Photonic Band Gaps and Local Self-Uniformity: New Perspectives on Disordered Optical Media

by

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A thesis submitted in partial fulfillment for the degree of Doctor of Philosophy

in the Advanced Technology Institute and Department of Physics Faculty of Engineering and Physical Sciences

January 2017
Declaration of Authorship

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Date: 10/01/2017
Simple connections between structure and optical response empower us with essential intuition to engineer complex optical functionalities. In this thesis, I study photonic crystals, quasicrystals and amorphous materials to quantify the structural properties that give rise to photonic band gaps (PBGs). Along the way, I develop two novel perspectives on the optical analysis of arbitrarily-structured media: generalised photonic band structure and local self-uniformity (LSU). Generalised photonic band structures reproduce the Bloch-wave band structure of photonic crystals but, crucially, also yield naturally unfolded complete dispersion relations for aperiodic materials. Using generalised band structures, I demonstrate that the overall form of a material’s dispersion relation is determined by the non-zero momentum transfers of its structure factor. I observe in great detail the fractal-like PBG spectra of a pair of Penrose photonic quasicrystals. Here, I demonstrate that, in most cases, the Penrose PBGs form through a mechanism of Bragg scattering-induced standing wave formation. The fundamental gap of each structure, however, is attributed to spatially localised scattering resonances. I also fabricate and characterise hyperuniform gold metasurfaces. Fluorescence emission characterisation reveals a statistically isotropic distribution of momentum states within the light cone; this property is shown to result from the metasurface structure factor. In the second part of this thesis I introduce LSU as a continuous measure of the extent to which a network possesses an optimal PBG-forming structure. Specifically, LSU measures the geometrical and topological similarities of the local vertex environments in a network of uniform valency. I demonstrate that both known optimal photonic crystal structures and disordered PBG-forming networks possess significant LSU. Further, I produce the first known designs of amorphous gyroid networks. Amorphous gyroids possess significant LSU and can exhibit a sizeable complete PBG; these PBGs are validated experimentally by performing microwave transmission experiments on centimetre-scale alumina prototypes ($\varepsilon_r = 9.5 \pm 0.3$ at 22 GHz). Using ensembles of both amorphous gyroids and planar hyperuniform networks, I demonstrate the striking correlation between LSU and PBG-forming ability. I rationalise the success of LSU by advancing a picture of photonic tight binding in high index connected networks. This picture explains the origin of PBGs in both ordered and disordered connected networks, and suggests why the diamond architecture possesses the largest known PBG. To conclude, I explore the possibility that amorphous gyroids exist in the wing scales of butterflies. I reveal that the microstructure in the scales of Pseudolycaena marsyas possesses substantial amorphous gyroid character and demonstrate that the butterfly’s reflectance spectrum can be effectively reproduced by amorphous gyroid microstructures.
Research Outcomes


British patent application no. 1601838.4. Inventors: Sellers, S. R. & Florescu, M. Filed in the name of the University of Surrey. Patent covers amorphous gyroids and their use in optical applications.
Foremost, I am tremendously grateful to my supervisor Marian Florescu. Marian has been the fundamental enabler of this project in a variety of ways: in the very beginning, he secured funding for my studies at short notice; he has worked tirelessly to secure quality computing hardware for our research group; his door was always open and he was prepared to spend his own time in bringing me up to speed. Most importantly, Marian steered the direction of the research without dictating it, and had sufficient confidence in me to let me explore my own personal interests. I am most grateful to have been given this freedom; without it, this project would not have been so rewarding, and the research quality would have suffered accordingly.

There are many others from within the ATI that deserve my thanks. From the teaching staff, I owe Vlad Stolojan for his time, skills and indefinite use of his SEM stub holder. Without Vlad, I would have no butterfly micrographs and would never have discovered the useful tools of the microstructural studies unit. Similarly, I thank David Cox for taking the time to help me on the SEM, and for providing sage wisdom regarding sample preparation; I would never have thought to pick up single butterfly scales with a one-bristle paintbrush by myself. Further, I thank Peter Aaen who assisted with acquiring my funding, and provided much useful advice on project management.

I’m grateful to all my colleagues in the research lab - Tim, Ross, Matt & Joe - for helping me out whenever I needed some instantaneous advice. I’m also thankful to George Gantzounis for stimulating physics chats over coffee. In particular, George has contributed to a number of projects in this thesis. He calculated the density of states plot for the TE Penrose photonic quasicrystal. He also helped to perform FDTD simulations of the gold metasurface experiments.

Looking beyond the ATI, I’m grateful to have had the opportunity to work with collaborators from both King’s College London and San Francisco State University. Michele Gaio, Marta Castro-Lopez and Riccardo Sapienza were key players in the hyperuniform gold metasurfaces work. In particular, Marta was responsible for the nano-fabrication and performed the optical characterisation experiments. Weining Man and Shervin Sahba were very kind to host me in San Francisco for a week. Thanks go to Weining for taking time out of her busy schedule to play around in the lab, and to give me lifts to and from the university. I’m also grateful to Shervin for his assiduous data collection and his tips on worthwhile places to visit in the city. Together, Weining and Shervin were instrumental in performing the microwave characterisation of amorphous gyroid.

Thanks to Keita Matsumoto and Maxwell Barclay of the Natural History Museum, London. Keita is responsible for the wonderful through-focus photographs of the Cyphochilus candidus and Lepidiota stigma specimens; it’s a shame the pictures can’t be bigger, because the tiffs are 70 MB in size and super sharp. Max was very accommodating and it was a pleasure to be exposed to the eccentricities of life as a curator of one of the world greatest collections of our natural heritage. Thanks also go to Laszlo Biró and Zófia Vértesy of the Hungarian Academy of Sciences; they provided the TEM section of a Pseudolycaena marsyas scale, and gave further information concerning their original study. Further thanks are due to: Silvia Vignolini for providing SEM
images of *Cyphochilus* spp. scale cross sections; Miroslav Hejna for his well-written thesis, which was key in developing a robust implementation of the WWW algorithm; and Normand Mousseau for providing us with a 1000-vertex amorphous silicon CRN.

From my fellow scientists, I would also like to single out Uwe Scheithauer of Fraunhofer IKTS, Dresden. Uwe worked very carefully to ensure that the alumina amorphous and single network gyroid models were printed to a high quality. This process took some iteration, and - I’m told - midnight working. Realisation of these structures was very important to me, and I’m glad to have had Uwe on board to make them a reality.

Without this PhD, I would never have met my beautiful girlfriend Navi. She has been there throughout the project and has been with me every step of the way. Thank you Navi for giving me space to think; for putting up with what must have felt like an endless process; for helping me to concentrate when I was unwilling; and for believing in me throughout. I am very glad to finally complete this project; it brings us a step closer to making our future together a reality.

It is immensely clear to me that this project would not have happened without my parents. Indeed, from their perspective, this document has been 26 years in the making. I’m very lucky to have a Mother and Father who are so generous. For as long as I can remember, they have nurtured me both physically and mentally; their role in what academic success I have had cannot be underestimated. Thank you Mum for helping me to cultivate a love of science, and for proof-reading and appreciating this whole document. Thank you Dad for instilling in me an appreciation for words, and the artistry of their ordering; I hope that this shines through herein.
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Abbreviations

BCC  Body Centred Cubic
BCP  Block CoPolymer
BZ   Brillouin Zone
CRN  Continuous Random Network
DOS  Density Of States
EBZ  Extended Brillouin Zone
FCC  Face Centred Cubic
FDTD Finite Difference Time Domain
FEM  Finite Element Method
FFT  Fast Fourrier Transform
FIB  Focussed Ion Beam
HPU  Hyperuniform
LCM  Lithography-based Ceramic Manufacturing
LDOS Local Density Of States
LSU  Local Self-Uniformity
MPB  MIT Photonic Bands
NA   Numerical Aperture
PAD  Photonic Amorphous Diamond
PBC  Periodic Boundary Condition
PBG  Photonic Band Gap
PC   Primitive Cube
PDG  Partially Disordered Gyroid
PML  Perfectly Matched Layer
PMMA Poly Methyl MethAcrylate
PWEM Plane Wave Expansion Method
SAXS Small Angle X-ray Scattering
SEM  Scanning Electron Microscope
SNG  Single Network Gyroid
SP   Shortest Path
Abbreviations

S-SC  Super-SuperCell
TE    Transverse Electric
TEM   Transmission Electron Microscope
TFSF  Total Field Scattered Field
TM    Transverse Magnetic
TSSF  Total Scattering Structure Function
VNA   Vector Network Analyser
WS    Wigner-Seitz
WNN   Wooten-Winer-Weaire
XRD   X-Ray Diffraction
To my parents
Chapter 1

Introduction

“From a long view of the history of mankind - seen from, say, ten thousand years from now -
there can be little doubt that the most significant event of the nineteenth century will be
judged as Maxwell’s discovery of the laws of electrodynamics.”

Classical electromagnetism is one of the great theories of science. Its encapsulation in the
four Maxwell equations was a profound synergy of over a century’s worth of observational and
theoretical physics. In this way, the theory owes as much to Maxwell as it does to each member
of a stellar supporting cast of towering scientific figures; that the theory remains relevant today
is testament to the enduring power of good science.

This thesis contains research at the frontiers of contemporary electromagnetism and, in particu-
lar, its application in materials that may play a key role in next-generation photonic technologies.
The main thrust of the work is to advance the understanding of fundamental physics surrounding
the formation of photonic band gaps. To facilitate this, I develop two major novel perspectives
on electromagnetism in structured media. In the first instance, I formulate the concept of gen-
eralised band diagrams and demonstrate the calculation of complete dispersion relations for both
periodic and aperiodic media. In the second instance, I re-formulate the ideal structural prop-
erties of a photonic band gap material. These properties are summarised in an order measure
- termed local self-uniformity - that can classify arbitrarily-structured networks of fixed valency
by the extent of their locally automorphic character.
1.1 Context

Electronics has changed the way we live. Our ability to manipulate electrical signals at microscopic lengthscales has ushered in an age of information. Personal computing devices, and the communications infrastructure that connects them together, depend on electronic logic performed by nanoscale transistor arrays. The development of these technologies over the past fifty years has been principally enabled by progressive miniaturisation. In 1965, transistor sizes were on the order of 50 $\mu$m; contemporary microcircuits employ transistors that are only 14 nm across. Now, however, further miniaturisation looks set to bring more problems than benefits. These problems include: the fundamental limitations imposed on transistor size by quantum tunnelling; heat build-up due to microcircuit density; and synchronisation issues caused by laggy metallic interconnects.

Industry is increasingly turning to optical technologies to resolve these problems. Hybrid electro-optical devices are expected to form an intermediate stage between current computing architectures and new all-optical or quantum computing paradigms. Specifically, optical interconnects can provide high bandwidth, low-lag connections to facilitate parallelisation between distinct conventional computing units. Such interconnects already exist at the rack level of high performance clusters and are expected to steadily infiltrate the computing architectures themselves.

Beyond computing, all-optical signal processing is a dream of the telecommunications industry. The information age places huge and ever-growing demands on global telecommunications infrastructures. Increased integration of optical components is a key step towards meeting future data capacity requirements.

The field of photonics is concerned with developing the physics, materials and devices that can enable these next-generation optical technologies; put succinctly, it is the science of controlling and manipulating light. In this thesis, I focus in particular on developing and understanding photonic materials that exhibit interesting optical properties as a result of their sub-wavelength structure.

The most striking examples of sub-wavelength structure are related to colouration. For instance, the iridescent colours of a soap bubble are a thin film interference effect. Light is reflected from both the inner and outer surfaces of the soap film. A phase difference exists between these two reflected beams; this difference is determined by the angle of incidence on the film. Different frequencies thus interfere constructively at different observation angles and the bubble appears multi-coloured and iridescent.

Sub-wavelength structures are employed by a wide variety of living creatures as a means of generating colour; these architectures can be a valuable source of ‘bio-inspiration’ for the design and fabrication of photonic devices. Pollia berries, for instance, may inspire the production of sustainable cellulose-based coloured materials for paints and dyes (Figs. 1.1a - d). The scales of Cyphochilus spp. beetles are the most brilliant white of all known low refractive index structures (Fig. 1.1e & f). This colour results from scattering by the disordered network contained within the scales; imitating this network can facilitate the design of ultra-white materials.
In general, the existence of photonic architectures in living creatures is contingent on the structure’s ability to spontaneously assemble itself. Studies of the development of these architectures can inspire next-generation manufacturing techniques in which photonic architectures, under appropriate conditions, can self-assemble.

Self-assembly processes can produce light controlling architectures with a remarkable degree of structural order. For instance, scales of the beetles Lamprocyphus augustus and Entimus imperialis are known to contain a three-dimensional structure in the form of a diamond network (Fig. 1.2a - d). The structure comprises a continuous network of the biopolymer chitin that is arranged and inter-connected like the carbon atoms in a diamond crystal. The structure’s wavelength-scale features preferentially scatter green light, thus lending the beetles their green camouflage. Similarly, the wing scales of numerous Lycaenid and Papilionid butterflies are filled with a chitin network in the form of a single network gyroid crystal; these architectures are responsible for the butterflies’ striking colourations. These naturally occurring diamonds and gyroids have been intensely studied because, when fabricated in high refractive index material, they can possess a complete photonic band gap.

The photonic band gap (PBG) was first proposed nearly thirty years ago as an electromagnetic analogue of the electronic band gap in semi-conductors and insulators. A PBG is a frequency region of the electromagnetic spectrum within which a material, by virtue of its sub-wavelength structure, supports no propagating solutions to the Maxwell equations. Light cannot travel through a PBG material; incident light whose frequency lies within the band gap will be perfectly reflected. Examples of artificial structures which can exhibit a complete photonic band gap include diamonds, single network gyroids, honeycombs, cubic scaffolds and inverse opals (Fig. 1.2e & f).

Periodic structures which support a complete PBG are known as photonic crystals. They were conceived both for their ability to control spontaneous emission and as means of probing the physics of localised states of light.
In the first instance, an emitter placed inside a photonic crystal, and emitting at a frequency within the PBG, cannot radiate; no propagating electromagnetic modes exist into which the emitter can inject photons. Taking this further, the introduction of a single mode into a PBG material can be used to enhance the light-matter interaction. This is typically achieved by creating a structural inhomogeneity inside the photonic crystal about which a defect electromagnetic mode forms. Single defect modes have been successfully used to create high quality factor cavities for lasing and information processing.

In the second instance, photonic crystals were proposed as a means of achieving the Anderson localisation of light. Anderson localisation is a phenomenon in which the propagation of waves through a medium breaks down as a result of structural disorder. The electromagnetic modes of disordered PBG materials are typically, for frequencies around the PBG edge, spatially localised. It is thus possible that sub-diffusional light transport may occur in suitably prepared disordered photonic crystals. Several groups claim to have observed the Anderson localisation of light in three-dimensions; these claims remain controversial and work to observe this elusive wave phenomenon is ongoing. Nevertheless, disordered PBG structures and other random materials have been harnessed to create novel random lasers. Specifically, their localised electromagnetic modes can act as impromptu laser cavities (Fig. 1.3A & B); these random lasers have potential applications in medical treatment, biological sensing and display technologies.

Researchers have since realised that, beyond demonstrating interesting new physics, photonic crystals can empower advanced optical signal processing. To begin, signals must be controllably routed through a photonic crystal component. This routing is enabled by designing a chain of structural defects along some path through the crystal. Specifically, defects are engineered to support electromagnetic cavity modes within the PBG; these cavity modes then couple to form an extended waveguide mode through which a signal can be passed. Functional light-based
devices may then be engineered by interacting waveguides and cavity resonances according to the designer’s vision.

In particular, much research, which is broadly dubbed silicon photonics, is focussed on the realisation of photonic crystal-based devices in planar semi-conductor architectures. Silicon photonic components are thus compatible with existing nano-fabrication paradigms and can be readily integrated into next-generation microcircuits. For instance, on-chip laser architectures may be realised by coupling a gain material to a resonant cavity. Miniature filters can be constructed by using a cavity to modify a signal that is inserted via a waveguide; a channel-drop filter, for example, uses a cavity to split out the signal frequencies for which it is resonant. The introduction of optically non-linear materials adds yet more degrees of control. For instance, a buried InGaAsP layer inside a simple cavity can be used as an all-optical random access memory (RAM) device. The memory functions by illuminating a non-linear cavity with a bias laser; the cavity is then flipped on and off resonance by ‘write’ and ‘reset’ pulses from a control laser.

Photonic crystals are thus a valuable enabling technology in the development of optical components. Recent research has shown, however, that a material does not need to be crystalline in order to possess a complete photonic band gap. Sizeable PBGs are now known to exist in two-dimensional hyperuniform materials, a unique three-dimensional amorphous network, and various quasicrystalline architectures. These materials exhibit both desirable optical characteristics and interesting unexplained behaviours that have caught the attention of the photonics community.
Figure 1.4: Electron micrograph of the mineral decagonite (A) - one of only two known natural quasicrystals and found at a meteor impact site. Diffraction pattern of decagonite (B) showing crystallographically-forbidden 10-fold rotational symmetry. Quantum cascade laser based on a Penrose quasicrystal (C) and associated electric field distribution of a lasing mode (D). Panels A & B reproduced from Bindi et al.\textsuperscript{76}, panels C & D from Vitiello et al.\textsuperscript{77}

Quasicrystals, like crystals, possess long-range structural order and exhibit point-like diffraction patterns. Unlike crystals, however, quasicrystals are aperiodic and their diffraction patterns can display crystallographically-forbidden rotational symmetries\textsuperscript{68,69} (Fig. 1.4A & B). Quasicrystals were a controversial research subject in the years immediately following their discovery\textsuperscript{70}. Now their existence and structure have been accepted, but the circumstances through which natural quasicrystals can form remain unclear\textsuperscript{71}. Importantly, the potential application of quasicrystals in photonics has generated significant interest\textsuperscript{72}.

Quasicrystals exhibit a number of interesting optical properties. Foremost, they typically possess high order average rotational symmetries; their optical properties are thus less dependent on device orientation. Further, quasicrystals have fractal-like reciprocal spaces with features at all intensity scales (Fig. 1.4B); as a result, they exhibit rich interactions with light. Amongst these rich interactions, it has been shown that quasicrystals can support many different complete photonic band gaps at once\textsuperscript{65,73–75}. These PBGs exist at different energy scales and thus may allow the simultaneous processing of light signals with distinctly different frequencies. In the case of Penrose quasicrystals, research has tried to establish how these multiple PBGs form, tentatively linking them to intense features of the Penrose reciprocal space\textsuperscript{74,75}.

The current lack of evidence to explain the origin of the Penrose fractal PBG spectrum illustrates a key theme of research in complex materials: regular theoretical methods cannot always be applied. Many theoretical methods in the analysis of electrons in solids, which have since been adapted to photonics, are contingent on the translational periodicity of space\textsuperscript{78}; these methods, therefore, only make sense when applied in crystalline materials. Photonics thus has excellent
tools for calculating the optical properties of photonic crystals but is significantly limited in its ability to analyse aperiodic systems.

Looking beyond quasicrystals, hyperuniform materials (Fig. 1.5) have recently emerged as a new amorphous state of matter with interesting optical properties. Hyperuniform structures possess reduced density fluctuations at long lengthscales and are characterised by diffraction patterns which are zero in a region around the reciprocal space origin. As a result, they exhibit significant short range structural order but are otherwise disordered. It has been shown that hyperuniform materials are transparent to long wavelength radiation and may be used as random lasers. Most significantly, both two and three-dimensional hyperuniform structures exhibit sizeable photonic band gaps. Because of their disorder, photonic engineers thus have extra freedom to engineer optical cavities and curved waveguides.

