained from the models using three different filling fractions. These material volume
fractions are estimates of the initial uncompressed structure, \( \phi_s = 0.4 \), the material
volume fraction of the structure after the largest modelled compression is made in the
theoretical models, \( \phi_s = 0.43 \), and the material volume fraction of the structure after
the largest compression is made in the experiment, \( \phi_s = 0.46 \). The full-width half-
maximum values of each transmission curve were calculated to be 0.264, 0.252 and
0.234, in reduced frequency units, for material volume fractions of \( \phi_s = 0.4 \), \( \phi_s = 0.43 \)
and \( \phi_s = 0.46 \), respectively. Therefore showing that, not only do the stop-band widths
change upon compression but also that, the stop band-widths are expected to be re-
duced by a smaller amount in the model than for the experimental case. Figures 8.9(a)
and (b) also show that, at the final maximum compression, the frequency position of
the stop-bands is also likely to differ slightly between the modelled and experimentally
determined data.

The stop-band movement that is observed upon compression in the theoretical
data is comparable to that observed in the experimental data with respect to the red-
and blue-shifting that occurs and also with respect to the frequency changes of
each stop-band that result upon compression. At the maximum compression of 77.8%,
the frequency shifts, in reduced units, of each of the stop-bands were calculated to be
approximately 0.057, 0.033 and 0.165 for the \([01\bar{1}]\), \([00\bar{1}]\) and \([10\bar{1}]\) bands, respectively, in
both the TM and TE polarised data. In each case these were found to be slightly smaller
shifts than were measured from the experimental data. This difference is likely to arise
from the difference in filling fractions and plane spacings between the experimental and
Figure 8.9: (a) The theoretically modelled transmitted magnitude data obtained at normal incidence from a series of gyroid arrays with systematically varied filling fractions. The material volume fraction of a gyroid array comprising the same materials as that used in the experimental and theoretical models was varied from $0.26 \leq \phi_s \leq 0.74$. (b) Line plots displaying the theoretically-determined transmitted magnitude at filling fractions of $\phi_s = 0.4$, $\phi_s = 0.43$ and $\phi_s = 0.46$. The values correspond to the material volume fractions of the initial uncompressed array, the theoretically modelled array at maximum compression and an estimate of that of the physical model used in the experiment at maximum compression, respectively.

In order to verify the origin of the blue-shifting band that is observed in both the experimental and theoretical data, time-averaged electric field plots were calculated from theoretical models at the upper frequency band-edge of the [10¯1] stop-band. Figure 8.10 displays such a field plot when a compression of 10 mm, or 88.9%, was made to the sample and TE light was incident to the array. The periodicity of electric field in the [10¯1] direction is identifiable in figure 8.10. The band edges of the [10¯1] stop-bands transmit relatively low magnitudes, and so are not the same as the 100% transmission expected from an ideal photonic crystal possessing no absorption. For this reason, the 'standing waves' that form at the band-edges of this stop-band are not perfectly transmitting. As a result, the configuration of electric fields within the gyroid array, presented in figures 8.10(a) and (b), shows higher intensities towards the top surface of the array compared to the base of the array. However, the direction of electric field periodicity present in these electric field plots is clearly observable and confirms the origin of the [10¯1] stop-band.

As a result of this confirmation it is possible to conclude that, for a gyroid array, the stop-band frequency position of the [00¯1] band and the crossing frequency of the [10¯1], [10¯1], [01¯1] and [0¯1¯1] bands offer a unique band separation behaviour when under com-
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Figure 8.10: The theoretically-determined time-averaged electric fields present in the gyroid photonic crystal at the upper edge of the \([10\bar{1}]\) band across the \(\hat{x} - \hat{z}\) plane within the structure. (a) Time-averaged electric fields plotted across the central \(\hat{x} - \hat{z}\) plane through the array. (b) Time-averaged electric fields plotted only in the dielectric regions of the 3D array. In this case only the top three unit cells of the structure are shown. The data was obtained when a compression of 10 mm, or 88.9%, was made to the structure, using TE linearly polarised incident radiation. A periodicity of electric field in the \([10\bar{1}]\) direction is clearly identifiable.
pression in the [\bar{1}00] direction. Due to the geometry possessed by the gyroid structure, the frequency of the [001] and [10\bar{1}] stop-bands overlap at normal incidence and produce similar dispersion behaviour. The orientations of the set of effective planes that give rise to each of these stop-bands are distinctly different. Therefore the application of a compression, and the resulting concurrent expansions defined in this chapter, increases the plane spacing in the [00\bar{1}] direction and decreases the plane spacing in the [\bar{1}0\bar{1}] direction. This consequently separates the two stop-bands into two clearly identifiable independent bands, as one is red-shifted and one is blue-shifted. This can only occur for structures that possess a [00\bar{1}] stop-band at the crossing point of the [10\bar{1}], [\bar{1}0\bar{1}], [01\bar{1}] and [0\bar{1}\bar{1}] bands when uncompressed. In chapter 5, two other minimal surface structures that possess an interconnecting framework were characterised. The [10\bar{1}], [\bar{1}0\bar{1}], [01\bar{1}] and [0\bar{1}\bar{1}] crossing frequencies of the P- and D-surface photonic crystal structures both occur at different frequencies to the [00\bar{1}] stop-band at normal incidence and so a compression is not required to individually resolve these bands. Therefore the [\bar{1}0\bar{1}] and [00\bar{1}] bands are present at different frequencies when uncompressed and as a result this behaviour will not be observed for the P- and D-surface structures.

8.6 Conclusions

A compliant 3D gyroid photonic crystal array has been characterised electromagnetically when under compression. The compression, made in the [\bar{1}00] direction, results in a symmetric expansion in all directions orthogonal to this compression. The set of compressions were made on a sample that had an initial material volume fraction of $\phi_s = 0.4$ and initial unit cell length of 9 mm. The sample was chosen to be a $10 \times 10 \times 10$ unit cell array in order to reduce asymmetric bowing under compression and also so that the incident face of the sample was always larger than the full-width half-maximum of the Gaussian incident beam, when under compression. A series of compressions were made to the sample and it was probed with both TE and TM microwave radiation. The sample was rotated over a polar angle range of $-45 \leq \theta \leq 45$ as defined by figures 4.5 and 8.2. The expansions in the [010] and [001] directions were measured and the maximum expansion was determined to be along the centre of the sample, where the maximum power of the emitted microwave beam is incident upon it. The expansion was found to be slightly smaller at the edges of the sample, where they were adjacent to the plates used to compress the sample, due to friction effects. The theoretical modelling that was used as an approximated analogy of the experimental set-up assumed that the structure expanded uniformly, at a rate determined by the maximum observed expansion value, determined experimentally. The experimental and theoretical data displayed similar band movement behaviour with regards to
the respective frequency shifts of each stop-band, resulting from the compression and simultaneous expansions that were made to the sample. The stop-bands were found both to red- and blue-shift. Whilst the red-shifting bands reduced in frequency at comparable rates, the blue-shifting band produced a larger increase in frequency over the same analysed compression distances. The novel part of this work was revealed upon the reduction in frequency of the [00\bar{1}] band and the increase in frequency of the [10\bar{1}] band. At normal incidence, when no compression is made, the [00\bar{1}] and [10\bar{1}] bands overlap in frequency and similar dispersion behaviour is observed. This can be seen clearly in the data presented in chapter 5, by figures 5.12 and 5.13. The geometry of the gyroid is such that the [10\bar{1}], [\bar{1}0\bar{1}], [01\bar{1}] and [0\bar{1}\bar{1}] band crossing point occurs at the same frequency as the [00\bar{1}] band, when no compression is made to the array. The orientations of the sets of effective planes that give rise to the [00\bar{1}] and [10\bar{1}] stop-bands are distinctly different. The application of a compression in the [\bar{1}00] direction, and the resulting concurrent expansion in all orthogonal directions, increases the plane spacing in the [00\bar{1}] and decreases the plane spacing in the [\bar{1}0\bar{1}] direction. As a result, the previously overlapping bands separate as the [00\bar{1}] band is red-shifted and the [10\bar{1}] band is blue-shifted. This is particularly novel and can only occur for a specific geometry that gives rise to a [00\bar{1}] stop-band at the crossing point of the [10\bar{1}], [\bar{1}0\bar{1}], [01\bar{1}] and [0\bar{1}\bar{1}] bands that require a compression in order to be individually resolved. Only upon changing the dimensions of the array in the direction perpendicular to the incident beam is it possible to uncover the two bands as separate entities in the transmission response by inducing diverging stop-band frequencies.
Chapter 9