The existence of a sizeable PBG in two-dimensional hyperuniform networks cannot be explained in the conventional picture of PBG formation. PBGs are typically viewed as a result of coherent scattering by the lattice planes of a crystal. In this process, which is called the Bragg mechanism, scattering by the crystal’s lattice planes causes, at a critical wavevector, standing waves to form. The energetic interaction between these electromagnetic standing waves and the underlying periodic material distribution causes a spectral gap to open. Hyperuniform materials are disordered and possess no lattice planes. More technically, their reciprocal spaces exhibit no Bragg peaks; they contain only a single isotropic scattering ring that is too diffuse to produce a zero group velocity state.

This problem is mirrored in three-dimensions by the existence of a sizeable, complete PBG in photonic amorphous diamond (PAD). PAD is a disordered network of four-coordinated vertices that is derived from computational models of amorphous silicon. Just like two-dimensional hyperuniform structures, its reciprocal space contains only a single diffuse scattering ring that cannot account for its PBG-forming ability.
Together, the band gaps in PAD and hyperuniform networks demonstrate that current understanding of PBG formation processes is incomplete. This incomplete understanding can be extended to include traditionally well-understood photonic crystal architectures. Specifically, it is known that (nearly) all the known photonic crystals with a large PBG are based on the diamond network\textsuperscript{92} (the exception being single network gyroid which exhibits a comparably large gap). The single largest known PBG is found in a rod-connected diamond network; diamond is thus known as the champion structure. However, it is not understood what property of the diamond structure leads to such a large PBG - I refer to this as the champion structure problem\textsuperscript{92}. Given the fundamental similarities between the PBGs in diamond and photonic amorphous diamond\textsuperscript{61}, a solution to the champion structure problem seems likely to clarify PBG formation mechanisms in aperiodic structures.

1.2 Thesis Overview

The focus of this thesis is to clarify the connection between a material’s structure and its ability to form a complete photonic band gap. I concentrate primarily on PBG formation in aperiodic media, specifically Penrose quasicrystals, hyperuniform materials, and glassy networks. Along the way I develop a number of tools, perspectives and materials, all of which are novel scientific contributions.

In particular, I make significant progress towards formalising the generalised photonic band structure of an arbitrarily-structured material. To achieve this, I resolve the ‘Bloch-character’ of modes by projecting the electric or magnetic field distributions into a plane wave basis; this is referred to as the spectral function method. The spectral function method yields a complete spectral (frequency-momentum) decomposition of a structured medium’s eigenmodes; this decomposition forms a natural generalisation of photonic band structure to aperiodic media. I apply the method to resolve the complete dispersion relations of hyperuniform materials and Penrose quasicrystals. Specifically, I demonstrate that a material’s diffraction pattern exerts a key influence on its dispersion relation through Bragg processes. I further show that several of the PBGs in Penrose quasicrystal-derived materials are a direct result of Bragg processes, but that the fundamental PBG forms through a different mechanism.

In the latter half of the thesis, I clarify the mechanism that is responsible for large PBGs in high refractive index connected networks. By surveying the known types of PBG-supporting architectures, I conclude that vertex symmetry and local structural and topological uniformities are the key properties of materials that exhibit a large PBG. I formulate these observations into a generalised symmetry measure - termed local self-uniformity (LSU) - that classifies networks of fixed valency by the extent of their locally automorphic character. To investigate the connection between LSU and PBGs, I use a simulated annealing protocol to generate the first known amorphous gyroid networks. I find that amorphous gyroids can exhibit a sizeable complete PBG, and that the size of an amorphous gyroid’s PBG is directly linked to the magnitude of its LSU. Then, moving temporarily to the laboratory, I confirm my PBG calculations by fabricating ceramic amorphous gyroid networks and observing their PBGs using a microwave transmission method. To conclude, I show that large PBGs form in connected networks through a process
of generalised resonant scattering and local standing wave formation. I demonstrate this by studying the electromagnetic modes of isolated network units, and argue that these properties are locally preserved when a network is assembled within a photonic tight-binding regime. An understanding of PBG formation through generalised resonant scattering can both explain LSU’s success as a measure of PBG-forming ability and suggest a solution to the champion structure problem.

In the final chapter, I seek to demonstrate that optical-scale amorphous gyroid-like structures exist within the natural world. The observation of such a structure, and the subsequent study of its development, may possibly enable the fabrication of aperiodic complete PBG materials through self-assembly. In particular, I demonstrate that gyroid crystals that include small amounts of topological disorder can account for the observed diffraction patterns of gyroid-containing green hairstreak butterfly scales. Following this, I present a microstructure in the scales of the butterfly *Pseudolycaena marsyas* which exhibits substantial amorphous gyroid character. Subject to certain assumptions, I demonstrate that *P. marsyas*’ reflectance spectrum can be effectively reproduced by amorphous gyroid microstructures.

Briefly, the structure of the thesis is as follows. In **chapter two** I provide an introduction to key concepts in the analysis and modelling of structured materials; I introduce the total scattering structure function, the pair correlation function and the structures of crystals, quasicrystals, glassy networks and hyperuniform materials.

**Chapter three** explores electromagnetism in dielectric media, numerical solution protocols for the Maxwell equations, and the basic physics of the photonic band gap. In particular, I present the current understanding of PBG formation; this comprises the Bragg mechanism in photonic crystals, and the Mie scattering mechanism in planar dielectric cylinder arrays. Following this, I employ finite difference time domain simulations to argue for the existence of a generalised resonant scattering mechanism of PBG formation in planar network architectures.

In **chapter four**, I formulate the spectral function method and apply it to calculate the generalised band structures of various periodic and aperiodic planar architectures. First, I present the band structure of a honeycomb photonic crystal and analyse the Bragg processes involved. I then demonstrate the significant influence of Bragg processes on the generalised band diagrams of hyperuniform materials. Finally I explore the dispersion relations of pair of Penrose quasicrystal architectures. Specifically, I index the Penrose reciprocal space in detail and use spectral functions to identify the Bragg processes that are responsible for the Penrose PBGs.

**Chapter five** explores the impact of reciprocal space engineering on the properties of planar metasurface devices. Hyperuniform gold metasurfaces are fabricated and characterised by light scattering and fluorescence emission. In particular, our experiments show that hyperuniform metasurfaces exhibit directional emission that, through the calculation of generalised band diagrams, is understood to be a result of the major isotropic Bragg process of the metasurface reciprocal space.

**Chapter six** describes the formulation and measurement of local self-uniformity. I explore the different types of PBG-forming architecture in two and three dimensions, arguing that the successful architectures comprise simple vertices that are connected in a network that is locally
uniform in both its geometry and topology. The technical concepts of LSU - \( n \)-trees, spatial similarity and LSU distributions - are all defined, and an algorithm is formulated for measuring the spatial similarity of arbitrarily disordered trees. I present example LSU distributions of honeycomb and diamond networks, both ordered and disordered, to illustrate these concepts.

**Chapter seven** describes the design and characterisation of amorphous gyroid networks and presents evidence that LSU is a successful measure of PBG-forming ability. I describe a modified Wooten-Winer-Weaire algorithm for generating amorphous gyroids. I characterise the geometry, structure factors and LSU distributions of amorphous gyroids. My collaborators and I fabricate prototype amorphous gyroid components in aluminium oxide and demonstrate their PBGs using a microwave transmission method. I then demonstrate the striking correlation between LSU and PBG size in both amorphous gyroid and planar hyperuniform connected networks. I close with an extended discussion of LSU’s efficacy as measure of PBG-forming ability.

In **Chapter eight**, I explore evidence for the possible existence of an amorphous gyroid in butterfly wing scales. I review existing work on colouration in *Papilio nireus* and *Parides sesostris* as case studies in the physics of structural colour. I then present existing X-ray scattering results for *Callophrys rubi*. I model the *C. rubi* scale structure and show that a partially disordered gyroid fits the diffraction results better than a perfectly ordered level-set gyroid. Next I present micrographs of the structure in *Pseudolycaena marsyas* wing scales, highlighting its disordered three-dimensional interconnectivity. By deriving a plausible complex refractive index for the apparent pigmentation of the structure, I show that amorphous gyroid models can effectively account for *P. marsyas*’ blue coloration. Finally, I present an overview of some alternative microstructures in butterfly wing scales and avian feather barbs that exhibit amorphous gyroid character.

In **Chapter nine**, I formulate some conclusions and remark on possible directions for future work.
Chapter 2

Structuring of Matter

The wavelength-scale structure of a material is intimately related to its optical properties. The study and manipulation of structure is therefore a key method for engineering light-controlling architectures. Photonics typically focuses on controlling light with wavelengths between the visible (400 - 700 nm) and microwave (centimetre-scale) regimes. Photonic structures are thus defined by characteristic features which are orders of magnitude larger than the inter-atomic lengthscales of crystals. In this sense, we are typically interested in engineering ‘microstructure’ - structure that is invisible to the naked eye, but is supra-molecular in its scale. Nevertheless, the structure of many photonic band gap materials is identical to, or often inspired by, common atomic structures. It is thus important to remember that, although we may refer to ‘diamond’ or ‘amorphous silicon’ structures, photonic structures exist at much larger lengthscales.

This chapter has two major purposes. Primarily, it serves as an introduction to both the principal structures that have been studied in the context of photonic engineering and the means by which these structures are characterised. Beyond this, the chapter tries to present a holistic picture of structure, portraying different structural classes not as fundamentally unrelated, but rather as points or regions in a continuous spectrum of order and disorder. This continuous evolution from order to disorder is most clearly observed in a structure’s reciprocal space.

To begin, I devote some considerable effort to introducing the reciprocal space and grounding it in reality by linking it to a structure’s diffraction pattern. I introduce also the radial distribution function as an alternative direct space means of characterising structural order. Following this, I explore the three major classes of photonic structure in a sequence of decreasing structural order. I begin by defining translationally periodic structures - crystals - and exploring their direct space and reciprocal space properties. Following this, I explore quasicrystals; these are materials which possess many of the same properties as crystals but exhibit no translational periodicity. In particular, I focus on quasicrystals derived from Penrose tilings. In the final section, I discuss amorphous materials, outlining two types of structure - continuous random networks and hyperuniform point patterns - that have been widely applied to photonic engineering.
2.1 Characterising Order and Disorder

2.1.1 The Total Scattering Structure Function

Light passing through a material may be scattered by regions of charge density, producing scattered wavefronts which interfere to generate intricate diffraction patterns. The study of these diffraction patterns, and the back-calculation of the structures that produce them, is known as crystallography.

In the case of atomic-scale structures, crystallographers perform X-ray scattering experiments to probe the angstrom-scale structure of the material. X-ray diffraction (XRD) methods can also be applied to supra-molecular-scale structures so long as fine scattering angles may be resolved. Small angle X-ray scattering (SAXS) can thus be used to probe the nature of structures with nanometre and micrometre-scale characteristics. In this section, I consider an arbitrarily structured weakly-scattering material and derive the form of its diffraction pattern. This is a key result which plays a major role in probing the structure of arbitrarily complex materials.

Consider an elastic scattering event by a single scattering centre. Incident light with wavevector $k_i$ is scattered onto outgoing light with wavevector $k_s$ through an angle $2\theta$. The momentum transfer vector $q$ is defined as

$$q = k_s - k_i. \quad (2.1)$$

This definition is illustrated in Fig. 2.1A. Using the elasticity of the scattering process (ie - that $|k_i| = |k_s| = k$) we see that the modulus of the momentum transfer vector is

$$q = 2k \sin \theta. \quad (2.2)$$

We now consider scattering from a complex distribution of air and another arbitrary material. Let the distribution be described by an aperture function $\Sigma(r)$ which represents the relative scattering strength at each point. For our purposes, $\Sigma$ need only qualitatively represent the

\[ \text{Figure 2.1: Definition of the momentum transfer vector } q \text{ (A), Schematic diagram of scattering from two volume elements } dV \text{ and } dV' \text{ from which the phase difference between the two scattered wavefronts can be determined (B).} \]
relative scattering strength, taking for instance values of zero and unity for air and material respectively. All that matters is that $\Sigma$ accurately reflects the underlying material distribution.

We illuminate the distribution with a plane wave, wavevector $k_i$, and observe the scattering in the farfield. Each infinitesimal volume element of the distribution scatters light as a point scattering centre. We assume that scattering strength is independent of the scattering angle $\theta$. We also assume that the distribution is weakly scattering such that the field which drives scattering from each volume element is just the incident plane wave; this is the first Born approximation.

Let two volume elements $dV$ and $dV'$ be located at positions $r$ and $r'$ respectively (Fig. 2.1B). We observe the scattered radiation in the farfield such that light detected from $dV$ and $dV'$ shares the same wavevector $k_s$. There exists a phase difference between wavefronts arriving from $dV$ and $dV'$; we write this phase difference $\Delta \phi$ as

$$\Delta \phi = (r' - r) \cdot k_i + (r - r') \cdot k_s = (r - r') \cdot q. \quad (2.3)$$

The total wave amplitude $A$ at the observation point is proportional to the sum over the complex amplitudes of all scattered beams. We integrate over all possible choices of the volume element $dV'$, modulating each element by the aperture function at that point. We therefore write $A$ as

$$A(q) = \int \Sigma(r') e^{-i(r-r') \cdot q} dV'$$

$$= e^{-i r \cdot q} \int \Sigma(r') e^{i r' \cdot q} dV'. \quad (2.4)$$

The observed amplitude is thus proportional to the three-dimensional Fourier transform of the aperture function. The intensity $S$ we detect is proportional to the square modulus of the amplitude. Thus we observe a distribution of intensity

$$S(q) = A(q) A(q)^* = \left| \int \Sigma(r') e^{i r' \cdot q} dV' \right|^2. \quad (2.5)$$

As formulated, the scattered intensity is a function of the momentum transfer vector $q$. The $d$-dimensional domain spanned by $q$ on which $S(q)$ is defined is called reciprocal space. Note that reciprocal space is not a constructed quantity; it is a ‘momentum transfer’ space of which we observe a projection when we perform a diffraction experiment.

$S(q)$ is an important quantity which fully describes the observed diffraction pattern of a material. It is often called the structure factor in the fields of optics and amorphous materials. It should be noted, however, that ‘structure factor’ has a different meaning for crystallographers; it refers to the Fourier transform of the material distribution within a crystal’s unit cell. $S(q)$ is best termed the total scattering structure function (TSSF); this reflects its relevance in describing
diffraction from both ordered and disordered structures. In this thesis, the terms TSSF and structure factor are used interchangeably and are understood to refer to $S(q)$ as defined by Eqn. 2.5.

The TSSF can be interpreted as the square magnitude of the coefficients of the aperture function when projected into a continuous plane wave basis. The TSSF will thus naturally reflect the presence of structural correlations within the scattering distribution. As we shall see, these correlations can result from perfect translational periodicities, as in a crystal, or characteristic structuring on a local length-scale, as in aperiodic and amorphous media. The TSSF is thus an invaluable probe of the structural order, or lack of it, in a distribution of material.

Often it is useful to present the TSSF as a one-dimensional function of the magnitude of the momentum transfer. The TSSF may be azimuthally averaged by summing its intensity in a shell of radius $q$ and dividing by the surface area of the shell. For a two-dimensional crystal, we define the azimuthal average of $S(q)$ as

$$
S(q) = \frac{1}{2\pi q} \int_0^{2\pi} S(q) \ qd\phi,
$$

where $qd\phi$ is the line element in a 2D polar coordinate system in reciprocal space. For a three-dimensional crystal, the azimuthal average of the TSSF is defined as

$$
S(q) = \frac{1}{4\pi q^2} \int_0^{2\pi} \int_0^\pi S(q) \ q^2 \sin\theta d\theta d\phi,
$$

where $q^2 \sin\theta d\theta d\phi$ is the surface area element of a spherical polar coordinate system.

### 2.1.2 The Pair Distribution Function

The pair distribution (or pair correlation) function of an ensemble of particles characterises the variation in local density as a function of distance from a reference particle. It measures the likelihood of finding a particle at this distance relative to the ideal gas case.

We consider an array of $N$ point particles with positions $\{r_i\}$. For a single particle $j$, the number of particles at radial distance $r$ from $j$ may be written as

$$
n_j(r) = \sum_{i \neq j}^N \delta(r - r_{ij}),
$$

where $r_{ij} = |r_i - r_j|$ and $\delta$ is the Dirac delta. We can construct a measure of the average number of particles at radial distance $r$ from any given particle by averaging $n_j(r)$ over all choices of particle $j$. We write this as

$$
n(r) = \frac{1}{N} \sum_j^N n_j(r) = \frac{1}{N} \sum_j^N \sum_{i \neq j}^N \delta(r - r_{ij}).
$$
For a non-interacting ideal gas-type system, the expected number of particles in a spherical shell of thickness $\Delta r$ is $4\pi r^2 \Delta r \rho_0$, where $\rho_0$ is average number density of the system. The pair distribution function $g_2(r)$ is then defined as

$$ g_2(r) = \frac{n(r)}{4\pi r^2 \rho_0} \quad (2.10) $$

where $n(r)$ is normalised to its ideal gas value. A $g_2(r)$ value of unity suggests an absence of structural correlations; the number of particles with separation $r$ is exactly equal to an unstructured ideal gas. Strong fluctuations of $g_2(r)$ about unity reveal the existence of positional correlations between particles; values greater than and less than unity show that the corresponding inter-particle separation is favoured and suppressed respectively.

Fig. 2.2A illustrates the concept underpinning the pair distribution function. We choose a particle $j$ (shaded black, centre) and construct sampling windows as spherical shells, of radius $r$, centred on $j$. For each $r$ we count the number of nearby particles $n_j(r)$ that fall within the sampling window. The histogram that results from averaging this process over all choices of $j$, and subsequent normalisation to the expected value of an uncorrelated structure, is the pair distribution function.

**Figure 2.2:** Illustration of the radial distribution function $g_2(r)$. $g_2(r)$ measures the expected number of particles in a shell of radius $r$ from a given particle (A), normalised to the ideal gas value (panel reproduced from Ref. [93]). $g_2(r)$ for a theoretical ideal gas is a constant (B). In a crystal, $g_2(r)$ is strongly peaked according to the discrete inter-particle separations (C). A typical amorphous material has short range peaks which decay to the ideal gas value at large $r$ (D).
Figs. 2.2B-D show a number of example pair distribution functions. Panel B shows the ideal gas case, for which the expected number of particles in a shell is everywhere $4\pi r^2 \Delta r \rho_0$. The function is constant, showing no enhancement or suppression of the expected value as a function of distance. Panel C shows an extreme opposite; the pair distribution function of a perfect crystal, which possesses positional order at all length scales, comprises an infinite set of sharp peaks. Panel D shows the pair distribution function of an amorphous material - an intermediate state between translationally periodic order and uncorrelated disorder. The distinct peaks at small $r$ reveal the presence of coordination shells and short-range positional order. At large $r$, the function tends to unity showing that the position of distant atoms is uncorrelated.

The pair distribution function is thus a useful tool for characterising the extent to which an arrangement of points is structurally ordered. Peaks in $g_2(r)$ are associated with preferential inter-particle separations and are indicative of order. The magnitudes, breadths and decay of these peaks with increasing $r$ describe the strength of this order and the lengthscales over which it exists. However, $g_2(r)$ has limited utility as a tool for determining the type of structural order that is present in a point pattern; this complex structural information is lost by its projection into a single dimension.

2.2 Translationally Periodic Media

Structurally periodic materials are ubiquitous. Innumerable simple chemical compounds and elemental metals adopt crystalline atomic structures and periodic tilings of the plane are often right beneath our feet. In this section, I review the characteristics of translationally periodic structures. First, crystals are defined as a combination of a Bravais lattice and a motif. To illustrate, the structure of the honeycomb network is presented. The structure factor of a crystal is its reciprocal lattice - a dual lattice in momentum transfer space; this is illustrated for honeycomb. Key features of reciprocal space, in particular the Brillouin zone, are discussed.

2.2.1 Lattices and Motifs

Periodic materials possess a set of translational symmetries. Within an infinite crystal there exist special vectors, termed lattice vectors, along which the structure can be translated onto an exact copy of itself. Points which are separated by a lattice vector are thus rendered identical and indistinguishable. The process of building a crystal is then reduced to choosing a set of indistinguishable points, as defined by the lattice vectors, and then decorating each point with an arbitrarily complex distribution of material, termed the crystal’s motif.

Consider a $d$-dimensional crystal. We express its lattice vectors in the lattice basis - a set of $d$ linearly independent vectors which span the space under consideration. The basis vectors are labelled $a_i$, where $i = 1, 2...d$.

The Bravais lattice is defined as the set of points which are accessible by traversing the basis vectors in integer combinations. In 3 dimensions for instance, the points $\mathbf{r}_{lmn} = la_1 + ma_2 + na_3$
for integers \( l, m \) and \( n \) describe a Bravais lattice. We use the symbol \( \mathbf{R} \) to refer to a general lattice vector - that is any vector in the Bravais lattice.

It is possible to prove through group theoretical considerations that there exist 14 distinguishable Bravais lattices in three dimensions \(^{78}\). Their distinguishability arises from the relative orientations and magnitudes of their basis vectors. The finite set of possible Bravais lattices restricts the symmetries that are possible within a crystal. It is, for instance, forbidden for a crystal to possess a ten-fold rotational symmetry; no corresponding Bravais lattice exists and thus such a structure cannot be periodic in space.

Once we have a lattice, we must specify a motif; this is a set of instructions describing the distribution of material about a single lattice point. Placing a spherical atom at every lattice point constitutes the most simple motif. In this case, the symmetry group of the lattice (the point group) is identical to the overall symmetry of the crystal (the space group).

More generally, lattice points are decorated with arbitrarily complex structures. These decorations need not have the same symmetries as the Bravais lattice. This mixing of symmetries creates many more possible crystal symmetry groups. Overall, a crystal belongs to one of 230 possible space groups and is derived from one of the 14 possible Bravais lattices \(^{78}\).

As a typical example of the combination of a lattice and a motif we consider the structure of a two-dimensional honeycomb. We specify this as:

\[
\begin{align*}
\textbf{Basis vectors} & \quad \textbf{Motif} \\
\mathbf{a}_1 &= a\hat{x} & \text{Place vertices at } 0 \& (\mathbf{a}_1 + \mathbf{a}_2)/3. \\
\mathbf{a}_2 &= a(\hat{x}/2 + \hat{y}\sqrt{3}/2) & \text{Join neighbouring vertices with edges.}
\end{align*}
\]

The underlying lattice of the honeycomb is the so-called triangular lattice (Fig. 2.3A). It is described by the basis vectors of Eqn. 2.11. The lattice is decorated by placing points (vertices) at every lattice point, and every lattice point plus \((\mathbf{a}_1 + \mathbf{a}_2)/3\). Each of these vertices is then connected to its three nearest neighbour vertices by a rectangular slab of material. The resulting honeycomb network is shown in Fig. 2.3B.
Often we specify a crystal’s motif as its primitive unit cell. The primitive unit cell is a volume that can be stacked to perfectly fill space. The cell is filled with an arbitrarily complex distribution of material and the crystal is built by placing a copy of it at every lattice point. For a given crystal there exists a continuum of possible choices of primitive unit cell depending on how it is defined relative to the lattice points. By definition the primitive cell contains a single lattice point. In the case of honeycomb, the parallelogram formed by the crystal’s basis vectors (Fig. 2.3A, purple) shares each corner with four other such parallelograms. It thus contains a single lattice point and represents a possible primitive cell of the crystal. In general, the parallelopiped of any crystal’s basis vectors is a primitive cell.

We often use another type of unit cell - the Wigner-Seitz (WS) cell - to visualise a crystal’s geometry. The WS cell is defined around some chosen lattice point \( a \). It is the volume of space for which any point therein is closer to \( a \) than any other lattice points in the crystal. This volume, being derived from a Bravais lattice, can tile space perfectly and contains exactly one lattice point. The shape of the WS cell and the distribution of material within it reveal the overall symmetry of the lattice and the local symmetries of the crystal respectively. It is thus a very useful tool for visualising crystalline distributions of matter.

The WS cells of the triangular lattice and honeycomb networks are shown in orange in Fig. 2.3. Prior to decoration with the motif (A), the cell is an empty hexagon which possesses all the symmetries of the underlying triangular lattice. The WS cell of the honeycomb network contains a three-fold vertex of material (B). It is clear that this cell, and the honeycomb network by extension, is less symmetric than the triangular lattice from which it is derived. The WS cell has exactly one half of the rotational and one half of the mirror symmetries of a bare hexagon.

Using the concepts of the lattice and unit cell, we may express the aperture function of any general crystalline distribution as

\[
\Sigma(r) = \sigma(r) \ast \sum_i \delta(r - R_i) = \sum_i \sigma(r - R_i), \tag{2.12}
\]

where \( \sigma(r) \) is the aperture function of the primitive unit cell and \( \ast \) denotes a convolution operation. Convolution with a comb of Dirac deltas - one placed at each lattice point - produces a periodic array of primitive cells.

### 2.2.2 The Reciprocal Lattice

The structure factor of a general crystalline distribution may be calculated by Fourier transformation of Eqn. 2.12.
Structuring of Matter

\begin{equation}
S(q) = \left| \mathcal{F}[\sigma(r) \ast \sum_i \delta(r - R_i)] \right|^2 \\
= \left| \mathcal{F}[\sigma(r)] \right|^2 \left| \mathcal{F}[\sum_i \delta(r - R_i)] \right|^2 \\
= \left| \sigma(q) \right|^2 \left| \sum_i \delta(q - G_i) \right|^2,
\end{equation}

where \( \mathcal{F} \) is a Fourier transform operator and we made use of the convolution theorem. \( \sigma(q) \) is the Fourier transform of the unit cell’s aperture function; this is the *crystallographic* structure factor, and distinct from the TSSF. In the final line, we use the result that the Fourier transform of the direct lattice is itself a Bravais lattice with lattice vectors \( G_i \); this is proved in Appendix A. This new lattice is termed the reciprocal lattice. It is constructed with the reciprocal lattice basis vectors \( b_i \), where

\begin{align}
b_1 &= 2\pi \frac{a_2 \times a_3}{a_1 \cdot a_2 \times a_3}, \\
b_2 &= 2\pi \frac{a_3 \times a_1}{a_1 \cdot a_2 \times a_3}, \\
b_3 &= 2\pi \frac{a_1 \times a_2}{a_1 \cdot a_2 \times a_3}.
\end{align}

We use the symbol \( G \) to represent an arbitrary lattice point in the reciprocal lattice; it is expressed in the reciprocal lattice basis as

\begin{equation}
G = hb_1 + kb_2 + lb_3,
\end{equation}

where \( h, k \) and \( l \) are integers. Importantly, it can be shown that the point group of the reciprocal lattice is identical to the point group of the direct lattice - both lattices possess the same symmetries. Eqn. 2.13 demonstrates that the TSSF of a periodic structure is zero for all momentum transfer vectors that are not equal to a reciprocal lattice vector \( (q \neq G) \). The diffraction pattern is thus a lattice of bright spots. The brightness of these spots is modulated according to the square modulus of the crystallographic structure factor at the corresponding momentum transfer \( q \).

To illustrate this, we calculate the TSSF of the honeycomb network. Specifically we take the fast Fourier transform (FFT) of the aperture function described by the material distribution of Fig. 2.3B. This TSSF is shown in Fig. 2.4A.

The light spots of the honeycomb diffraction pattern correspond to the points of the reciprocal lattice. The basis vectors of the reciprocal lattice may be calculated via Eqn. 2.14. In the case of a 2D lattice, we set \( a_3 = \hat{z} \) and ignore this artificial extra dimension. The reciprocal basis vectors of a honeycomb are thus

\begin{align}
b_1 &= \frac{2\pi}{a} \left[ \hat{x} - \frac{1}{\sqrt{3}} \hat{y} \right], \\
b_2 &= \frac{2\pi}{a} \left[ \frac{2}{\sqrt{3}} \hat{y} \right].
\end{align}
These basis vectors are shown in red in Fig. 2.4A. It transpires that they describe a triangular lattice; the triangular lattice is thus its own reciprocal space dual. It should be noted that not all Bravais lattices possess this property; the triangular lattice, along with a few other lattices, is a special case.

The Wigner-Seitz cell of the reciprocal lattice, shown as an orange hexagon in Fig. 2.4A, is an extremely important construction. It is the basic unit of the reciprocal lattice and is called the first Brillouin zone. Any arbitrary vector in reciprocal space may be mapped into the first Brillouin zone by addition of a $G$ vector.

The azimuthally averaged TSSF (according to Eqn. 2.6) is presented in Fig. 2.4B. It shows intense peaks where the magnitude of the momentum transfer is equal to a $G$ vector. Note that peaks have different total intensities as a result of their modulation by the crystallographic structure factor (Eqn. 2.13).

### 2.2.3 Connection with Structural Order - Bragg’s Law

Reciprocal lattice points correspond to the possible momenta that a crystal can impart to a photon. These scattering events can be connected to coherent reflection from planes in the crystal via the Bragg formulation of diffraction.

We can depict a lattice as a set of stacked atomic planes with an inter-plane separation $d$ (Fig. 2.5A). The structure is illuminated with a plane wave of wavevector $k_i$ and we consider the outgoing state $k_s$ to be a result of specular reflection from the lattice planes. The beam is incident at an inclination of $\theta$ to the planes and is thus scattered through an angle $2\theta$. 
Consider a bright spot in the structure’s diffraction pattern. This spot arises when the reflections from the lattice planes interfere constructively. This condition is met when the path difference between reflected beams from adjacent planes is a single wavelength $\lambda$. At this bright spot, we may state that

$$\lambda = 2d \sin \theta.$$  \hfill (2.17)

Using the relationship between the momentum transfer and the scattering angle (Eqn. 2.2), we may replace $\sin \theta$ to observe that

$$q = G = \frac{2\pi}{d},$$  \hfill (2.18)

where $q$ is equal to a reciprocal lattice vector because the bright spot is a point in the reciprocal lattice. $G$ vectors can therefore be associated with scattering from a particular set of lattice planes defined by the inter-planar spacing $d$. Further, we note that, because the lattice plane bisects the scattering angle, $q$ is normal to the lattice planes under consideration (Fig. 2.5A). A $G$ vector is therefore normal to its associated lattice planes, and its magnitude is trivially related to the interplanar spacing.

The specific planes in the direct lattice associated with a $G$ vector can be determined through Miller indices. We specify a particular $G_{hkl}$ by its coefficients $h$, $k$ and $l$ in the reciprocal lattice basis (Eqn. 2.15). The plane defined by the points

$$p_1 = \frac{1}{h}a_1$$
$$p_2 = \frac{1}{k}a_2$$
$$p_3 = \frac{1}{l}a_3$$

\hfill (2.19)

**Figure 2.5:** Bragg’s law and Bragg planes. An incident plane wave $k_i$ is specularly reflected onto a state $k_s$ by a stack of lattice planes (A); reciprocal lattice points are observed when the scattering angle satisfies $\lambda = 2d \sin \theta$. Honeycomb lattice illustrating a number of Bragg planes (B), specifically (100) (green), (110) (red) and (120) (orange).
is the associated Miller plane; it is typically represented by its Miller indices \((hkl)\). It is easy to show that the normal to an \((hkl)\) plane is parallel to \(G_{hkl}\). Once all Miller planes of a specific type are identified, the spacing between the planes is then given by \(2\pi/|G_{hkl}|\).

A number of Miller planes are shown for the honeycomb structure in Fig. 2.5B and the \(G\) vectors associated with these planes are labelled in Fig. 2.4A. Planes are defined by their intercepts with the lattice basis vectors according to Eqn. 2.19. (110) planes (red) thus pass through the corners of the primitive unit cell. (100) planes (green) are parallel to \(a_2\); the position of their intercept with \(a_2\) is undefined and intersection does not occur. In honeycomb, the (110) and (100) planes are equivalent under the symmetry operations of the point group.

Planes with higher order Miller indices tend to be more closely spaced. (120) planes (orange) have a small inter-planar spacing. Note also that the distance between lattice points in a (120) plane is larger than for a lower order plane. The existence of the (120) plane is thus contingent on the presence of well-defined structural order over a lengthscale of 2 unit cells. An ideal honeycomb is perfectly ordered on all length scales and thus the observation of high order Bragg reflections will be limited only by our ability to experimentally probe large scattering angles. Disordered crystals, however, are not perfectly periodic. High-order Miller planes, contingent on structural order at long lengthscales, become poorly defined and it may not be possible to observe these peaks in the diffraction pattern.

Fundamentally, the TSSFs of crystals reveal their well-defined structural order as a result of periodicity. The existence of \(G_{hkl}\) peaks in the diffraction pattern for both low and high-order Miller planes shows that the structure contains strong structural correlations at all length scales.
2.3 Quasiperiodic Media

The theoretical framework of crystallography was laid out in the 19th century. The assumption of translational periodicity allowed all possible crystal symmetries to be theoretically determined and catalogued. As an experimental science, crystallography was truly born at the turn of the century. The discovery of ultra-short wavelength electromagnetic radiation - X-rays - allowed diffraction experiments to be conducted at the atomic and molecular level.

It was well known that, as translationally periodic media, the farfield diffraction patterns of crystals should comprise distinct intense spots of light. Once this basic periodicity had been confirmed, crystallographers focussed on determining the fundamental atomic content of a structure's unit cell\textsuperscript{95}. The formulation of Bragg’s law, the crystallographic structure factor and other fundamental tenets of crystallographic analysis led to to the successful characterisation of the structure of countless simple materials.

Over several decades, crystallography developed into a mature and well-understood field. The determination of the structure of dauntingly complex biochemical molecules, such as vitamin B12, insulin and DNA, crowned a golden era for the discipline\textsuperscript{96}. It was certainly possible to believe that the nature of regularly structured, as opposed to amorphous, matter had been thoroughly understood. All that remained, it seemed, was to continue cataloguing the countless natural and artificial structures that were still to be characterised.

In 1984, however, Shectman et al.\textsuperscript{68} observed a fascinating and crystallographically impossible diffraction pattern. The sample, a single crystal of a rapidly cooled Al-Mn alloy, displayed all the characteristics of the icosahedral symmetry group. It was well known that such symmetries were forbidden by the crystallographic restriction theorem and the discovery, which was inexplicable by conventional means, caused a serious stir.

The new finding was leapt upon by Levine and Steinhardt\textsuperscript{69}, condensed matter theorists who were familiar with recent mathematical interest in aperiodic tilings of the plane. The study of aperiodic tilings, foremost amongst them the Penrose tiling, revealed a great menagerie of possible aperiodic but nonetheless highly-ordered structures\textsuperscript{97,98}. It was known that aperiodic tilings could be generated by projection of a hyperlattice into a lower dimensional subspace, and that the diffraction pattern of the resulting structure should comprise a discrete set of densely-packed Bragg-like peaks. With the periodicity requirement relaxed, aperiodic tilings could display crystallographically forbidden rotational symmetries.

The new form of matter was dubbed a ‘quasicrystal’ (short for quasi-crystalline), and the study of quasicrystals was not without controversy. In particular, the mechanism through which a quasicrystal might form was hotly debated. It seemed that the formation of long range deterministic order in a quasicrystal was incompatible with the necessarily local process of crystallisation from a melt. Eventually Jeong and Steinhardt\textsuperscript{99} were able to show that the Penrose tiling, amongst other possible aperiodic structures, uniquely maximises the density of a specific atomic cluster. Suitably chosen quasicrystal formation conditions, in which the Penrose-forming cluster is energetically favoured, should thus lead to formation of a quasicrystal.
Sheetman’s discovery of the first quasicrystal, for which he received a Nobel prize, catalysed much broad and high impact research. In particular, quasicrystals have been observed in a variety of metal alloy systems\textsuperscript{68,100} and natural realisations have been discovered at meteorite impact sites\textsuperscript{71,76}. Quasicrystals have even been observed in medieval Islamic art\textsuperscript{101} and as a nearly-optimal structure in densely packed solid tetrahedra\textsuperscript{102}. Of fundamental interest to this thesis is the study of light propagation in quasicrystal structures. Their Bragg-like total scattering structure functions lend them interesting light scattering properties\textsuperscript{72}. The Penrose structure in particular is known to support multiple distinct photonic band gaps\textsuperscript{67,74,75}, the physical origins of which have not yet been explained.

In the section that follows, some of the basic concepts of quasicrystals are introduced. I focus on the Penrose tiling, discussing its basic geometry and common methods by which aperiodic tilings may be computationally generated. I save the discussion of the optical properties of Penrose structures for Chapter 4.

### 2.3.1 Definition of Quasiperiodicity

Consider the function \( f(x) = \sin(2\pi x) + \sin(2\pi \alpha x) \) where \( \alpha > 1 \) is a constant. If the function is periodic, there exists some region \( 0 \leq x \leq x_0 \) within which both sine waves have completed an integer number of periods. This periodic condition can be written as

\[
2\pi x_0 = 2\pi \alpha x_0 - 2\pi n,
\]

where \( n \) is an integer equal to the difference between the number of complete cycles performed by each sine wave. The condition implies that

\[
x_0 = \frac{n}{\alpha - 1}.
\]

However, it is clear that \( x_0 \) must itself be an integer. This is only possible if \( \alpha \) is a rational number. If \( \alpha \) is irrational then the function never repeats; it is said to be almost periodic. Formally, we say that a function \( f \) is almost periodic if, for each \( \varepsilon > 0 \), there exists a relative dense set of translations \( \{a\} \) such that

\[
|f(x + a_i) - f(x)| < \varepsilon,
\]

where \( a_i \in \{a\}\).\textsuperscript{97} The qualifier ‘relative dense’ means that there is a number \( A_\varepsilon \) such that in each interval of length \( A_\varepsilon \) on the number line there exists a translation \( a \).

It can be proved\textsuperscript{103} that an almost periodic function can be expanded as a Fourier series; we may thus write

\[
f(x) = \sum_n c_n e^{-iG_n x}.
\]
The Fourier spectrum of such a function is thus a countable sum of delta function-like peaks, and this fingerprint can be used as a diagnostic of almost-periodicity. The ideas of almost periodic functions may be generalised to functions of $n$ variables. We say that a function $f(r)$ is quasiperiodic (or incommensurate) if its Fourier transform $f(k)$ may be expressed as

$$f(k) = \sum_{h_1 \ldots h_n} F(h_1 \ldots h_n) \delta(k - h_1 b_1 - \ldots - h_n b_n)$$

(2.24)

where the $n$ vectors $b_i$ form a rationally independent set\(^{97}\). A set of vectors is rationally independent if a linear combination of the member vectors with rational coefficients is zero if and only if all the coefficients are zero. The set of Fourier wavevectors $M^*$ is called a Fourier module of rank $n$. The members of the Fourier module pack reciprocal space densely at all lengthscales. Strictly speaking, quasiperiodic functions are only almost periodic in the limit where the rank of their Fourier module tends to infinity\(^{95}\). For practical purposes, however, quasiperiodicity is much more relevant.

The Fourier transform of a quasicrystal thus comprises a countable set of delta function-like peaks (Eqn. 2.24). The diffraction patterns of quasicrystals therefore possess a striking resemblance to the TSSFs crystals (Eqn. 2.13). In general however, the Fourier module of a $d$-dimensional crystal has rank $d$, while the Fourier module of a $d$-dimensional quasicrystal has rank $> d$. In other words, the reciprocal lattice of a crystal may be indexed by a basis vector set of size equal to the crystal’s dimension. The reciprocal space of a quasicrystal, however, can only be indexed by a basis vector set of size greater than the crystal’s dimension. The reciprocal quasi-lattice is thus described by an over-complete rationally independent basis set and thus comprises a dense set of delta-like peaks that may display crystallographically forbidden symmetries.