Conclusions

In this thesis the investigation of many naturally occurring photonic crystal structures have been described. These include optical structures found on the wings/elytra of butterflies and beetles and also scaled-up replicas of triply periodic bicontinuous cubic structures designed for the microwave regime. The opening chapters of this thesis provide a background to structural colour in nature. The brief overview of structural colour in nature presented in chapter 2 reviews a selection of previously published work in the field regarding some birds, butterflies, beetles, aquatic life and flora that produce colour through the interaction of light with periodic structures. The sheer diversity of structural geometries and optical effects that are produced by these organisms was highlighted. In chapter 3 the theory regarding the mathematical and physical concepts that are used to determine the origin of structural colour and photonic band-gaps was described in detail. Additionally, the basic electromagnetic theory regarding reflection and transmission at a dielectric interface was introduced and constructive and destructive interference was discussed. Later in chapter 3 photonic crystal theory was outlined. This theory includes the mathematical description of electric field configurations within mixed dielectric media. Alongside each part of the mathematical description, an equivalent physical description was also given in order to provide the full interpretation of how electric field behaviour in periodic media gives rise to a photonic band-gap. In this chapter rotational symmetry and full-and-complete band-gaps were discussed with respect to quasi-ordered photonic crystals. This new breed of photonic crystal geometries can possess high orders of rotational symmetry, unobtainable by more ordered, highly-periodic structures. The experimental and theoretical methods that were employed to probe and characterise the naturally occurring photonic crystals under investigation in this thesis were reviewed in chapter 4. These methods were used alongside the mathematical and physical concepts outlined in chapter 3 in order to fully characterise the electromagnetic response of a selection of naturally occurring photonic
9. Conclusions

9.1 Triply periodic bicontinuous cubic photonic crystals

In chapter 5 the experimental and theoretical electromagnetic characterisations of the three basic bicontinuous cubic structures, forming from the P-, D- and G-surfaces, in the microwave regime were described. The scalability of Maxwell’s equations, outlined in chapter 3, allows the characterisation of optical structures to be performed on scaled-up replicas when probed with longer incident wavelengths. The fabrication process was undertaken on the millimetre scale and used dielectric materials that possessed similar permittivities to the naturally occurring optical counterparts found in butterflies and beetles. The resulting experimentally and theoretically determined dispersion graphs were plotted over an extensive polar and azimuthal angle range. The experimental and theoretical data match each other extremely well. This allowed the physical origin of each photonic stop-band to be determined by electric field profiles obtained by theoretical modelling alongside geometric theoretical analysis. The structural origin of each stop-band was attributed to the various sets of, and orientations of, periodic planes that are present at various directions in each structure, identified by their respective directional Miller indices. In doing this the photonic responses of these naturally occurring photonic crystal structures were electromagnetically characterised. Each structure under characterisation displayed a difference in transmission response when probed with linearly polarised TE radiation when compared to TM radiation. 2D photonic crystal structures are known to possess very different photonic band-gap responses when linearly polarised TM and TE radiation is incident upon them. However, this effect is often reduced in 3D photonic crystal structures. The difference in stop-band width when TE and TM polarisation is incident upon each structure under investigation in chapter 5 arises from the electric field configurations of standing waves set up at frequencies that form the edges of each stop-band. The boundary conditions outlined in chapter 3 must be observed when electric and magnetic fields cross a boundary. In addition to this the geometry of a structure can appear extremely different when an electric field is rotated by 90° and travelling in the same direction. Consequently different incident polarisations result in different concentration factors for a particular standing wave configuration in a particular geometry. This arises due to the relative orientation of electric field with respect to the dielectric struts that form the structure. In addition to the general geometry of the structure, the connected nature of the structures under investigation is also important in determining the difference in the band-width response of each stop-band when using different incident linear polarisations [20]. The theoretical modelling undertaken on each structure allowed electric
field concentration values to be calculated for the frequencies at the upper and lower band-edges of each transmission stop-band. The relative differences in concentration factors between different incident polarisations confirmed the hypothesis that incident linear polarisation and the geometry of a connected 3D photonic crystal structure can lead to different stop-band widths for certain stop-bands. In addition to this, linear polarisation conversion within the chiral gyroid structure was found to occur along the [111] directions but not along the [00̅1] direction. The absence of polarisation conversion along the [00̅1] chiral axis was attributed to the $4_1$ symmetry of the gyroid unit cell along this direction.