### 2.3.2 Penrose Tilings

Numerous shapes, such as hexagons, squares and parallelograms, are known to tile a two-dimensional plane in a periodic way. The tilings they produce can be described within the formalism of crystal structures, and the rotational symmetries they may possess are thus limited. An aperiodic tiling, on the other hand, is an arrangement of tiles that both fills space perfectly and cannot be constructed from a single repeating unit. The most famous example of an aperiodic tiling is the Penrose tiling (Fig. 2.6B). In this section, I introduce the geometry of Penrose tilings, two methods for generating arbitrarily large systems and the nature of the tiling’s TSSF.

Penrose showed that it is possible to produce an aperiodic tiling using a combination of two rhombic prototiles\(^{104}\) (Fig. 2.6A). Both rhombs comprise sides of equal length $d_0$. The ‘fat’ rhomb has internal angles of $108^\circ$ and $72^\circ$ and the ‘skinny’ rhomb angles of $144^\circ$ and $36^\circ$.

To create a Penrose tiling, the prototiles are arranged edge-to-edge subject to a set of tile matching rules. The rhombs are marked with coloured arrows along each edge. Adjacent tile edges must possess arrows of the same colour and orientation. Further, when arranging tiles they may only be rotated in the plane (no out-of-plane flips are allowed). Fig. 2.6B shows
Figure 2.6: The two Penrose prototiles are the ‘fat’ and ‘skinny’ rhomb (A). They may be arranged according to the matching rules to form a Penrose tiling (B). Families of quasi-Bragg planes exist within the structure, of which a selection are overlaid in colour.

an example Penrose tiling arising from the composition of ‘fat’ and ‘skinny’ rhombs. In reality, generation of a tiling by sequential tile addition is not guaranteed to produce a pattern of infinite extent. Specifically, we may reach a point at which further addition of tiles violates the matching rules. As we shall see, there exist several methods for overcoming this problem and generating arbitrarily large Penrose tilings.

The Penrose tiling possesses many interesting properties. Firstly, it is locally isomorphic; every finite pattern inside a circle of radius $R$ is repeated within a circle of radius $2R$. In this way, the Penrose tiling is weakly periodic. More specifically, it has been proved the Penrose tiling is in fact quasiperiodic.

Secondly, Penrose tilings possess a scaling property. The tiling may be deflated by subdivision of the Penrose rhombs into Robinson triangles. The matching rules enforce tile configurations such that the Robinson triangles can then be composed into a different Penrose tiling, produced by a new set of smaller rhombic prototiles. The existence of a deflation operation implies the existence of an equally deterministic inflation operation, in which the existing prototiles are composed into a new set of larger rhombs. A single Penrose tiling is thus governed by a hierarchy of related inflated and deflated structures. This imposes strong constraints on where a single prototile may be placed, and is the reason why sequential tile addition usually generates tilings which cannot be extended infinitely.

2.3.3 Pentagrid Method

Following Penrose’s initial work, Dutch mathematician De Bruijn developed a thorough algebraic theory of the Penrose tiling. This included methods for generating infinitely large Penrose tilings in a finite number of steps. I shall explore two such methods here.
The first method used a so-called ‘pentagrid’ to determine the positions of the Penrose rhombs. We begin with the following observation. Opposite sides of a rhomb are parallel to one another. If we choose a rhomb and a pair of opposite sides, we may form a ribbon by adding rhombs to that pair of opposite sides and then continuing in a similar fashion. Fig. 2.7A shows a number of shaded ribbons propagating through a tiling.

We observe that a single rhomb is uniquely defined as the intersection between two such ribbons. Further, the ribbons, although they oscillate back and forth, appear to be approximately described by straight lines (Fig. 2.7A). The location of the crossing point between lines describing intersecting ribbons lies within the shared rhomb. We imagine that the positions of all rhombs might be predicted by the intersection points of an appropriately constructed collection of lines, each one representing a ribbon.

A pentagrid is just such a collection of lines. A grid is a set of equally spaced parallel lines. A pentagrid comprises five such grids, each rotated by a multiple of $2\pi/5$ with respect to one another. An example pentagrid is shown in Fig. 2.7B. De Bruijn showed that it is possible to associate the four vertices of a rhomb with each grid intersection point, and further that a collection of rhombs constructed in this way satisfies the Penrose tile matching rules. Remarkably, he also showed that every Penrose tiling results from a pentagrid.

Using the pentagrid construction method, it can be shown that there are a finite number of vertex types in a Penrose tiling. These vertices are shown in Fig. 2.8. All vertices in a tiling can be classified as one of the eight types shown, differing only by a rotation in the plane.

**2.3.4 Cut and Project Method**

De Bruijn went on to explore the connection between the pentagrid formulation and the projection of a high-dimensional lattice into a lower dimensional subspace. In particular, he showed that a Penrose tiling may be obtained by intersecting a 5D simple cubic lattice with specific 2D
hyperplanes. This idea forms the basis of the ‘cut and project’ method - a common means of Penrose tile generation. Here I explore a one-dimensional version of the cut and project method to develop an intuition about the process. I then describe the process for generating a Penrose tiling through the projection method.

Consider a 2D square lattice of points with primitive unit cell $\Omega$ (Fig. 2.9A). We choose a direction in the crystal $r_{\parallel}$ - this will form the surface onto which the lattice is projected. The perpendicular direction to the projection surface is labelled $r_{\perp}$. Consider now sliding $\Omega$ along $r_{\parallel}$, maintaining its orientation throughout. We use $\Omega$ as a sampling window; the set of points which fall within the window are connected with a line. Finally we produce a tiling of the subspace $r_{\parallel}$ by projection of the sampled points parallel to $r_{\perp}$. This tiling comprises a chain of intervals of length $a$ and $b$, corresponding to the projections of the horizontal and vertical edges of the unit cell respectively.

In the limit where the length of $r_{\parallel}$ tends to infinity, the ratio of the number of type-$b$ tiles to type-$a$ tiles tends to the gradient of $r_{\parallel}$. Clearly, if the chain is to be periodic this ratio must be a rational number. We may thus generate an aperiodic chain by setting the gradient of $r_{\parallel}$ to be irrational.

To investigate whether the chain is truly quasiperiodic, as defined by Eqn. 2.24, we investigate the properties of its Fourier transform. The transform may be calculated in the higher-dimensional space and then projected into the subspace. Our objective is to calculate the transform of the direct product between a square lattice of delta functions and the extended sampling window (red lines of separation $d$, Fig. 2.9A). The transform of the direct lattice is simply its reciprocal lattice. The transform of the sampling window is of the form $\delta(r_{\parallel})\text{sinc}(r_{\perp}d/2) - a$ sinc function at the origin, oriented along $r_{\perp}$. The transform of the direct product is the convolution of the reciprocal lattice and the sinc function; we thus place a properly oriented sinc function at each reciprocal lattice point. Finally we project this convolution onto the line $r_{\parallel}$. This process is illustrated in Fig. 2.9B.

We note that the Fourier transform of the chain is everywhere zero, except where the sinc functions intersect $r_{\parallel}$. It therefore comprises a set of delta functions of variable intensity. This
A one-dimensional representation of the cut and project method of quasicrystal generation. A quasiperiodic chain may be generated by projecting the points sampled by the window $\Omega$ onto the line $r_\parallel$ (A). The Fourier transform is also calculated by projection (B); we convolve the reciprocal lattice with the transform of the sampling domain, and project onto $r_\parallel$.

proves the quasiperiodicity of the chain as defined by Eqn. 2.24. In the case where the gradient of $r_\parallel$ is chosen to be the golden ratio $\tau = (1 + \sqrt{5})/2$ the resulting quasiperiodic projection is called a Fibonacci chain$^{97}$. The cut and project method is an extremely useful formulation. It is easily generalised to higher-dimensional cases$^{106,108}$ in which it can generate a variety of quasicrystal structures including Penrose tilings, generalised Penrose-like structures and 3D icosahedral structures. The cut and project process for generating a Penrose tiling may be summarised as follows.

Consider a five dimensional cubic hyperlattice. The vertices of the lattice may be represented as integer combinations of the basis vectors $(a_1, a_2, a_3, a_4, a_5) = \{[1, 0, 0, 0, 0], [0, 1, 0, 0, 0], [0, 0, 1, 0, 0], [0, 0, 0, 1, 0], [0, 0, 0, 0, 1]\}$. We split the five-dimensional space into a parallel and perpendicular subspace as before. The parallel subspace is spanned by the two vectors

\begin{align*}
x_1 &= [2, -\sigma, -\tau, -\tau, -\sigma] \\
x_2 &= [0, \tau \beta, \beta, -\beta, -\tau \beta],
\end{align*}

while the three vectors that span the perpendicular subspace may be written as

\begin{align*}
x_3 &= [2, -\tau, -\sigma, -\sigma, -\tau] \\
x_4 &= [0, \beta, -\tau \beta, \tau \beta, -\beta] \\
x_5 &= [\sqrt{2}, \sqrt{2}, \sqrt{2}, \sqrt{2}, \sqrt{2}],
\end{align*}

where $\sigma = 1 - \tau$ and $\beta = \sqrt{3 - \tau}$.$^{108}$ We then define a five-dimensional acceptance window $\Omega$ which corresponds to the primitive unit cell of the hypercubic lattice. The window is scanned continuously throughout the parallel subspace, and the 5D position vector of any lattice point that falls within the window is recorded. The set of lattice points sampled by the window is then
projected into the parallel subspace. To perform this projection, we note that the 5D lattice vectors may each be projected into the plane according to

\[
\begin{align*}
    a_1 &= [2, 0] \\
    a_2 &= [\tau - 1, \tau \beta] \\
    a_3 &= [-\tau, \beta] \\
    a_4 &= [-\tau, -\beta] \\
    a_5 &= [\tau - 1, -\tau \beta].
\end{align*}
\] (2.27)

These 5 vectors then form a rationally independent basis in the plane with which the projection of any 5D lattice point may be expressed.

As described above, the cut and project method can be used to generate perfect aperiodic Penrose tilings. In the computational modelling of disordered structures, however, it is often advantageous to possess complex periodic unit cells. The complex matter distribution described by tiling the large periodic unit can be an excellent approximation to the aperiodic structure of interest. Such large periodic units are typically referred to as supercells.

The cut and project formalism can be implemented ‘approximately’ to generate supercells that resemble true Penrose tilings. The approximation is made by substituting rational values in place of \(\tau\) in the definition of the parallel subspace (Eqn. 2.25). The gradient of the hyperspace cut described by \(x_1\) and \(x_2\) thus becomes rational, and the set of lattice points sampled by \(\Omega\), and by extension the projection of the set into the plane, becomes periodic.

\(\tau\) is typically approximated as the ratio of consecutive terms of the Fibonacci sequence. The sequence of possible \(\tau\) values thus takes the form

\[
\tau \approx \left[ \frac{1}{1}, \frac{2}{1}, \frac{3}{2}, \frac{5}{3}, \frac{8}{5}, \frac{13}{8}, \ldots \right].
\] (2.28)

As the approximate value of \(\tau\) becomes more accurate, the period with which the tiling repeats in the parallel subspace increases. The size of the supercell, as measured by the total number of Penrose vertices contained, thus also increases in parallel. Further, it is known that the periodic approximate tiling generated by any particular rational approximation of \(\tau\) contains exactly two points at which the Penrose tile matching rules are violated\(^{67}\). These violations are necessary to force an artificial periodicity in the parallel subspace, but are otherwise undesirable. Higher order periodic approximate supercells are thus favoured, as these minimise the density of tiling defects.

2.3.5 Penrose Structure Factor

As in the two-dimensional case, it is possible to calculate analytically the TSSF of a Penrose tiling using the cut and project method\(^{109}\). The process is instructional and reveals the vectors of the Penrose Fourier module, but is otherwise cumbersome and applicable only to tilings comprising
delta functions at the vertices. Instead, in this thesis I calculate quasicrystalline structure factors via FFTs of their aperture functions. The structure factor of a Penrose tiling, comprising delta functions at the vertices and calculated by the FFT method, is shown in Fig. 2.10A.

The Penrose structure factor possesses a remarkable 10-fold rotational symmetry which is evident in the numerous decagonal rings of diffraction maxima. Such symmetry is forbidden in a translationally periodic structure and immediately suggests quasiperiodic character. Inspection of the high-resolution azimuthally averaged structure factor shows the clear delta function character of the peaks (Fig. 2.10B). Despite the high resolution of the calculation, weak peaks resolve to a background signal due to the density with which they pack the reciprocal space.

The Fourier module of the Penrose structure factor has rank 5. All peaks in the pattern correspond to vectors of the form $G_{hklmn} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3 + m\mathbf{b}_4 + n\mathbf{b}_5$, where the primitive vectors $\mathbf{b}_i$ form a rationally independent set and may be expressed as

$$
\mathbf{b}_i = \frac{2}{d_1} \left( \hat{x} \cos \left( \frac{\pi (i-1)}{5} \right) + \hat{y} \sin \left( \frac{\pi (i-1)}{5} \right) \right),
$$

where $d_1 = d_0 \sqrt{(4 - \tau^2)}$ is the length of the long diagonal of the skinny Penrose rhomb\textsuperscript{110}. As already observed, the structure factor of a quasicrystal shares many characteristics with the reciprocal lattice of a crystal. Scattering maxima are delta function-like in character and peaks may be indexed with an appropriate reciprocal space basis. The Fourier modules of $d$-dimensional crystals have rank equal to $d$, while the modules of $d$-dimensional quasicrystals have rank greater than $d$. The reciprocal space of a quasicrystal is thus densely packed by Fourier wavevectors.

The diffraction maxima of a quasicrystal can be interpreted through a generalisation of Bragg’s law. We may view each scattering process as the result of coherent reflection from quasi-Bragg
planes in the structure - Fig. 2.6B shows a number of such planes. The magnitude of the reciprocal lattice vector $G_{hklmn}$ is related to the interplanar spacing according to Eqn. 2.18. Peaks associated with large $|G_{hklmn}|$ values correspond to closely spaced quasi-Bragg planes in which the vertices are separated by large distances. Many such peaks are visible, which thus indicates the presence of strong long-range structural correlations in the tiling. The structure factor thus effectively describes the structural order in a Penrose quasicrystal; it has delta function-like peaks with crystallographically forbidden symmetries, an effective 10-fold rotational symmetry and strong long-range structural correlations.

### 2.4 Amorphous Materials

The progression from crystalline to quasi-crystalline is a natural first step towards structural disorder. Both crystals and quasicrystals are deterministically structured; the former is governed by the lattice and material distribution in the primitive cell, while the latter may be seen as a projection of a perfectly ordered hypercrystal.

In a projection of the hyperlattice into a lower dimensional subspace, the quasicrystal loses its translational periodicity. In spite of this, quasicrystals exhibit strikingly high order rotational symmetries as evidenced by the Penrose tiling structure factor (Fig. 2.10A). Results for the transmission of radiation as a function of incident angle through quasicrystals clearly demonstrate these average rotational symmetries.$^{66,111}$

Consider now a material which is both translationally aperiodic and rotationally isotropic at a statistical level. Such a material represents a natural next step towards structural disorder, in which we replace the discrete (average) rotational symmetries of quasicrystals with an average continuous rotational symmetry.

A trivial example of this type of structure is a Poisson-distributed point pattern in the plane. A Poisson point pattern can be considered ‘perfectly’ random; it models a set of non-interacting particles and represents a two-dimensional ideal gas. Fig. 2.11A shows the total scattering structure function of a Poisson point pattern. Its uniform intensity distribution shows that the structure possesses no significant structural correlations at any lengthscale. No preferential separation exists between the scattering centres and no radiation is scattered coherently to produce significant features in the diffraction pattern. Note that the dark ring towards the edge of the figure is a result of the finite radius of the cylinders with which the point pattern is modelled; it corresponds to the first minimum of the Airy disc of a single cylinder, and not to a structural feature of the point pattern.

Poisson point patterns are just a single example of structures that possess both translational aperiodicity and average rotational isotropy. Countless structures are known which are qualitatively ‘less random’. For example, consider the structure factor shown in Fig. 2.11B. No Bragg-like peaks are discernible; the TSSF cannot be represented by the basis vectors of a Fourier module, thus implying that the structure is non-deterministic. However, the TSSF displays a high intensity annulus that must result from semi-coherent light scattering. This partially coherent
Figure 2.11: The difference between random and amorphous media as demonstrated by their structure factors. The structure factor of a random material (A) is a uniform speckle pattern without any notable features. The structure factor of an amorphous material (B) usually contains a high-intensity ring as a result of semi-coherent scattering from structural correlations.

scattering suggests the existence of a preferred inter-scatterer distance, and demonstrates the existence of structural correlations in the material.

The TSSF of Fig. 2.11B is typical of so-called ‘amorphous’ materials. Amorphous structures are aperiodic matter arrangements with an average rotational symmetry. However, unlike in random media, the positions of scattering centres, although non-deterministic, are correlated at a local level. The amorphous material responsible for the structure factor of Fig. 2.11B is a disordered honeycomb; this structure is shown in Fig. 2.12A where the local structural correlations are clear.

2.4.1 Glassy Networks

Glasses are amorphous materials that typically result from the rapid cooling of a liquid\textsuperscript{112}. Many examples of glassy structures are known. These include amorphous silicon\textsuperscript{113}, silicate (a major component of window glass), glassy graphene\textsuperscript{114} and amorphous ice\textsuperscript{115}. A number of glassy networks of dielectric material have been shown to support sizeable photonic band gaps\textsuperscript{62,63}; the structure of glass is therefore of fundamental optical interest.

The genesis of the current understanding of glassy structure can be traced to work from 1932 by W. H. Zachariasen\textsuperscript{116} that introduced the concept of a continuous random network (CRN). A CRN comprises a number of points (vertices) which are non-deterministically positioned in space. The points are then interconnected by edges. As applied to the structure of a glass, a point represents the position of an atomic species and an edge between two points models a region of electron density corresponding to a chemical bond.

The CRN description of a glass is well-illustrated by the two dimensional graphene glass shown in Fig. 2.12A. Graphene comprises $sp^2$ hybridised carbon atoms that favour the formation of three covalent bonds in the plane (the extra electron sits in a non-hybridised $p$ orbital that is normal to the plane of the $sp^2$ orbitals). All carbon atoms will seek to satisfy their bonding requirements by bonding to 3 other carbons and the structure of perfect graphene is a honeycomb (Fig. 2.3B).
Irradiation of graphene with an electron beam causes significant damage to the structure; atoms may be knocked out, and covalent bonds broken and reformed. This process fundamentally alters the topology of the graphene, introducing local strains that deform the atomic positions and creating non-hexagonal rings. The resulting structure, which I model in Fig. 2.12A, comprises atoms which are all trivalently bonded. The atomic positions, however, are non-deterministic and the network topology is markedly different to the crystalline case. The pair distribution function of glassy graphene (Fig. 2.12B) demonstrates the existence of a preferred inter-particle separation and strong positional correlations which fade to the ideal gas value at long range.

The most famous example of a continuous random network is the CRN model of amorphous silicon (a-Si); this is illustrated in Fig. 2.12D. Elemental silicon forms 4 covalent bonds. These bonds repel each other such that they are maximally separated around their root atom. The potential energy of a single silicon atom is thus minimised when its bonds point to the corners of tetrahedron. High quality a-Si CRNs, of which Fig. 2.12D is an example, have been computationally modelled. Each vertex in the network strictly satisfies the silicon bonding requirement, and is connected to 4 other vertices. The CRN contains a multitude of topological defects and, in order to accommodate these defects, the edge configuration about each vertex is only approximately tetrahedral; the network may thus be considered a connected arrangement of structurally deformed tetrahedral units. The pair distribution function of the CRN model, shown in Fig. 2.12C, is typically amorphous.

The CRN representation of amorphous silicon was a great stride in the modelling of amorphous structures. Theoretical total scattering structure functions and pair distribution functions, as predicted by the CRN models, are in good agreement with pair distribution functions obtained through X-ray diffraction studies; the model is thus accepted as the general basis of amorphous silicon structure.

However, the exact structure of amorphous silicon remains a controversial subject. CRN a-Si is understood to refer to a connected network which has not crystallised in any way; the network

---

**Figure 2.12:** A paracrystalline disordered honeycomb network (A) embodies Zachariasen’s notion of a continuous random network. Its pair distribution function (B) is characteristically amorphous, showing strong short range correlations. The CRN model of amorphous silicon (D) is an excellent model of a 3D glassy structure; it is also of fundamental optical interest. Its pair distribution function (C) is also typically glassy.
contains no sizeable regions within which the topology matches that of the cubic crystalline phase. Using a fine electron beam probe, it has been shown that the variance in diffraction patterns, obtained by irradiating small volumes of a-Si samples, is fundamentally incompatible with the CRN hypothesis\textsuperscript{119}. Rather, reverse Monte-Carlo modelling suggests that the variance may be explained by a partially-crystallised random network model in which significant regions of the network are topologically crystalline.

The partially-crystallised random network structure is called the paracrystalline model. Most recently, direct observation of a two-dimensional graphene glass via high resolution electron microscopy has provided direct evidence of paracrystallinity\textsuperscript{114}. Graphene glass is observed to contain significant areas of 6-membered rings. These small crystallites are then interconnected through a continuous random network. These features may be resolved in the computational model of graphene glass in Fig. 2.12A.

The structure of glass thus remains an active field of research decades after Zachariasen’s proposal of the CRN model. The question of paracrystallinity is, however, not relevant in the field of optical metamaterials, whose structures are designed rather than observed. Throughout this thesis I therefore make no distinction between topologically homogeneous CRNs and paracrystalline CRNs. Rather, any ensemble of vertices and edges which is not specifically crystalline or quasi-crystalline is referred to as a CRN.

2.4.2 Hyperuniformity

2.4.2.1 Definition

The concept of hyperuniformity\textsuperscript{84} arose from theoretical studies of density fluctuations in point patterns. From an optical perspective, a hyperuniform material possesses a total scattering structure function $S(q)$ that tends to zero in the limit where $q \to 0$. More generally, the structure factor of hyperuniform materials is typically zero for a range of values around $q = 0$. Such structures are called ‘stealthy’\textsuperscript{85} and could be expected to display interesting light scattering properties. Indeed, hyperuniform materials have been shown to be effectively transparent to long wavelength radiation\textsuperscript{86}, and distributions of dielectric material derived from hyperuniform point patterns are known to possess complete photonic band gaps\textsuperscript{62,89,120}.

This section provides a brief introduction to concepts in the design of hyperuniform materials. First, I state the definition of a hyperuniform arrangement of points. Following this, I explore the connection between hyperuniformity and ground state configurations for systems of interacting particles. In particular, it is known that stealthy materials may be engineered by numerically optimising the positions of a point array until a ground state is found. Finally, the hyperuniform order parameter $\chi$, which describes the stealthiness of a particular point distribution, is introduced.

Consider a distribution of points in a $d$-dimensional domain $D$. We define an arbitrarily shaped convex sampling window $\Omega$, of characteristic lengthscale $R$, and locate the centroid of the window at position $x_0$. This configuration is shown for a 2-dimensional domain in Fig. 2.13A. We then
Figure 2.13: Definitions of hyperuniformity. The number variance of a \(d\)-dimensional point distribution (A) may be calculated by sampling with a convex window \(\Omega\) (purple) of centroid \(x_0\) and lengthscale \(R\). The number variance of a hyperuniform material scales as \(R^{d-1}\). Hyperuniform point patterns arise when particles interact through specific pair potentials. Typically, we consider a pair potential whose Fourier transform \(V(k)\) (B) is non-zero only within the region \(|k| < k_c\); hyperuniform materials correspond to ground states of the system.

count the number of points \(N_\Omega\) within the sampling window. The variance \(\sigma_\Omega^2\) of the number of points within \(\Omega\) may be written as

\[
\sigma_\Omega^2 = <N_\Omega^2> - <N_\Omega>^2,
\]

where angle brackets denote an ensemble average over the position of the sampling window centroid. Consider the case where the point arrangement is random; a Poisson point pattern is a good illustration of this (Fig. 2.13A). For a large sampling domain \(\Omega\), the number variance within \(\Omega\) will grow with the volume of the sampling window. We may say that \(\sigma_\Omega^2 \sim R^d\). It can be shown that the slowest rate at which the number variance may grow is \(R^{d-1}\). A hyperuniform point pattern is thus defined as an arrangement of points for which the number variance of points within a sampling window is proportional to the surface area of the sampling window. This condition is equivalent to the statement that the total scattering structure function of the point distribution is vanishing in the limit where \(q \to 0\).

Hyperuniformity is a characteristic of a broad class of structures. All crystalline and quasicrystalline point distributions are known to be hyperuniform (since their TSSFs are vanishing for \(q \to 0\)). It is also possible to generate non-deterministically structured amorphous hyperuniform materials, of which several are shown in Fig. 2.14. The process of generating amorphous hyperuniform structures is elegantly linked to the question of finding the ground state of a set of interacting particles\(^{85,121,122}\). I now present a brief outline of this process.

### 2.4.2.2 Classical Ground States and Stealth

Consider an array of \(N\) interacting point particles in a 3-dimensional domain \(\Omega\). Let the domain be cubic, with side length \(L\), and be subject to a periodic boundary condition. The possible wavevectors of a plane wave in \(\Omega\) are thus quantised; they may take values \(\mathbf{k} = \hat{x}2\pi\alpha/L + \cdots\)
\[ \hat{y}2\pi\beta/L + \hat{z}2\pi\gamma/L. \] The particles interact through a pair potential function \( V(r) \), where \( r \) is the vector between two points. The total potential energy of the system may be written as

\[ \Phi = \sum_{i=1}^{N} \sum_{j=i+1}^{N} V(r_i - r_j). \] (2.31)

The pair potential function may be represented as a Fourier series in the possible wavevectors of the domain; assuming that the pair potential is even such that \( V(r) = V(-r) \), we write

\[ V(r) = \frac{1}{\Omega} \sum_{k} V(k) \cos(k \cdot r). \]

Substitution of this expansion into Eqn. 2.31 shows that

\[ \Phi = \frac{1}{\Omega} \sum_{k} V(k) \sum_{i=1}^{N} \sum_{j=i+1}^{N} \cos(k \cdot (r_j - r_i)) = \frac{1}{\Omega} \sum_{k} V(k)c(k), \] (2.32)

where we have defined the quantity \( c(k) = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \cos(k \cdot (r_j - r_i)) \).

We now choose the functional form of the interaction potential in the Fourier domain. We choose a potential that is non-zero only in a finite region around \( k = 0 \); we write

\[ V(k) = \begin{cases} V_0 & : |k| < k_c \\ 0 & : |k| > k_c \end{cases}, \] (2.33)

where \( V_0 > 0 \) is a constant and \( k_c \) is a critical radius in reciprocal space. This potential is illustrated in Fig. 2.13B, in which the potential is seen to only take non-zero values in the neighbourhood of \( k = 0 \). The corresponding real space potential \( V(r) \) is found by inverse Fourier transformation of \( V(k) \) as defined in Eqn. 2.33; it is easy to show\(^{122}\) that \( V(r) \) corresponds to an oscillating soft potential with a global maximum at \( r = 0 \). For such a potential, Eqn. 2.32 tells us that any realisation of the point particles which minimises all \( c(k) \) for which \( |k| < k_c \) will be a ground state of the system.

We now consider what form the ground state particle configurations of the point distribution take. To make progress, let us consider the total scattering structure function \( S(q) \) of the particle array; \( S(q) \) may be calculated according to Eqn. 2.5 in which the aperture function is taken as \( \Sigma(r) = \sum \delta(r - r_i) \). It is easily shown that the TSSF satisfies

\[ S(q) = N + 2c(q). \] (2.34)

Minimal values of the TSSF thus occur for corresponding minimal values of \( c(q) \). Further, since it is a real-valued non-negative quantity, the TSSF takes a minimum value of 0. Accordingly, we observe that \( \min[c(q)] = -N/2 \) and that any particle array whose TSSF is zero for all \( |q| < k_c \) will be a ground state of the system.

Computationally, ground states of the system may be accessed by optimisation of the particle positions until the TSSF of the array is zero within the critical region \( |q| < k_c \).\(^{85,122}\) We note, however, that \( S(q = 0) \) can never be set to zero as it is necessarily equal to \( N^2 \). In spite of this,
Figure 2.14: Hyperuniform point patterns and their total scattering structure functions for a selection of $\chi$ values. Hyperuniform point patterns are characterised by a region around $q = 0$ within which their TSSFs are zero. As the stealthiness of the pattern - as measured by $\chi$ - increases, structural correlations within the point pattern become more pronounced and significant local geometric order begins to develop.

Ground states possess TSSFs which tend to zero in the limit where $q \rightarrow 0$; ground states of the system are thus hyperuniform.

Hyperuniform systems constructed in this way are called ‘stealthy’. The systems may be characterised with a dimensionless parameter $\chi$ - the stealthiness - which is defined as

$$\chi = \frac{M(k_c)}{dN},$$

where $d$ is the dimensionality of the system (here $d = 3$) and $M(k_c)$ is the number of wavevectors within the critical reciprocal space region for which the pair potential is non-zero. The stealthiness thus describes the proportion of wavevectors for which the TSSF has been set to zero relative to the total number of degrees of freedom in the particle array.

Fig. 2.14 presents three hyperuniform point patterns for a selection of $\chi$ values; the top row shows detail from the point pattern while the bottom row shows the corresponding TSSF. In each case, the patterns were generated by application of conjugate gradient optimisation to minimise the values of the TSSF in the region $|q| < k_c$. For each structure, we observe a hyperuniform ‘exclusion region’ about the $q$ space origin throughout which the structure factor has been set to zero. As the $\chi$ value increases (A → C → E) the radius of the exclusion region increases and the point distributions become progressively more correlated. At $\chi = 0.6$ (Figs. 2.14E & F) the structural correlations of the point pattern are clearly apparent; there is a favoured interparticle separation and the local particle arrangement resembles that of a triangular lattice. The
parameter $\chi$ can thus be used to tune the magnitude of structural correlations and geometrical order within the point pattern\textsuperscript{62}.

### 2.4.2.3 Delaunay Tessellation

The prototypical design protocol for hyperuniform structures, as discussed above, is based on the optimisation of an array of point scattering centres\textsuperscript{85,122}. For photonic applications, however, connected network architectures are also desirable because they can support sizeable photonic band gaps\textsuperscript{62}. Such networks can be constructed from arbitrarily structured point patterns using a tessellation protocol based on the Delaunay triangulation algorithm\textsuperscript{123}; this protocol is illustrated in Fig. 2.15.

The Delaunay tessellation protocol comprises the following steps. To begin, we choose a seed point pattern (Fig. 2.15, blue points) that possesses desirable geometrical characteristics; for instance, the point pattern could be quasicrystalline, hyperuniform or simply random. Next, we enforce a periodic boundary condition and apply a Delaunay triangulation algorithm to the point pattern. In general, a triangulation subdivides a planar object into edge-sharing triangles. As applied to a point pattern, triangles are formed by connecting together three nearby points. The Delaunay triangulation is, in most circumstances, a uniquely defined triangulation that maximises the smallest angle of each component triangle\textsuperscript{123}; it thus suppresses the occurrence of deformed, thin triangles. The Delaunay triangulation of a seed point pattern is shown as thin blue lines in Fig. 2.15.

![Figure 2.15: Generation of a connected network from a seed point pattern through Delaunay tessellation. To begin, we choose a seed point pattern (blue points) and form its Delaunay triangulation (thin blue edges). The centroid of each Delaunay triangle is used to define a new set of points (black points). The centroids of edge-sharing triangles are then connected to form the tessellated network (red edges).](image-url)
Once triangulated, a new set of points is created by placing a point at the centroid of each Delaunay triangle (Fig. 2.15, black dots). In the final step, these new points are connected to form a continuous network. Specifically, any given Delaunay triangle is edge-sharing with exactly three other triangles; only the centroids of edge-sharing triangles are connected, thus forming a strictly trivalent network (shown as the red network, Fig. 2.15). For a seed pattern comprising $N$ vertices, the Delaunay tessellated network consists of $2N$ new vertices and $3N/2$ edges which enclose $N$ cells.
Chapter 3

The Photonic Band Gap

3.1 Electromagnetism in Mixed Dielectric Media

The macroscopic form of the Maxwell equations relates the electric field strength $E$ and the magnetic flux density $B$ to the total charge density $\rho$ and current density $J$. It is common to split the charge density into free and bound charge components ($\rho = \rho_f + \rho_b$) and the current density into contributions from the free, magnetisation and polarisation currents ($J = J_f + J_m + J_p$). We may then write the Maxwell equations in macroscopic form as

$$\begin{align*}
\nabla \cdot D(r,t) &= \rho_f \\
\nabla \cdot B(r,t) &= 0 \\
\nabla \times E(r,t) &= -\frac{\partial}{\partial t} B(r,t) \\
\nabla \times H(r,t) &= J_f + \frac{\partial}{\partial t} D(r,t),
\end{align*}$$

where the source terms are the free charge $\rho_f$ and the free current $J_f$. The auxiliary fields $D$ and $H$ are the electric displacement field and magnetic field strength respectively. They are defined as

$$\begin{align*}
D &= \varepsilon_0 E + P \\
H &= \frac{1}{\mu_0} B - M,
\end{align*}$$

where the fields $P$ and $M$ are the polarisation density and magnetisation of a material respectively.

The Maxwell equations as stated above are a very general statement of the classical theory of electromagnetism. To solve these equations in a particular circumstance, we must specify a suitable set of constitutive relations that link the $E$ field to the $D$ field, and the $B$ field to the $H$ field. Quite generally we can expand the polarisation density and magnetisation vectors as power series. We write
\[ P_i = \varepsilon_0 \left[ \sum_j \chi^{(1)}_{ij} E_j + \sum_{j,k} \chi^{(2)}_{ijk} E_j E_k + O(E^3) \right] \]  
\[ M_i = \sum_j \xi^{(1)}_{ij} H_j + \sum_{j,k} \xi^{(2)}_{ijk} H_j H_k + O(H^3) \]  

where the tensors \( \chi^{(n)} \) and \( \xi^{(n)} \) are the \( n \)-th order electric and magnetic susceptibilities of the material respectively. To arrive at a suitable set of constitutive relations we begin to simplify the problem. First, we specify that the materials are non-magnetic such that the magnetisation is equal to zero. Next we specify that the magnitude of the electric field is sufficiently small that we may neglect the contribution of second-order and higher electric susceptibilities. Further, we consider only isotropic materials in which the polarisation density is strictly parallel to the applied \( E \) field. We therefore write the first order susceptibility as \( \chi^{(1)} I_{ij} \) where \( I \) is the identity matrix; the polarisation becomes

\[ P_i = \varepsilon_0 \chi^{(1)} \sum_j I_{ij} E_j = \varepsilon_0 \chi^{(1)} E_i \]  

We may now write the required constitutive relations as

\[ D = \varepsilon_0 \varepsilon_r E \]  
\[ B = \mu_0 H , \]  

where we define the relative permittivity \( \varepsilon_r = 1 + \chi^{(1)} \) and the refractive index \( n = \sqrt{\varepsilon_r} \).

We consider specifically a collection of mixed lossless dielectric media; this could be, for instance, an arbitrary distribution of vacuum and a single type of dielectric. The relative permittivity is thus strictly real and is a discontinuous step-like function of position \( \varepsilon_r(\mathbf{r}) \), the value of which is dictated by the material occupying position \( \mathbf{r} \). As dielectrics, the materials possess no free charge \( \rho_f \). We specify also that there exist no free currents in the region under consideration. The Maxwell equations may then be written as

\[ \nabla \cdot [\varepsilon_r(\mathbf{r}) \mathbf{E}(\mathbf{r}, t)] = 0 \]  
\[ \nabla \times \mathbf{E}(\mathbf{r}, t) + \mu_0 \frac{\partial}{\partial t} \mathbf{H}(\mathbf{r}, t) = 0 \]  
\[ \nabla \cdot \mathbf{H}(\mathbf{r}, t) = 0 \]  
\[ \nabla \times \mathbf{H}(\mathbf{r}, t) - \varepsilon_0 \varepsilon_r(\mathbf{r}) \frac{\partial}{\partial t} \mathbf{E}(\mathbf{r}, t) = 0. \]  

To summarise, we have arrived at a set of Maxwell equations (Eqns. 3.9) that describe the propagation of light through an arbitrary distribution of dielectric material. There are no sources of \( \mathbf{E} \) and \( \mathbf{H} \) in the region under consideration, and so the equation set is homogeneous. All dielectrics are assumed to be non-magnetic, linear and isotropic. The equations hold for lossy dielectric material, but we specify nonetheless that \( \varepsilon_r \) is real. Although these assumptions seem quite restrictive, we shall see that these simple systems can demonstrate a wealth of interesting
physics. Further, the simple model is a solid foundation on which to build theories appropriate for more complex materials.

3.2 The Maxwell Eigenvalue Formulation

Eqns. 3.9 can be cast into a very useful form; they may be formulated as a Hermitian eigenvalue problem. Such problems have been thoroughly studied throughout the mathematical and physical sciences. The field modes that solve the eigenvalue problem (the eigenvectors) are thus known to possess many useful properties.

We begin by looking for a separable solution for $\mathbf{E}$ and $\mathbf{H}$. In particular, we take the temporal component of the solution to be time harmonic with frequency $\omega$. We write $\mathbf{E}(\mathbf{r}, t) = e^{-i(\omega t + \varphi)} \mathbf{E}(\mathbf{r})$ and $\mathbf{H}(\mathbf{r}, t) = e^{-i\omega t} \mathbf{H}(\mathbf{r})$. Substitution of these expressions into Eqns. 3.9 and rearranging yields two possible eigenvalue problems. The $\mathbf{E}$ field obeys

$$\frac{1}{\varepsilon_r(\mathbf{r})} \nabla \times [\nabla \times \mathbf{E}(\mathbf{r})] = \frac{\omega^2}{c^2} \mathbf{E}(\mathbf{r}), \quad (3.10)$$

while the $\mathbf{H}$ field is governed by

$$\nabla \times \left[ \frac{1}{\varepsilon_r(\mathbf{r})} \nabla \times \mathbf{H}(\mathbf{r}) \right] = \frac{\omega^2}{c^2} \mathbf{H}(\mathbf{r}). \quad (3.11)$$

These two equations are both eigenvalue problems. We see that the operation of some differential operator on the field reproduces the field multiplied by a scalar eigenvalue. We define operators $\hat{\Theta}_E$ and $\hat{\Theta}_H$ and rewrite equations Eqn. 3.10 and 3.11 to show their eigenvalue form clearly.

$$\hat{\Theta}_E \mathbf{E}(\mathbf{r}) = \frac{\omega^2}{c^2} \mathbf{E}(\mathbf{r}) \quad (3.12)$$

$$\hat{\Theta}_H \mathbf{H}(\mathbf{r}) = \frac{\omega^2}{c^2} \mathbf{H}(\mathbf{r}) \quad (3.13)$$

It is sufficient to solve one of either Eqn. 3.12 or Eqn. 3.13 to determine everything about the possible field modes (although we note that we have not yet specified the zero divergence conditions imposed on $\varepsilon_r(\mathbf{r}) \mathbf{E}(\mathbf{r})$ and $\mathbf{H}(\mathbf{r})$ by the Maxwell equations; we return to this point later). We must therefore choose one, but which should we solve? At this point it is useful to define the inner product of two vector fields $\mathbf{F}(\mathbf{r})$ and $\mathbf{G}(\mathbf{r})$ as

$$\langle \mathbf{G} | \mathbf{F} \rangle = \int \mathbf{G}^* \cdot \mathbf{F} \, d^3r. \quad (3.14)$$

We adopt a bra-ket style notation to denote an inner product. In this context, a Hermitian operator $\hat{H}$ on a vector field is an operator that satisfies the relation $\langle \mathbf{G} | \hat{H} \mathbf{F} \rangle = \langle \hat{H} \mathbf{G} | \mathbf{F} \rangle$. A Hermitian operator has many useful properties, proofs of which can be found in many standard
texts. In particular, its eigenvalues are necessarily real and eigenfunctions having different eigenvalues are necessarily orthogonal with respect to the inner product. We can prove that $\hat{\Theta}_H$ is Hermitian through an integration by parts

$$
\langle G|\hat{H}|F\rangle = \int G^\ast \cdot \nabla \times \left( \frac{1}{\varepsilon_r(r)} \nabla \times F \right)
= \int \left( \frac{1}{\varepsilon_r(r)} \nabla \times G^\ast \right) \cdot \nabla \times F
= \int \nabla \times \left( \frac{1}{\varepsilon_r(r)} \nabla \times G^\ast \right) \cdot F
= \langle \hat{H} G|F\rangle,
$$

(3.15)

where this property is contingent on the reality of $\varepsilon_r$. We assert that the surface terms in the above integration can be made to vanish for cases of interest. The system is either finite, in which case the fields will decay to zero for sufficiently large distances, or the system is periodic, and any surface integrals performed over the boundary of the periodic domain will vanish.