Not only was the origin of this difference in linear polarisation response identified, but also each set of data from each structure was compared and contrasted with each other. In a publication by Michielsen et al. [9], \textit{P. sesostris} was identified to possess the G-surface and in chapter 6 of this thesis the weevil \textit{Eupholus magnificus} was identified to contain the D-surface structure. Consequently, these characterisations of bicontinuous cubic photonic crystals were also used in the further analysis of the weevil \textit{Eupholus magnificus} and the butterfly \textit{Parides sesostris} in later chapters.

### 9.2 \textit{Eupholus magnificus}

In chapter 6 the investigation into the structural mechanisms that provide the weevil \textit{Eupholus magnificus} with its coloured patterns was described. \textit{E. magnificus} is adorned with striped bands of two different coloured hues, yellow and blue, on its elytra. The colour from each band was found to be produced by photonic structures as opposed to pigment. However, the coloured hues of each band appear constant when viewed over different angles, much like a pigmented colour. As beetles can not generally create the chemical pigments necessary to produce these coloured hues [29], they must adapt photonic crystals in order to achieve angle-independent coloured patterns. In using structural colour to do this, the resultant colour is intensely vivid, something only achievable by structural colour. \textit{E. magnificus} was discovered to produce the two coloured hues on its elytra by the use of two different 3D photonic geometries. The photonic structures that produce each coloured hue were discovered to be contained within tiny 50 $\mu$m sized scales positioned on the exoskeleton of the weevil. Each individual scale is not visible by an observer, however, the ensemble additive optical effect produced by many scales in each coloured band is observable. The materials available to the weevil to fabricate a photonic structure are limited, and so the high refractive index contrast necessary to produce a non-iridescent ordered 3D photonic crystal structure is unobtainable. The weevil overcomes this fabrication issue by implementing two different methods; one for each elytral coloured hue. To produce the yellow elytral stripes...
the weevil adapts an ordered photonic crystal geometry, that would normally be iridescent, into a domained configuration. This produces an angle-independent coloured appearance to an observer. Each domain possesses the same ordered photonic crystal geometry but is arranged at a different orientation with respect to its neighbouring domains. The 3D photonic crystal structure present in these scales was determined to be based on the FCC Bravais lattice symmetry. Image analysis was performed on SEMs of the periodic structure and were found to resemble the diamond structure produced by the D-surface. Each intra-scale structural domain will reflect a different wavelength due to the iridescent nature of the single photonic crystal used, but the ensemble effect produced from many domains results in the production of an average, angle-independent coloured appearance. In this case, the weevil is using the iridescent nature of the photonic crystal to its advantage by means of domaining. The blue elytral band produces its angle-independent coloured appearance by a contrasting quasi-ordered structural approach. The quasi-ordered structure was found to produce an angle-independent coloured hue directly, without the need for domaining. The quantification of a level of disorder, quasi-order and order in the form of Voronoi analysis and entropy calculations has provided the first step to a possible benchmark for the difference between disorder and quasi-order; something that is not currently well known.

*E. magnificus* uses two contrasting methods to produce an angle-independent coloured appearance involving two types of structure with differing structural order. The D-surface that creates the interconnecting diamond network in the scales from the yellow elytral band naturally forms from a surface of minimum energy by a self-assembly process. The structure that forms the quasi-ordered photonic system is also an interconnecting network of two materials, much like the D-surface structure, and so may be self-assembled in a similar way. As they are present concurrently on the same weevil, it may be that the same fabrication methods are used by the weevil to produce both structures. The processes that lead to the introduction of an element of disorder into an ordered, periodic, naturally occurring structure may be of interest with respect to the fabrication of highly isotropic quasi-ordered photonic structures with 12-fold rotational symmetry like that discovered in *E. magnificus*. The discovery and identification of the structures present on this weevil may inspire such control in quasi-ordered fabrication methods once the mechanism behind the formation of naturally occurring weevil photonic crystal structures is known.

### 9.3 *Parides sesostris*

In chapter 7 the gyroid photonic crystal structure found in the butterfly *Parides sesostris* was investigated. *P. sesostris* encases its 3D gyroid photonic crystal structure
inside individual scales present on the dorsal side of its wings. It also uses a domaining approach to its intra-scale ordered 3D photonic crystal structure arrangement in order to suppress iridescence. In addition to this, the surface structure present on the top-side of each scale aids this suppression of iridescence by introducing light into each domain at a diffracted angle, consequently resulting in highly diffuse scattering from these scales. This was shown directly through scatterometry. The 3D gyroid photonic crystal structure that exists within each scale was identified by Michielsen and Stavenga in 2008 [9] and the filling fraction and lattice constant was also identified. This chapter examined how these parameters are optimised within the butterfly scales in order to aid iridescence suppression. By systematically varying the filling fraction of the gyroid structure and modelling its electromagnetic response, the filling fraction used by *P. sesostris* was determined to be optimised to produce a maximised reflected band-width. A large reflected band-width is a feature usually associated with complete band-gaps and, therefore, angle-independent reflections of a specific frequency range. Generally this property is achieved by using a large refractive index contrast, something that is inaccessible to *P. sesostris*. The extremes that *P. sesostris* goes to in order to suppress iridescence by the use of the more obvious embellishments within and upon each individual scale indicates that an optimised filling fraction is likely to also be a design feature that *P. sesostris* has evolved, alongside the more drastic features, in order to suppress iridescence from its wing scales. This fundamental feature has been previously overlooked as a method used by *P. sesostris* in order to suppress iridescence from its scales.

The electromagnetic characterisation of the gyroid photonic crystal structure presented in section 5.6 was performed on a structure that closely mimicked that found within the scales of *P. sesostris*. Subsequently, the dispersion graphs obtained by experimental and theoretical methods closely represent the response of the *P. sesostris* gyroid. In chapter 7, *P. sesostris* was shown to produce a maximised reflected band-width by optimising the filling fraction of the gyroid photonic crystal used. The extent of overlap of frequencies in the characterised stop-bands produced by the gyroid replica, over the 45° polar angle range, will be reduced or may not be present at all if any other filling fraction was used by *P. sesostris*. This is a further indicator that *P. sesostris* uses a highly tuned filling fraction in order to enhance its reflected bandwidth, consequently minimising the angle-dependence of its reflected colour [13].

In addition to this optimisation, the number of unit cells present in the depth of each scale has also been shown to be optimised, both for producing a reflection response with the maximum possible intensity and also for minimising the prevalence of additional Fabry-Perot type resonances that occur within the structure. Namely, the number of unit cells in the depth of *P. sesostris* wing scales is the minimum number of unit cells
necessary to produce a reflectance response that approximates that of a semi-infinite array.

The work performed in chapter 5 can also be related to the colour reflections that emanate from the intra-scale gyroid photonic crystal found on \textit{P. sesostris}. The lattice constant identified by Michielsen et al. [9] was applied to the reduced frequency axes in the dispersion graphs presented in section 5.6. From this it was determined that, in addition to green wavelengths, a large proportion of the colour reflections from this structure was in the blue wavelength range of the visible spectrum. In recent literature it was discovered that a membrane covering each scale on \textit{P. sesostris} contained a pigment which selectively absorbs blue wavelengths [164], resulting in a highly tuned green colour reflection from these scales.