Integration by parts applied to $\hat{\Theta}_E$ shows that it is not a Hermitian operator. Solutions to Eqn. 3.12 are thus not guaranteed to possess the useful properties associated with Hermitian eigenvalue problems. We therefore focus our efforts on solving the magnetic field problem (Eqn. 3.13).

Solutions to the magnetic field eigenvalue problem possess several useful properties. As already observed, two distinct solutions $H_i$ and $H_j$ are orthogonal with respect to the inner product. In particular, we may choose the amplitudes of the solutions to be orthonormal such that $\langle H_i|H_j\rangle = \delta_{ij}$. Further, $\hat{\Theta}_H$ is a linear operator. Any full solution of the Maxwell equations for $H(r)$ can thus be written as a linear superposition of functions $H_i(r)$ that solve the eigenvalue problem. We may write

$$
H(r) = \sum_i \alpha_i H_i(r),
$$

(3.16)

where $\alpha_i$ is a scalar weight. Finally, we define a quantity $U_f$ as the Rayleigh quotient of the operator $\hat{\Theta}_H$. We write

$$
U_f(H) = \frac{\langle H|\hat{\Theta}_H H\rangle}{\langle H|H\rangle},
$$

(3.17)

Consider a small perturbation $\delta A$ applied to $H$. Let us calculate the change $\Delta_f$ in the Rayleigh quotient as a result of this perturbation; we define this change as $\Delta_f = U_f(H + \delta A) - U_f(H)$. Working to first order in $\delta$ (which is true in the limit of a small perturbation), it can be shown that $\Delta_f = [(\delta A|G) + (G|\delta A)]/2$, where $G$ is given by

$$
G(H) = \frac{2}{\langle H|H\rangle} \left( \hat{\Theta}_H H - \frac{\langle H|\hat{\Theta}_H H\rangle}{\langle H|H\rangle} H \right).
$$

(3.18)
The difference $\Delta f$ must vanish at local maxima or minima of the Rayleigh quotient. In particular, $\Delta f$ must equal zero for all possible choices of the perturbing vector field $A$. As a result, we conclude that $G$ must be identically zero at local maxima and minima. Looking at Eqn. 3.18, we see that $G$ is vanishing when $H$ is an eigenstate of the operator. Solutions to the eigenvalue problem are thus stationary points of the Rayleigh quotient. Further, the value of $U_f$ at these points is exactly the eigenvalue $\omega^2/c^2$.

It is possible to re-express the Rayleigh quotient using Eqns. 3.9 & 3.2 as

$$U_f(H) = \frac{\langle \nabla \times E | \nabla \times E \rangle}{\langle E | \varepsilon_r(r) E \rangle} = \int \frac{|\nabla \times E|^2 \ d^3r}{\int \varepsilon_r(r)|E|^2 \ d^3r}. \quad (3.19)$$

This is a particularly useful expression which we refer to as the electromagnetic energy functional. From Eqn. 3.19, we see that $U_f$, and by extension the eigenvalue, is minimised when the quantity $\int \varepsilon_r(r)|E|^2 \ d^3r$ is maximal. The frequency of a field mode is thus minimised when the electric field is concentrated in regions of high relative permittivity. As we scan from low frequency to high frequency, we should observe progressive exclusion of the electric field from high relative permittivity regions.

### 3.3 Numerical Solutions to the Maxwell Equations

Although several useful statements about the nature of the solutions to Eqn. 3.13 have just been made, the explicit forms of the allowed $H$ fields are yet to be determined. It is not generally possible to find analytical solutions for $H$ in the case of arbitrarily complex distributions of dielectric material. Instead, a numerical method is typically employed. There exist a number of well-developed numerical methods for solving the Maxwell equations; these can broadly be divided into frequency-domain and time-domain approaches.

Frequency-domain methods typically proceed by expansion of the $E$ or $H$ fields in some chosen set of time-harmonic basis functions $\{f\}$. To achieve this, we write $H = \sum_i c_i f_i(r)e^{-i\omega t}$; the time-dependence then naturally falls out (as in Eqns. 3.10 & 3.11), leaving a set of coupled partial differential equations in the unknown expansion coefficients $c_i$. These equations form a linear system that may be solved using regular matrix methods; each eigenvector and eigenvalue pair describes a field mode and its associated eigenfrequency. To render the computation tractable, the basis set is truncated; it is limited to a number of basis functions that ensures good convergence while minimising the memory requirements and calculation runtimes. In general, frequency-domain methods are suitable tools when the dispersion relation (the wavevector-frequency dependence of light propagating through a structure) is the principal quantity of interest.

The plane wave expansion method (PWEM) is the most common example of this type of frequency-domain approach. In the PWEM, the electromagnetic fields of a periodic unit cell are determined through expansion of $H(r)$ as a truncated Fourier series. Expansion coefficients and eigenfrequencies are calculated numerically and the eigenmodes of the unit cell can
then be reconstructed. Well-implemented plane wave expansions require modest memory and
can execute rapidly. Plane wave expansion methods are thus an ideal choice for probing the
electromagnetic properties of periodic structures, but, depending on the implementation, solvers
may be limited to simulating domains comprising dielectrics with real-valued permittivities only.

Wannier functions present an alternative complete basis in which to expand the magnetic field\(^{126}\). Wannier functions are localised basis states whose symmetries reflect those of the system under
consideration. The use of Wannier functions can greatly reduce calculation memory overheads
and runtimes without compromising on accuracy. However, Wannier functions must be con-
structed from the results of a PWEM calculation; this restricts their use as an exploratory tool
for novel architectures but renders them useful for defect engineering in established materials\(^{126}\).

Finite element methods (FEM) are an alternative paradigm of frequency-domain numerical ap-
proaches\(^{127}\). FEM calculations begin by discretising the system under consideration into a space-
filling mesh of irregular polyhedral elements (typically triangles in two-dimensions and tetrahedra
in three-dimensions). Within each element, the electromagnetic fields are represented using a
polynomial approximation of variable order. The distinct elements are pieced together by ensur-
ing tangential continuity of the electric and magnetic fields at any shared face. Field eigenmodes
and eigenfrequencies of the system are then found using a variational method\(^{127}\). Finite element
methods support adaptive meshing; accurate results are facilitated by increasing the mesh den-
sity around key features of the system. However, the FEM solution scheme is computationally
expensive; it is thus typically used to probe only a few frequencies of interest\(^{80}\).

The finite difference time domain (FDTD) approach is the most common time-domain numerical
solution paradigm\(^{127,128}\). It is a robust method that can simulate the behaviour of arbitrarily
structured samples comprising materials with a complex refractive index. The FDTD method
employs a rectangular Yee grid to discretise the electric and magnetic fields in time and space.
Central differences are then used to approximate the temporal and spatial partial derivatives and
to step the fields forward in time. Together with time-domain information, FDTD calculations
employ a Fourier post-processing step to calculate spectral properties of the system. In particular,
FDTD can generate electric and magnetic field eigenmodes (although these modes do not form
a complete basis set), reflection and transmission spectra, scattering cross sections and farfield
scattering patterns. FDTD is widely used on account of its power and flexibility. However,
FDTD is not without its disadvantages. In particular, the rectangular grid introduces sampling
errors where material interfaces are not parallel to a grid axis; this can create spurious sharp
interfaces which are problematic when simulating metals. Further, complex FDTD calculations
require a large amount of time and memory.

Each of the above methods has its own advantages and disadvantages and it is important to
choose an appropriate approach for a given problem case. The plane wave expansion and FDTD
methods are employed widely throughout this thesis; the PWEM is ideal for rapid calculation of
photonic crystal dispersion relations and FDTD provides a versatile fallback method for complex
non-periodic systems. For this reason, the following two sections present more detailed sketches
of these two methods.
3.3.1 Finite Difference Time Domain Method

The finite difference time domain (FDTD) method is a powerful numerical method for solving the fundamental form of Maxwell’s equations (Eqns. 3.1). The method is based on the discretisation of space and time into grids. The grids store an array of values representing the current and past states of the electric and magnetic fields. The spatial and temporal derivatives of the fields are then calculated through finite differences between stored field values.

The fundamental FDTD algorithm was proposed by Kane Yee\(^{129}\). Yee’s insight was to employ a special framework for gridding space and time. In discretising the electromagnetic fields, it is natural to formulate a grid in which the electric and magnetic fields are co-located, with the values of the two fields thus being stored at identical locations. Instead, FDTD employs a Yee grid, comprising a pair of distinct grids which separately record the magnetic and electric fields. The two grids are staggered by half a grid spacing, with the result that a randomly chosen grid point will contain either magnetic or electric field data, but not both.

A central difference scheme is employed to numerically estimate the partial derivatives. Consider a scalar field \(\phi(x)\) which is sampled by a grid with spacing \(\Delta x\). We may estimate the derivative at a point \(x_0\) through a central difference method as

\[
\frac{\partial \phi}{\partial x} = \frac{\phi(x_0 + \Delta x) - \phi(x_0 - \Delta x)}{2\Delta x}.
\]  

Central difference estimation is accurate to terms of the order of the square of the grid spacing; it is substantially more accurate than simple Newton-like forward and backward difference methods\(^ {128}\).

To illustrate the utility of the Yee grid formulation, we consider a one-dimensional example. Consider a plane wave propagating in the \(x\) direction through a linear homogenous dielectric with permittivity \(\varepsilon_r\) and permeability \(\mu_r\). We specify that the plane wave is polarised along the \(y\) direction and that there is no free charge or current in the region under consideration. The Maxwell equations reduce to a pair of coupled equations\(^ {127,128}\) that we may write as

\[
\frac{\partial E_y}{\partial t} = -\frac{1}{\varepsilon_0 \varepsilon_r} \frac{\partial H_z}{\partial x},
\]

\[
\frac{\partial H_z}{\partial t} = -\frac{1}{\mu_0 \mu_r} \frac{\partial E_y}{\partial x}.
\]

Consider now meshing the Maxwell equations with a simple grid. Let the electric and magnetic fields be recorded at the set of points \(x = i\Delta x, i = 0, 1, 2,\ldots\). A spatial grid is defined at each grid point of a temporal grid that samples the fields at points \(t = j\delta t, j = 0, 1, 2,\ldots\). The spatial and temporal derivatives at a given point in space-time may then be expressed as finite differences according to Eqn. 3.20. Taking the central difference about a point \((x, t)\), Eqn. 3.22 becomes

\[
H_z|_{x}^{t+\delta t} = H_z|_{x}^{t-\delta t} = \frac{\delta t}{\mu_0 \mu_r \Delta x} \left[ E_y|_{x+\Delta x}^{t} - E_y|_{x-\Delta x}^{t} \right] 
\]
where $H_z |^t_x$ represents the value of the $H_z$ field component at time $t$ and position $x$ and so on. We see that the $H_z$ component of the magnetic field at $t + \delta t$ is determined by two $E_y$ values at adjacent spatial grid points at time $t$, and the value of $H_z$ at the same grid point at time $t - \delta t$. This relationship is illustrated in Fig. 3.1A in orange. Let us now step backwards in time to write two separate finite difference equations for the terms $E_y |^{t-\delta t}_x$ and $E_y |^{t+\delta t}_x$ in Eqn. 3.23. Using Eqn. 3.21, we may write

\begin{align}
E_y |^{t-\delta t}_x &= E_y |^{t-2\delta t}_x - \frac{\delta t}{\mu_0 \mu_r \Delta x} \left[ H_z |^{t-\delta t}_x - H_z |^{t-\delta t}_{x-2\Delta x} \right] \\
E_y |^{t+\delta t}_x &= E_y |^{t-2\delta t}_x + \frac{\delta t}{\mu_0 \mu_r \Delta x} \left[ H_z |^{t-\delta t}_x + H_z |^{t-\delta t}_{x+2\Delta x} \right].
\end{align}

These equations are visualised in Fig. 3.1A in green and pale blue. Taken together, Eqs. 3.23-3.25 suggest the Yee grid. We note that we may evolve the electric and magnetic fields in time by only storing half the total field information. Electric field components may be stored at even time grid points $(t - 2\delta t, t, t + 2\delta t$ etc) and odd spatial grid points $(x - \Delta x, x + \Delta x$ etc). Magnetic field components may be stored at odd time grid points and even spatial grid points. Together, enough information is stored to ‘leapfrog’ the fields forward in time, calculating the $E$ field and $H$ field at consecutive non-simultaneous time steps. By storing only half the field information, we can calculate central differences on the intervals $\delta t$ and $\Delta x$ with grids of effective spacing $2\delta t$ and $2\Delta x$. This translates to huge memory savings when applied to three-dimensional Yee grids.
The method has been generalised to three dimensions; a fully 3D Yee grid is shown in Fig. 3.1B. Each unit cell of the grid stores the 6 field components, each offset by a half a grid step. The Yee grid is also conveniently formulated to allow quick determination of the Maxwell curl equations. We see that any electric (magnetic) field component is both normal to and enclosed by a planar loop of magnetic (electric) field components; Fig. 3.1C highlights an electric field component and its associated magnetic field loop (red). The Yee grid thus facilitates the formulation of the integral form of Maxwell’s equations using finite differences. These integral formulations are extremely useful for formulating accurate material boundary conditions at sub-grid lengthscales\textsuperscript{128}.

The FDTD method is a vital tool in computational electrodynamics. It has been thoroughly researched and developed since Yee’s seminal 1966 paper. To write a fast, dependable and accurate FDTD implementation that addresses the many subtleties of numerical stability and boundary condition implementation is beyond the scope of this thesis. All FDTD calculations reported herein thus employ a commercial industry-grade FDTD solver by Lumerical Solutions Inc\textsuperscript{130}.

A typical FDTD experiment comprises a finite region of space whose edges obey user-determined boundary conditions. Common FDTD boundary conditions include periodic boundary conditions (PBCs) and perfectly matched layers (PMLs).

PBCs simulate an infinitely periodic domain in which the simulated region is taken as the unit cell. Radiation leaving one side of the domain simultaneously re-enters on the opposite side (with a phase difference if desired). PBCs thus allow the simulation of photonic crystals and other periodic arrays of scattering centres.

PMLs are a vital boundary condition that allow the simulation of ‘open’ domains, for instance a scattering centre in free space. We may define the impedance of a material of permittivity $\varepsilon_1$ and permeability $\mu_1$ as $Z_1 = \sqrt{\mu_1/\varepsilon_1}$. A wave incident on an interface between two materials will transmit perfectly without reflection when the materials’ impedances are matched ($Z_1 = Z_2$). The PML comprises a material that is both impedance matched to its adjoining region in the simulation domain and possesses a complex permittivity and permeability\textsuperscript{127}. Waves incident on a PML are thus unreflected, and decay exponentially with distance as they propagate through it. A thin layer of PML cladding can thus simulate an open region of space by allowing radiation to ‘escape’ without reflection.

Objects of interest are placed within the simulation domain and illuminated with a variety of electromagnetic sources; these sources are typically point-like radiating dipoles or finite plane wave sources. Monitors - user-defined sub-regions of the FDTD domain - may then be set-up to measure physical quantities of interest. FDTD solvers employ an impulse response method, in which the illuminating pulse $s(t)$ comprises a broad distribution of frequencies $s(\omega)$. Measured electric and magnetic fields are recorded as a function of time ($E(r, t)$), and then Fourier transformed on-the-go to determine the frequency response ($E(r, \omega)$). An impulse response may also be returned by dividing the frequency response $E(r, \omega)$ by the spectral amplitude $s(\omega)$ of the illuminating pulse. Monitors thus return spectral quantities, typically field eigenmodes $E(r, \omega)$ and $H(r, \omega)$ or transmitted powers $T(\omega)$. 
FDTD solvers are ideal tools for probing a system’s internal and near-field electromagnetic behaviour. Further, FDTD solvers can predict the electromagnetic fields far away from a system, well-outside the defined FDTD domain, through a far-field transformation post-processing step. To perform a farfield transform, a complete set of near-field electric and magnetic fields are recorded by encapsulating the sample in a three-dimensional monitor box. All fields inside the monitor box are then set to zero and the box is clad in a skin of imaginary electric and magnetic current sources that can account for the newly-created discontinuities in the magnetic and electric fields\(^{128,131}\). By the surface equivalence theorem, this set of sources completely reproduces the electromagnetic fields outside of the monitor box. Farfield properties may then be estimated by forming a vector potential, at all distant points of interest, through an integration over all the source terms.

### 3.3.2 Plane Wave Expansion Method

The plane wave expansion method (PWEM) is based on the expansion of the \(H\) field as a truncated Fourier series. The resulting solutions are thus periodic and are only physically meaningful if the underlying dielectric material distribution is itself periodic. We therefore consider an infinite photonic crystal which is built on a given Bravais lattice with lattice vectors \(R\). The distribution of dielectric material is thus invariant under translation by a lattice vector; we write \(\varepsilon_r(\mathbf{r} + \mathbf{R}) = \varepsilon(\mathbf{r})\).

From this we can infer that the solution for \(H(\mathbf{r})\) must take a specific form in accordance with Bloch’s theorem (Appendix B). We therefore propose a ‘Bloch wave’ solution to Eqn. 3.13 of the form \(H(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} \tilde{H}_{k,n}(\mathbf{r})\), where the function \(\tilde{H}_{k,n}\) has the same periodicity as the Bravais lattice and \(k\) is an arbitrary vector in reciprocal space. We apply the solution labels \(n\) and \(k\) with some foresight, as these labels will uniquely identify a particular mode. Making use of the periodicity of \(\varepsilon_r(\mathbf{r})\) and \(\tilde{H}_{k,n}(\mathbf{r})\) we may expand these functions as a Fourier series in the reciprocal lattice vectors. We write

\[
\varepsilon_r(\mathbf{r}) = \sum_{\mathbf{G}} \kappa(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}} \quad (3.26)
\]

\[
H(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} \tilde{H}_{k,n}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{H}_{k,n}(\mathbf{G}) e^{i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}} \quad (3.27)
\]

The magnetic field is thus represented as a linear combination of plane waves with wavevector \(\mathbf{k} + \mathbf{G}\). The Fourier coefficients \(\kappa(\mathbf{G})\) are known, given that we know the form of \(\varepsilon_r(\mathbf{r})\). We seek to establish the unknown Fourier coefficients \(\tilde{H}_{k,n}(\mathbf{G})\). Substitution of equations (3.26) and (3.27) into the eigenvalue problem (3.11), together with application of the general result that \(\nabla \times [\mathbf{v} e^{i\mathbf{k} \cdot \mathbf{r}}] = i(\mathbf{k} \times \mathbf{v}) e^{i\mathbf{k} \cdot \mathbf{r}}\) for some constant vector \(\mathbf{v}\), yields the relation

\[
-\sum_{\mathbf{G}'} \kappa(\mathbf{G} - \mathbf{G}')(\mathbf{k} + \mathbf{G}) \times [(\mathbf{k} + \mathbf{G}') \times \tilde{H}_{k,n}(\mathbf{G}')] = \frac{\omega_{k,n}^2}{c^2} \tilde{H}_{k,n}(\mathbf{G}). \quad (3.28)
\]
This is the master equation for the plane-wave expansion. We choose an arbitrary $k$ vector and must then solve an infinite linear system of equations in the $H_{k,n}(G)$.