9.4 The tunable gyroid

In chapter 8, the effect of compressing a compliant gyroid, comprising air and a rubber polymer with refractive index of $n = 1.69$, was investigated. The compression was made to the gyroid in a direction perpendicular to the incident beam. A symmetric expansion was found to result in all directions perpendicular to the compression direction. Due to the unique configuration of stop-bands present in the gyroid dispersion graphs, the stop-band movement that resulted was found to be particularly novel. Upon compression, the resulting stop-band response was found to be a combination of red- and blue-shifting bands. The $[10\bar{1}]$ and $[00\bar{1}]$ bands were found to exhibit similar dispersion behaviour when light is incident upon the sample at increasing polar angles. In addition to this the geometry of the gyroid structure is such that the crossing frequency of the $[10\bar{1}]$, $[10\bar{1}]$, $[01\bar{1}]$ and $[0\bar{1}1]$ bands overlap the resonant stop-band frequency of the $[00\bar{1}]$ band at normal incidence. Consequently, the $[00\bar{1}]$ and $[10\bar{1}]/[10\bar{1}]$ bands appear as one stop-band when no compression is made to the array. As the compression, and the concurrent orthogonal expansion, is applied to the sample the $[10\bar{1}]$ and $[00\bar{1}]$ bands separate as they are blue- and red-shifted, respectively, and each band becomes individually resolvable. This response can only occur for structures that possess a $[00\bar{1}]$ stop-band at the crossing point of the $[10\bar{1}]$, $[10\bar{1}]$, $[01\bar{1}]$ and $[0\bar{1}1]$ bands when uncompressed. This stop-band arrangement was only found to occur for the gyroid structure out of the three bicontinuous cubic structures characterised in chapter 5.
9.5 Future work

9.5.1 Compliant structures

The compliant nature of the gyroid structure analysed in chapter 8 allows the entire structure to be deformed. The analysis described in chapter 8 was performed on a gyroid array under compression, conducted with radiation incident perpendicular to the direction of compression. Alterations to the compression mechanism will allow for the characterisation to be undertaken with incident radiation parallel to the direction of compression. The device used to conduct the experiments in section 8 has been modified to permit a larger percentage of microwave radiation to be transmitted through the compression plates. The modifications made to the device include the removal of a large proportion of the tufnol material used in its construction and its replacement with wood where necessary. As wood is relatively transparent to microwaves, this should allow the electromagnetic characterisation in the direction of compression to be undertaken.

In order to limit the amount of absorption present within the sample, the number of unit cells in the line of transmission through the sample can be reduced. This may uncover additional experimentally determined stop-band features previously undetectable at higher frequencies and aid comparative theoretical analysis. However, the addition of asymmetric bowing that may occur due to this size reduction may require adding additional parameters to the theoretical model that are not feasible due to the amount of processing power needed.

In addition to a compression, it is possible to apply further deformations to the gyroid array in the form of a shear or a torsional force. This would result in altering the electromagnetic response of the gyroid in a different manner to that already observed by applying a one dimensional compression. In particular, twisting the gyroid structure will alter the chiral symmetry of the gyroid and so may alter the circular polarisation and circular dichroism effects already observed from a similar gyroid structure [69]. In addition to this a torsional force will also drastically alter the linear polarisation conversion effects that are observable from the chiral structure and shown in chapter 5 of this thesis. In particular, the $4_1$ chiral axis does not show evidence of polarisation conversion due to its symmetry. By altering the twist of the $4_1$ chiral axis, strong polarisation conversion of the [001] stop-band, and others, may be observed.

9.5.2 The double gyroid

The double gyroid is a tricontinuous cubic structure comprising two gyroids, intertwined with one another by applying a reflection inversion and rotation to one component
Figure 9.1: A double gyroid structure fabricated for the microwave regime. The light and dark structures are single gyroid structures comprised of a solid polymer and air. A reflection inversion and rotation of the light gyroid results in the geometry of the dark gyroid. The interconnection of the two structures results in the production of the double gyroid structure presented here. Scale bar: 1 cm.