At this point, we note that a given plane wave can exist in a variety of polarisation states. The polarisation dictates the direction of the vector $H_{k,n}(G)$, which must be allowed to explore all allowable polarisations. We thus represent $H_{k,n}(G)$ in a basis of linear polarisation states $\hat{e}_1,G$ and $\hat{e}_2,G$, where these two vectors are mutually orthogonal and span the null space of the wavevector $k + G$. The polarisation unit vectors obey the relation

$$\hat{e}_1,G \times \hat{e}_2,G = k + G |k + G| ,$$

and thus form a right-handed coordinate system with the wavevector. We express the Fourier coefficient in this basis as $H_{k,n}(G) = h_1,G \hat{e}_1,G + h_2,G \hat{e}_2,G$. By restricting the polarisation states such that they are orthogonal to the wavevector, we ensure that each plane wave component is divergence-free. In doing so, we satisfy the as-yet unaddressed Maxwell equation $\nabla \cdot H(r) = 0$.

Expanding the $H_{k,n}(G)$ in this manner in equation (3.28) we can derive that

$$\sum_{G'} \kappa(G - G') |k + G||k + G'| \left( \begin{array}{cc} \hat{e}_2,G' \cdot \hat{e}_2,G & -\hat{e}_1,G' \cdot \hat{e}_2,G \\ -\hat{e}_2,G' \cdot \hat{e}_1,G & \hat{e}_1,G' \cdot \hat{e}_1,G \end{array} \right) \left( \begin{array}{c} h_1,G' \\ h_2,G' \end{array} \right) = \frac{\omega_{k,n}^2}{c^2} \left( \begin{array}{c} h_1,G \\ h_2,G \end{array} \right).$$

Eqn. 3.30 may be solved computationally by employing a finite plane wave basis. We choose a basis set of $G$ vectors of size $N$. Eqn. 3.30 then describes a set of $2N$ equations for the $2N$ unknown Fourier coefficients $h_1,G$ and $h_2,G$. Having chosen an arbitrary reciprocal space vector $k$, these $2N$ equations can be expressed as a simple linear system of the form $\sum_{ij} M_{ij} h_j = h_i \omega_{k,n}^2 / c^2$, where $h_i$ is a vector of the unknown Fourier coefficients. The eigenvalues of $M_{ij}$ describe a ladder of permitted frequencies $\omega_{k,n}$, which we label with the ‘band index’ $n$ from lowest to highest frequency. The associated eigenvectors are the magnetic field distributions $H_{k,n}(r)$.

It is computationally very difficult to simultaneously determine all the eigenvalues of a large matrix. For high resolution calculations or calculations for a 3D photonic crystal, we may find that the matrix has several hundred thousand entries. Such a large matrix is difficult to calculate, manipulate and store. Instead, the PWEM is normally implemented using an iterative technique to find the eigenvalues and eigenvectors. Iterative techniques are a powerful means of determining the first few eigenvectors and eigenvalues of extremely large matrices.

Iterative methods do not require that $M_{ij}$ be calculated and stored explicitly. Instead, we require a routine that describes how $\hat{\Theta}_H$ operates on a vector. In the Fourier basis, the operation of $\hat{\Theta}_H$ is encapsulated by Eqn. 3.28. For a given $k$ vector, the ground state (smallest) eigenvalue may be found by a power iteration process or unconstrained conjugate gradient minimisation of the Rayleigh quotient. Subsequent eigenvalues and eigenvectors may then be found by minimisation of the Rayleigh quotient subject to the constraint that the eigenvector being iterated remains orthogonal to all eigenvectors so far found.
All PWEM calculations in this thesis are executed using the MIT photonic bands package (MPB for short). MPB employs an iterative process to solve for the eigenvectors of $\hat{\Theta}_H$ in blocks (i.e. several at a time). A typical MPB calculation proceeds as follows. First, the simulation geometry is defined. This comprises a set of basis vectors and an associated unit cell with an arbitrarily complex motif. A periodic boundary condition is applied along the unit cell edges, with the result that solutions correspond to the field modes of an infinite array of unit cells. Secondly, we specify important resolution parameters. These include the mesh size, which determines the accuracy with which the dielectric material distribution is discretised, and the resolution, which dictates the number of spatial grid points per unit cell on which the fields are resolved. Thirdly, we supply a set of $k$ vectors for which the corresponding ladder of eigenvalues and eigenvectors will be found. The eigensolver can then be run and the modes of the electromagnetic field determined.

3.4 Photonic Band Structure

The propagation of light through any arbitrary structure can be described through its dispersion relation. The dispersion relation is a function that links the wavevector $k$ in a material to the allowed frequencies of propagation $\omega(k)$ at that wavevector. In structured media, the dispersion relation can become extremely complex. In particular, it can reveal the presence of photonic band gaps which appear as frequency regions within which allowed field modes cannot be generated by any choice of $k$. The photonic band structure, which we may calculate easily using a PWEM method, is a means of presenting and visualising the dispersion relation $\omega(k)$.

Consider the plane wave expansion master equation (Eqn. 3.28). We can solve the equation for any reciprocal space vector $k$. We therefore expect each of the eigenvalues, for a given $k$, to vary continuously as a function of $k$. If the band index $n$ is fixed, we expect variation of $k$ to produce a continuous string of eigenvalues $\omega_{k,n}$ which may be interpreted as a section of the structure’s dispersion relation. It is natural to expect that, in order to obtain a complete dispersion relation, $k$ should be allowed to vary freely in reciprocal space. However, it transpires that it is necessary to consider only a subset of possible $k$ vectors. The Bloch theorem (Appendix B) dictates that a set of magnetic field modes $H_{k,n}(r)$, labelled with wavevector $k$, obeys the relation $H_{k,n}(r+R) = e^{ik \cdot R} H_{k,n}(r)$, where $R$ is a lattice vector. Translation of the mode through a lattice vector thus leads it to acquire a phase factor of $e^{ik \cdot R}$.

Consider now a new set of magnetic field modes whose wavevector is $k + G$. The Bloch theorem tells us that

$$H_{k+G,n}(r+R) = e^{i(k+G) \cdot R} H_{k+G,n}(r) = e^{ik \cdot R} H_{k+G,n}(r),$$

(3.31)

where we have used the fact that $G \cdot R = 2n\pi$ for integer $n$. Under translation, such modes acquire an identical phase factor to those identified by wavevector $k$. The field modes $H_{k,n}$...
and $H_{k+G,n}$ are thus closely related. In fact, the set of field modes identified by wavevector $k + G$ is a subset of all the modes which may be labelled by wavevector $k$. We conclude that, in order to obtain a complete dispersion relation, we need only solve for sets of field modes whose wavevectors lie in the first Brillouin zone. This is because any vector $k'$ that lies outside the first BZ may be mapped onto a vector in the BZ by addition of an appropriate reciprocal lattice vector.

Further, it can be shown that the dispersion relation $\omega(k)$ possesses the full symmetry of the reciprocal lattice point group. It is therefore sufficient to determine the dispersion relation within the smallest region of the BZ for which the $\omega(k)$ values are not related by a symmetry operation. This region of the BZ is called the irreducible BZ, or irreducible wedge. The complete dispersion relation for the first BZ may be assembled from the $\omega(k)$ within the irreducible wedge by suitably chosen symmetry operations.

It is important to remark that the propagation direction, that is the orientation of the Poynting vector, of a particular Bloch mode $H_{k,n}(r)$ is not necessarily parallel to the wavevector $k$. It can be shown that the relevant quantity in defining the mode’s propagation direction is the group velocity $v_g = \nabla_k \omega(k)$, where $\nabla_k$ is the gradient with respect to $k$. Further, for a photonic crystal comprising real-valued and dispersionless dielectric material, it can be proved that the group velocity is equal to the velocity of energy transport $v_e$. The velocity of energy transport is defined as the spatial average (over the unit cell) of the time-averaged Poynting vector divided by the spatial average (again, over the unit cell) of the time-averaged electromagnetic energy density. Accordingly, the group velocity points in the average direction of energy transport.

The dispersion relation, as presented in a band structure, is a useful tool for inferring the presence and size of photonic band gaps, but is a rigorous proof of neither. To present a readily interpretable band structure, the $k$ space path along which eigenfrequencies are calculated typically explores only the important high symmetry points of the BZ. However, a rigorous proof of the existence of a PBG should probe the whole $k$ space of the irreducible wedge to demonstrate that no single $k$ vector generates an eigenfrequency in the gap region.

Fortunately, it is true that, in most cases of interest, the maxima and minima of a given band in the band structure almost always occur at the high symmetry points of the BZ. From these maxima and minima an accurate measurement of PBG size can be made. A more thorough proof of the existence of a PBG can be made by formulating the density of states $\rho(\omega)$ (the DOS). The DOS counts the relative abundance of field modes as a function of frequency; it may be defined as

$$\rho(\omega) = \sum_n \int_{BZ} d^3k \ \delta(\omega - \omega_{k,n}),$$  

(3.32)

where the integration runs over all $k$ vectors inside the first Brillouin zone. To calculate the DOS, the first Brillouin zone is meshed and a complete set of eigenfrequencies $\omega_{k,n}$ is calculated, using an eigensolver, at each $k$ point of the grid. The numerical integration can then be performed using a linear triangle or tetrahedron method (in two and three-dimensions respectively).
Complete PBGs may then be identified by frequency regions within which the DOS is exactly equal to zero.

### 3.5 Photonic Band Structures and Band Gaps

In the sections that follow, a number of band structures for important photonic crystals are presented. I investigate further the example of a honeycomb structure, demonstrating the possible photonic band gaps for transverse electric and transverse magnetic polarisation states. The band structures of the 3D champion photonic crystal - rod-connected diamond - and the near-champion single network gyroid architecture are also presented.

#### 3.5.1 Honeycomb Networks

In solving for the modes of a 2D photonic crystal, such as honeycomb, by plane wave expansion, the permittivity $\varepsilon_r(r)$ is allowed to vary in the $xy$ plane and the dielectric distribution is extended to infinity along the positive and negative $z$ directions without any change in its transverse cross section. In such a structure, partial derivatives of field components with respect to the $z$ coordinate become zero. It can then be shown that the Maxwell equations decouple to form two separate systems. One system couples the field components $H_z$, $E_x$ and $E_y$ while the other system couples the $E_z$, $H_x$ and $H_y$ components; these systems are called the transverse electric (TE) and transverse magnetic (TM) polarisation states respectively.

More generally, the separation of the field modes into TE and TM polarisations is linked to mirror symmetries of the system. We may define a mirror operator $\hat{O}_P$ which reflects a vector field in the plane $P$ according to $\hat{O}_P E(r) = \hat{M}_P E(\hat{M}_P r)$, where $\hat{M}_P$ is an operator which reflects a vector in $P$. Mode separation occurs only for positions and Bloch modes which satisfy the conditions $\hat{M}_P r = r$ and $\hat{M}_P k = k$. For a 3D photonic crystal, these conditions can only be met for particular Bloch modes at position vectors in the plane $P$. In 2D, however, the $xy$ mirror plane extends through the system and these conditions are absolutely true. The TE and TM field modes are decoupled at every point in the structure and we must therefore solve for both polarisation states separately.

---

![Figure 3.2](image)

**Figure 3.2:** The first Brillouin zone of a triangular lattice (A) showing the irreducible wedge (red) and the high symmetry points. Structure of a honeycomb assembly of dielectric cylinders optimised to maximise the fundamental TM PBG (B). Structure of a honeycomb network of dielectric walls optimised to maximise the fundamental TE PBG (C).
Fig. 3.3 shows the photonic band structure for a honeycomb arrangement of dielectric rods ($\varepsilon_r = 13$) in air. This structure is shown in Fig. 3.2B. The $x$ axis shows the Bloch wavevector, which is allowed to vary along a $k$ space path from $\Gamma \rightarrow M \rightarrow K \rightarrow \Gamma$, where these points are the high symmetry points of the BZ (Fig. 3.2A). The $y$ axis shows the allowed mode frequencies for a given $k$ vector. The frequency is typically presented as a normalised frequency, $af/c$, where $a$ is the spacing between adjacent unit cells of the crystal and $c$ is the speed of light. We see that, at a given $k$ vector, the frequencies of the allowed modes describe a discrete ladder of energies according to the eigenvalues of Eqn. 3.28. The eigenfrequencies evolve smoothly with varying Bloch wavevector, thus forming continuous bands.

Fig. 3.3A shows that TM modes (blue) and TE modes (red) can display markedly different band structures. Further, two large frequency regions between TM bands $2-3$ and $7-8$ (both shaded blue) exist within which there are no TM bands; none of the $k$ vectors investigated generates TM modes with frequencies within these regions. These frequency regions are thus photonic band gaps. Within the gaps, the structure cannot support propagating TM electromagnetic excitations; the structure will act as a perfect reflector for any incident TM radiation.

The size of a photonic band gap is measured using a dimensionless width given by the absolute frequency span $\Delta \omega$ of the gap divided by the central frequency $\omega_0$. The gap between TM bands $2-3$ in Fig. 3.3A has a width of 31.2%, and the gap from bands $7-8$ has width 13.9%. Within a particular photonic crystal architecture, the size of the photonic band gap is determined by two factors. These are the refractive index contrast between the scattering distribution and the surrounding medium, and the specific spatial configuration of dielectric within the unit cell.
Figure 3.4: 'The champion' photonic crystal in 2D is a honeycomb array of dielectric pillars connected by thin walls (A). This structure overlaps the fundamental TE and TM band gaps of honeycomb networks and pillar arrays to form the largest known complete PBG in 2D (shaded blue, B).

Typically we find that no PBG exists until the index contrast reaches an architecture-dependent threshold value. Above this value, the size of the gap increase monotonically with increasing index contrast. Maximising the size of a PBG at a given (sufficiently-large) index contrast is then reduced to finding the optimum distribution of dielectric within the unit cell. The nature of an optimum dielectric distribution is a fundamental question within photonic crystals research which forms the core of the latter part of this thesis. For now, it is sufficient to note that the radius of the dielectric cylinders in the honeycomb presented here has been numerically optimised to maximise the size of the first TM PBG.

The first TM gap, however, exists only for TM modes. The gap region contains a number of TE bands, showing that the structure still supports propagating TE excitations. Band gaps can exist for a single polarisation state or both polarisations at once. The second TM gap exemplifies the latter of these. It overlaps a smaller TE band gap between TE bands 5 – 6 (unshaded). This region, of width 9.5%, is said to be a complete band gap, in which strictly no modes, neither TM nor TE, are supported by the structure.

Sticking to a honeycomb arrangement of dielectric, the unit cell decoration can be optimised to yield a very large PBG for TE polarised modes. The corresponding structure, shown in Fig. 3.2C, comprises a connected honeycomb network of dielectric. The width of the dielectric walls has been numerically optimised to maximise the first TE gap.

The corresponding band structure is shown in Fig. 3.3B. An extremely large PBG of width 56% is evident between TE bands 1 – 2 (shaded in red). As before, the TE and TM band structures are very different, and the first TE gap is incomplete.
Taken together, the band structures of Fig. 3.3 suggest that a large complete PBG might be engineered at low frequencies by hybridising the pillar and network structures. The resulting photonic crystal comprises a honeycomb array of pillars which are interconnected by a thin network of dielectric. The structure was first presented by Fu et al.\(^{27}\), who calculated that the size of the complete PBG may be maximised by choosing cylinder radii of 0.155a and wall thicknesses of 0.035a. This structure is shown in Fig. 3.4A.

Fu’s optimum array of dielectric pillars and connecting walls possesses a complete PBG for TE and TM polarisations of width 24\%\(^{27}\). The band structure for this architecture is shown in Fig. 3.4B and the complete PBG is shaded in blue. The complete PBG of the honeycomb pillar/wall array is the largest known complete PBG in a 2D structure\(^{27}\). I call it the ‘champion’ structure in two dimensions.

### 3.5.2 The Diamond Network

I now exemplify the diamond network - the most well known of all photonic crystals. The diamond structure is based on an FCC lattice with a 2-point motif. The recipe for constructing diamond may be expressed as:

\[
\begin{align*}
\text{Basis vectors} & \quad \text{Motif} \\
\mathbf{a}_1 &= a(\hat{x} + \hat{z}) \quad \text{Place vertices at } 0 \& (\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)/4. \\
\mathbf{a}_2 &= a(\hat{x} + \hat{y}) \quad \text{Join neighbouring vertices with cylinders.} \\
\mathbf{a}_3 &= a(\hat{y} + \hat{z})
\end{align*}
\]

Each primitive cell contains 2 crystallographically distinguishable vertices. Each vertex is connected to its four nearest neighbours by a cylinder of dielectric. The four cylinders about a given vertex point to the corners of a tetrahedron, and the angle between any pair of cylinders that meet at a vertex is therefore \(\cos^{-1}(-1/3) \approx 109.5^\circ\). The Wigner-Seitz cell, shown in Fig. 3.5A, is a rhombic dodecahedron containing a single tetrahedral unit. Stacking of the WS cell produces a rod-connected diamond network as shown in Fig. 3.5B.

The Brillouin zone of diamond, like any FCC-based crystal, is a truncated octahedron. The truncated octahedron, shown in Fig. 3.5C, is highly isotropic in the sense that its surface deviates very little from the surface of a sphere. The irreducible wedge is shown in red and its high symmetry points are labelled.

Unlike the 2D case, a general point in a 3D photonic crystal does not lie in a mirror plane of the structure. As a result, all field components \(E_x, E_y, E_z, H_x, H_y\) and \(H_z\) are coupled through the Maxwell equations. TE and TM polarisation states mix together and the modes found by plane wave expansion cannot be associated with a single polarisation.

The photonic band structure for a rod-connected diamond photonic crystal with \(\varepsilon_r = 13\) is shown in Fig. 3.6. The structure possesses a large photonic band gap (shaded in purple) of width 31.4\% between bands 2–3. The dielectric fill fraction, which is 18.2\%, has been optimised to maximise the size of the fundamental PBG.
Unlike a 2D photonic crystal, which possesses a PBG only for radiation propagating in the plane of the structure, a 3D photonic crystal supports no modes for all possible propagation directions. In this sense, the PBG of three-dimensional photonic crystals is truly complete. The prospect of a complete 3D photonic band gap is the phenomenon, postulated by Yablonovitch\cite{26} and John\cite{25}, which fired contemporary interest in photonic crystals. As discussed in the introduction, complete gaps in 3D photonic crystals have numerous applications including high Q-factor confinement of light at lattice defects, the guiding of light through arbitrarily shaped waveguides, control over spontaneous emission rates and as a means of probing the Anderson localisation of light. These functionalities are facilitated by large PBGs, and architectures which possess sizeable PBGs are therefore valuable.

Researchers have therefore sought to determine the optimum architecture for maximising the size of the complete 3D PBG. Many complete gap structures have been found, including Yablonovite\cite{135}, woodpile\cite{136} and inverse opal\cite{29}. Interestingly, a survey by Maldovan and Thomas in 2004\cite{92} demonstrated that all but one of the known large complete PBG structures were based on the diamond morphology. The single largest PBG was found in the rod-connected diamond architecture. More recently, a topological optimisation technique\cite{137} has been applied to solve for the optimum dielectric distribution within a specified space group symmetry. The technique makes no assumptions about the form of the dielectric distribution, which is free to explore arbitrary shapes and topologies within the specified symmetry. The largest single complete gap observed was nonetheless found in a rod-connected diamond architecture.