Figure 9.2: A view perpendicular to a single face of the double gyroid structure. Each individual gyroid that forms the double gyroid structure is free to move independently. The translation of one gyroid while the other remains stationary is possible with this structure. This is highlighted by the two extreme translations, (a) and (c), with the intermediate equilibrium stage depicted in (b). Scale bars: 1 cm.
gyroid. A double gyroid structure suitable for analysis in the microwave regime has been fabricated with the stereolithography method outlined in section 4.6.1 and is presented in figures 9.1 and 9.2. The double gyroid is an achiral structure due to the opposing chiral handedness of the two component gyroids from which it is formed. Achirality results in the suppression of circularly polarised light effects including the dichroism effects present in the single gyroid [129]. Preliminary modelling data has been taken on a double gyroid with lattice constant $a = 1$ cm using TM polarised incident light and is presented in figure 9.3. The material volume fraction of the double gyroid was chosen to be $\phi_s = 0.394$, comprising two gyroid structures with filling fractions values of $\phi_s = 0.197$, or value of $t$ in equation 5.5 being $t = -0.9$, for each. Initial inspection of figure 9.3 shows the same general stop-band features as was observed for the single gyroid with a slightly smaller band-width up to the reduced frequency value of approximately 1. The introduction of solid material into the air gaps of a single gyroid is likely to change the concentration factor of each stop band and so a difference in band-width between the response of the single and double gyroid is expected. The double gyroid consists of two solid gyroids in air, and so are free to move with respect to one another as presented in figure 9.2. Figures 9.2(a) and (c) show the two extremes obtainable by laterally displacing an individual gyroid component within this structure. Figure 9.2(b) displays the structure at an intermediate equilibrium stage, with no lateral displacement. Altering the displacement between individual gyroids provides an additional parameter that may be altered and electromagnetically characterised. The band-widths of each stop-band are expected to change due to the
change in concentration factor that a lateral displacement of one component gyroid will induce. In addition to this, the displacement of a single gyroid with respect to another may also result in the change of effective plane spacings and so some stop-band frequencies may also change due to this. This dynamic structure can be investigated by using linear and circular incident polarisation when altering the displacement of a component gyroid within the structure.

9.5.3 Circular polarisation

In the microwave regime, it is possible to obtain circularly polarised light from linear polarisations by use of a birefringent lens alongside a source that emits linearly polarised radiation. By perturbing a component of linearly polarised light by a quarter wavelength, circularly polarised light can be obtained. This can only be performed over a narrow frequency band and so broadband horns will be replaced with several narrow band horns accompanied by the relevant birefringent lenses. In using several sets of narrow-band horns in this manner, a cumulative broadband response can be obtained. This set-up may be utilised in order to characterise the chiral gyroid structure and the achiral double gyroid using circularly polarised incident radiation. The gyroid has been identified to possess circular dichroism properties, particularly from the [100] 41 chiral axis. In particular, it is possible to characterise the deformable and dynamic gyroid and double gyroid structures using circularly polarised incident radiation. From this it is expected that a gyroid that is under a torsional or compressive force will experience a frequency shift in its reflection response due to the change in periodicity along the chiral axes. In addition to this, new chiral axes may be generated by applying a torsional force to a particular geometry. This may consequently induce additional circular polarisation-dependent band-gap responses. The synthetic fabrication of analogous structures suitable for probing in the optical regime are currently limited by the resolution of the equipment. In performing these measurements, it is possible to extensively characterise the analogous optical structures and their electromagnetic responses when under deformation upon which linearly and circularly polarised light is incident.

9.6 Publications

9.6.1 Papers

• C. Pouya, D.G. Stavenga & P. Vukusic, (2011) Discovery of ordered and quasi-ordered photonic crystal structures in the scales of the beetle *Eupholus magnificus*, Optics Express, 19, 11355.
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- C. Pouya & P. Vukusic, (2012) Electromagnetic characterization of millimetre-scale replicas of the gyroid photonic crystal found in the butterfly *Parides sesostris*, Royal Society Interface Focus. Published online ahead of print.

9.6.2 Presentations


- Poster presentation: C. Pouya, Ordered and quasi-ordered 3-Dimensional photonic crystals in the weevil *Eupholus magnificus*, BIOOPTICS 1st annual review, Harvard University, USA, November 2010.

- Oral presentation: C. Pouya, Electromagnetic characterisation of millimetre scale replicas of the gyroid photonic crystal found in the butterfly *Parides sesostris* in the microwave regime, Geometry of Interfaces, Primosten, Croatia, October 2011

- Poster presentation: C. Pouya, Electromagnetic characterization of millimetre-scale replicas of the gyroid photonic crystal found in the butterfly *Parides sesostris*, BIOOPTICS 2nd annual review, Georgia Technology Institute, Atlanta, December 2011.
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