Overall, rod-connected diamond possesses the largest known complete PBG; it is thus known as the champion structure.

### 3.5.3 Single Network Gyroid

The diamond structure is the champion photonic crystal morphology, but not by a significant margin. A drastically different structure - that of single network gyroid - has been shown to
Figure 3.6: The band structure for a rod connected diamond network, fill fraction 31.4% and $\varepsilon_r = 13$. A large complete photonic band gap is evident (shaded in purple). This is the largest known complete photonic band gap; diamond is therefore the ‘champion’ structure.

possess a large and near-champion PBC. Here, the single network gyroid structure is presented, some of its geometrical properties are outlined, and its band structure is calculated.

Single network gyroid (SNG) is known by several other names throughout the physical sciences including K4, the Laves graph and the SRS net. Throughout this thesis, the structure is referred to as single network gyroid. This emphasises its fundamental connection to the triply-periodic gyroid surface (although they are distinct structures).

Figure 3.7: The single network gyroid Wigner-Seitz cell is a truncated octahedron containing four vertex points and a two complete trihedral units (A). It may be stacked to form a single network gyroid crystal (B). The Brillouin zone of the BCC lattice is a rhombic dodecahedron (C); the irreducible wedge is marked in red and high symmetry points are labelled.
SNG is based on a BCC lattice with a 4-point motif. The recipe for its construction may be expressed as:

<table>
<thead>
<tr>
<th>Basis vectors</th>
<th>Motif</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \mathbf{a}_1 = a(\hat{x} + \hat{y} - \hat{z}) )</td>
<td>Place vertices at ( 0 ), ( (\mathbf{a}_1 - \mathbf{a}_2)/4 ),</td>
</tr>
<tr>
<td>( \mathbf{a}_2 = a(\hat{x} - \hat{y} + \hat{z}) )</td>
<td>( \mathbf{a}_2 - \mathbf{a}_3)/4 ) &amp; ( (\mathbf{a}_3 - \mathbf{a}_1)/4 ).</td>
</tr>
<tr>
<td>( \mathbf{a}_3 = a(-\hat{x} + \hat{y} + \hat{z}) )</td>
<td>Join neighbouring vertices with cylinders.</td>
</tr>
</tbody>
</table>

The SNG Wigner-Seitz cell, shown in Fig. 3.7A, is a truncated octahedron which contains 4 vertices. When stacked to form a crystal, each vertex is surrounded by three-nearest neighbour vertices, separated from them by a distance of \( a/\sqrt{2} \). Connection of every vertex to its three nearest neighbours by a dielectric cylinder then generates the SNG photonic crystal shown in Fig. 3.7B.

The major geometrical features of the SNG structure can be summarised as follows. Each vertex and its three nearest neighbours describe a planar figure in which three edges, each of length \( a/\sqrt{2} \), converge at the central vertex. The angle between cylinders at the central vertex is 120°. This figure is referred to as a trihedron. The SNG structure comprises a network of connected trihedra, four of which may be resolved in Fig. 3.7A. Two connected trihedra are not coplanar; their two trihedral planes intersect at a dihedral angle of \( \cos^{-1}(-1/3) \approx 109.5° \).

The SNG Brillouin zone is a rhombic dodecahedron - the BZ of a BCC lattice, shown in Fig. 3.7C. The irreducible wedge is highlighted in red and the high symmetry points are labelled.

![Figure 3.8: The band structure for a rod connected single network gyroid photonic crystal, fill fraction 17.9% and \( \varepsilon_r = 13 \). The structure exhibits a complete photonic band gap (shaded in purple) of width 28.1%. Of the known complete PBG architectures, SNG possesses the second largest gap after diamond; it is the ‘near-champion’ structure.](image)
The photonic band structure for a SNG photonic crystal with $\varepsilon_r = 13$ is shown in Fig. 3.8. The structure possesses a substantial photonic band gap (shaded in purple) of width $28.1\%$ between bands 2 − 3. The dielectric fill fraction, which is $17.9\%$, has been optimised to maximise the size of the fundamental PBG. We note that, as in Fig. 3.8, the band structure should include the additional high-symmetry point $H'$. This point lies outside the first BZ along the $\Gamma \to P$ direction, and is exactly halfway to the next $\Gamma$ point along this axis. An accurate measurement of the stop-gap size along the $\Gamma \to P$ direction (the [111] axis) must consider this extended $k$-space path\(^{140}\).

The $28.1\%$ PBG in SNG compares favourably with the $31.4\%$ in rod-connected diamond. SNG is the only known photonic crystal architecture which comes close to achieving as large a PBG as diamond. This conclusion is supported by topological optimisation\(^{137}\), which concluded that SNG displays the largest PBG of a distinctly non-diamond-like architecture. The SNG photonic crystal is therefore referred to as ‘near-champion’.

### 3.6 PBG Origins - The Nearly-Free Photon Model

#### 3.6.1 The Quarter Wave Stack

To begin, consider the dispersion of a free photon travelling along the $x$ axis in a homogeneous dielectric of refractive index $n$. We artificially divide the medium into empty unit cells of length $L$ and infinite extent perpendicular to the $x$ direction.

We suggest a Bloch-wave solution for the $H$ field and solve Eqn. 3.28 to build a band structure. The eigenmodes $H_{k,n}(r)$ of the magnetic field operator are simply plane-waves which obey the linear one-to-one dispersion relation $\omega = ck/n$. This behaviour is completely represented by the Bloch exponent of Eqn. 3.27; the lattice periodic function $\hat{H}_{k,n}(x)$ is therefore everywhere equal to unity.

The first Brillouin zone corresponds to the region $-\pi/L < k_x < \pi/L$, although the dispersion relation will be symmetrical about $k_x = 0$ and so we may reduce the zone to $0 < k_x < \pi/L$. A band structure may be calculated for a $k$ space path from $0 \to \pi/L$; this result, for the case where the homogeneous medium is a vacuum, is shown in Fig. 3.9A. The band structure may be viewed as folding of the light-line $\omega = ck/n$ back into the first BZ by addition of a suitable $G$ vector.

We now consider perturbing the dielectric distribution of the medium. We specify the perturbation as a quarter-wave stack of period $L$, comprising two materials with refractive indices $n$ and $n'$, where $n' > n$. The material distribution in the unit cell of the stack may be written as

$$
\varepsilon_r(x) = \begin{cases} 
n^2 & : 0 < x < \Delta \\
n'^2 & : \Delta < x < L 
\end{cases},
$$

where $\Delta = Ln'/n + n')$. The band structures for a number of different quarter-wave stacks for differing index contrasts $n : n'$ are shown in Figs. 3.9 B-D. We focus first on the nearly-free
Figure 3.9: Band structures for a collection of quarter-wave stacks. With no index contrast, (A), the band structure is a folded light-line. A small index contrast of $1:1.01$ is sufficient to open a small PBG (B). Increasing the contrast to $1:1.1$ increases the size of the PBG (C). A large index contrast of $1:3.6$ strongly perturbs the free space dispersion relation and produces large PBGs (D).

The photon case, where the index contrast is low and the dispersion relation strongly resembles the free space situation.

Consider preparing the unperturbed system in a plane-wave state with wavevector $k_x$. The perturbation is then switched on by increasing the value of $n'$ by a small amount.

The eigenstates of the quarter-wave stack are not plane waves. The initial plane wave state will therefore scatter on the stack’s unit cell, acquiring extra momentum according to the possible momentum transfer vectors of the structure. These momentum transfers are given by the reciprocal lattice vectors $G = 2j\pi/L$, where $j$ is an integer. Once scattered, a number of plane wave states with wavevectors $k_{x,j} = k_x + 2j\pi/L$ will exist throughout the stack.

In the low index contrast case, scattering is insignificant for most $k_x$ within the first BZ. This is because the magnitude of the lowest order scattered wavevector $|k_{x,-1}|$ is significantly larger than $|k_{x,0}|$. This scattering process is therefore suppressed as the wavevector of the scattered state lies well outside the light-line $k = n'\omega/c$ of the high index dielectric. The initial plane wave state is weakly affected by the perturbation, and the dispersion for $k_x$ away from the BZ edge is therefore linear and free-space-like (Figs. 3.9B & C).

As $k_x$ approaches the BZ edge, however, scattering becomes significant. Consider specifically the BZ edge wavevector $k_{x,0} = \pi/L$. The dominant scattering processes produces plane waves with $k_{x,-1} = -\pi/L$. This is a counter propagating state with an identical spatial periodicity. The initial and scattered plane wave states will interfere to produce an amplitude distribution $\Phi(x,t)$, where $\Phi$ is of the type
The Photonic Band Gap

$$\Phi(x,t) = e^{-i\omega t} \left[ e^{i\pi x/L} \pm e^{-i\pi x/L} \right] = \begin{cases} 
2e^{-i\omega t} \cos(\pi x/L) & : + \\
2ie^{-i\omega t} \sin(\pi x/L) & : - \end{cases}.$$  \tag{3.36}

Note that the two resulting states are labelled with distinct eigenfrequencies $\omega_+$ and $\omega_-$. Interference between the counter propagating states therefore produces standing waves. As standing waves, these modes do not transport energy and therefore have zero group velocity ($\nabla_k \omega(k) = 0$). As a result, the dispersion relation begins to bend down, and its gradient is reduced to zero at the BZ edge (Figs. 3.9 C & D).

A further important effect occurs when $k_x$ lies at the BZ edge. The standing waves in the first band at the BZ edge have a period of $2L$ - exactly double the period of the lattice. The electromagnetic energy distribution of these waves, which is proportional to $E \cdot E^*$, therefore has period $L$. The energy distribution can thus align throughout the lattice to localise either inside the high index dielectric, or inside the low index material. The electromagnetic energy functional (Eqn. 3.19) shows that localisation of the energy inside the high dielectric minimises the associated mode frequency. Localisation inside the low dielectric, on the other hand, will maximise the frequency.

Let us say that the $\sin(\pi x/L)$-type standing wave localises the electric field energy density maxima in the high index dielectric material. Translation of this state by $L/2$ localises the energy density in the low dielectric, and transforms it into the $\cos(\pi x/L)$-type standing wave. The two standing waves thus have different eigenfrequencies where $\omega_- < \omega_+$. Therefore, not only does the dispersion relation become flat at the BZ edge, but two possible modes with two distinct eigenfrequencies exist. The spectral gap between these two states is the photonic band gap.

The evolution of the PBG can be tracked as the refractive index contrast is increased. In the free space case there is, of course, no scattering at the BZ edge and no PBG forms (Fig. 3.9A). Perturbation of free space to a quarter-wave stack with a small index contrast of 1 : 1.01 is sufficient to open up a small PBG (barely visible, shaded red in Fig. 3.9B). Increasing $n'$ further to 1.1 shows clearly the flattening of the dispersion relation at the zone edge (Fig. 3.9C). With increasing index contrast, the spectral gap becomes larger as predicted by the electromagnetic energy functional. This trend is evident even in a high-index $n' = 3.6$ stack (Fig. 3.9D).

This analysis of the quarter-wave stack is borne out when the eigenmodes at the BZ edge are visualised. Fig. 3.10 plots the electric field modes and associated time-averaged energy densities just below and above the PBG for a variety of index contrasts. For an index contrast of 1 : 1.01 (Fig. 3.10A & B), the eigenmodes of the stack are almost exactly plane waves. Below the gap (A), the energy density is localised in the high dielectric (dark blue), and above the gap it is localised in the low dielectric (lighter blue). The situation is similar for an index contrast of 1 : 1.1 (Fig. 3.10C & D), although the energy density deviates from that of a simple standing wave.

The process of PBG formation retains the same character even in the high index case (Fig. 3.10E & F). The eigenmodes are clearly no-longer plane waves. However, the modes remain zero group velocity standing waves which are mutually orthogonal, just like the nearly-free photon case.
The PBG originates from localisation of field in dielectric of low and high refractive index below and above the gap respectively.

To summarise, PBGs in the nearly-free photon case can be seen to arise from the formation of two non-degenerate standing wave states at the BZ edge. Standing waves result from the Bragg scattering of the eigenmodes of the unperturbed system, in which the plane waves acquire extra
momentum from the reciprocal lattice. For this reason, this mechanism of PBG formation is known also as the Bragg mechanism. The band below the PBG localises electromagnetic energy density in the high index dielectric and is often called the dielectric band, while the band above the PBG localises the energy in the low index material and is often called the air band.

3.6.2 Generalisation to Higher Dimensions

It was suggested by both Yablonovitch\textsuperscript{26} and John\textsuperscript{25} that a complete photonic band gap in a three-dimensional material might be achieved by a generalisation of the mechanism of gap formation in a one-dimensional stack. Specifically, a material in which the refractive index is modulated periodically in 3 non-co-planar directions will possess a 3D reciprocal lattice that should Bragg scatter photons travelling along any given direction in the structure.

Re-visiting the band structures of the diamond Fig. (3.6) and single network gyroid Fig. (3.8) photonic crystals, we observe the signatures of strong Bragg scattering at the edges of the PBG. Points of zero group velocity are associated with the high symmetry points of the BZ, where plane wave states with wavevector $k$ are Bragg scattered onto states with wavevector $-k$. The dispersion relation flattens as the mode becomes standing wave-like, and two non-degenerate states are created according to the localisation of the electromagnetic energy density with respect to the dielectric distribution. A complete gap is opened at a threshold index contrast when the stop gaps along each reciprocal lattice direction are sufficiently large to overlap.

Analysis of the concentration of the electromagnetic energy density below and above the PBG has shown that the dielectric and air band picture holds true in three-dimensional photonic crystals. It should be noted, though, that the dielectric and air band picture is not evidence that a PBG results from Bragg scattering. Rather, the formation of dielectric and air bands is a natural consequence of the presence of a PBG, as Eqn. 3.19 generally states that a spectral gap may be associated with a discrete change in the localisation state of the electric field. This therefore says little about the fundamental origin of the gap.

Nonetheless, I illustrate the dielectric and air band picture here by continuing the example of the 2D honeycomb photonic crystal. The TE band structure for an optimum honeycomb network of dielectric walls with $\varepsilon_r = 13$ is shown in Fig. 3.11. As for diamond and single network gyroid photonic crystals, the honeycomb bands show a zero group velocity at the BZ high symmetry points and thus suggest that Bragg scattering plays a role in the formation of the gap. Four PBG edge modes are labelled in the band structure. The corresponding time-averaged electric field energy densities are shown in the four panels to the right.

Beneath the gap at the $M$ point, the electric field energy density is strongly localised in the dielectric network (inset 1). At the $M$ point above the gap, the field, and as a result the energy density, are strongly excluded from the high index material; the eigenfrequency of the mode is therefore raised (inset 3). The dielectric and air band picture is evident too in electric field energy density below (inset 2) and above (inset 4) the gap at the $K$ point.
Figure 3.11: Illustration of dielectric and air bands in an \( \varepsilon_r = 13 \) honeycomb network. TE band structure (left) shows a large PBG; 4 modes are labelled. The corresponding time-averaged electric field energy densities for these modes (right hand panels) show energy localisation in high index and low index dielectric below and above the gap respectively.

3.7 PBG Origins - Mie Resonant Scattering

So far only photonic crystals - dielectric structures which can be built from a fundamental repeating unit - have been discussed. We may view their photonic band gaps as arising from the Bragg scattering of plane wave states with wavevectors at the BZ edge. In order for standing waves to reliably form, this Bragg scattering must be exact; the momentum transfer must precisely equal twice the negative of the initial wavevector. This is possible in structures whose reciprocal lattices comprise delta function like peaks. The Bragg mechanism would therefore appear to preclude the existence of PBGs in amorphous distributions of dielectric. Amorphous structures are typically characterised by an average inter-scatterer lengthscale \( L \), and therefore possess first Brillouin zone-like reciprocal space resonances at \( q = 2\pi/L \). These resonances are broad, and the momenta they may transfer to a photon in a Bragg scattering event take on a broad distribution about \( 2\pi/L \). This disfavours the formation of standing waves, which requires two counter propagating plane wave states with exactly opposite wavevectors.

The discovery of a complete TM PBG in a two-dimensional amorphous distribution of dielectric cylinders\(^{141}\) might therefore be seen as surprising. Since then, many complete TM PBGs have been observed in amorphous arrangement of cylinders, both quasi-random\(^{142}\) and hyperuniform\(^{62}\). The distribution of electric field energy densities in these amorphous photonic structures conforms to the dielectric and air band picture\(^{143}\); this observation, however, has no bearing on the fundamental mechanism of gap formation. Importantly, as amorphous materials with broad reciprocal space resonances, the PBG origin cannot be attributed to the Bragg scattering mechanism.
3.7.1 Single Cylinder Mie Resonances

An alternative mechanism of PBG formation - typically called the Mie scattering mechanism - has been presented to explain TM gap formation in amorphous structures. A brief outline of this process following Rockstuhl, Peschel and Lederer\textsuperscript{142} and van de Hulst\textsuperscript{144} is presented below.

Consider an infinitely long dielectric cylinder of radius $R$ and relative permittivity $\varepsilon_2$ oriented with its cylinder axis along the $z$ direction. The cylinder is embedded in a homogeneous dielectric of permittivity $\varepsilon_1$. Plane wave radiation, electric field $E_{\text{inc}}$ polarised along $z$ and of wavevector $k_0$, is incident on the cylinder. The fields of the system are decomposed into the incident field $E_{\text{inc}}$ and the scattered field $E_{\text{scat}}$.

In the vicinity of the cylinder, the incident plane wave may be expressed as a sum over cylindrical waves originating from the cylinder centre as

$$E_{\text{inc}}(r, \theta) = \sum_{m=-\infty}^{\infty} i^m J_m (\sqrt{\varepsilon_1 k_0 r}),$$  \hfill (3.37)

where $r$ and $\theta$ are the radial and polar coordinates in the incidence plane, $J_m$ the $m$-th Bessel function and $i^m$ a coefficient. The scattered field may be decomposed in a similar way. Inside the cylinder it is decomposed into Bessel functions. Outside the cylinder it is decomposed into Hankel functions, and we may write

$$E_{\text{scat}}(r, \theta) = \sum_{m=-\infty}^{\infty} a^m H_m (\sqrt{\varepsilon_1 k_0 r}),$$  \hfill (3.38)

where $H_m$ is the $m$-th Hankel function and $a^m$ are the so-called Mie coefficients. Application of the Maxwell boundary conditions at the cylinder surface - that is that the tangential $E$ and $H$ field components must be continuous across the interface - enables an analytical expression for the Mie coefficients to be deduced. We may write

$$a^m = -\frac{\sqrt{(\varepsilon_1)} J_m (\sqrt{\varepsilon_2 k_0 R}) J'_m (\sqrt{\varepsilon_1 k_0 R}) - \sqrt{(\varepsilon_2)} J'_m (\sqrt{\varepsilon_2 k_0 R}) J_m (\sqrt{\varepsilon_1 k_0 R})}{\sqrt{(\varepsilon_1)} J_m (\sqrt{\varepsilon_2 k_0 R}) H'_m (\sqrt{\varepsilon_1 k_0 R}) - \sqrt{(\varepsilon_2)} J'_m (\sqrt{\varepsilon_2 k_0 R}) H_m (\sqrt{\varepsilon_1 k_0 R})},$$  \hfill (3.39)

where the primed notation represents a derivative with respect to the radial coordinate. A Mie resonance of the cylinder is such that the scattered field has a large Mie coefficient. Mie resonances appear for a vanishing denominator in Eqn. 3.39 and may be identified by inspection of the cylinder’s scattering cross section or Mie efficiency.

The scattering cross section $\sigma$ is a general measure of the scattering efficiency of an arbitrary system. It is defined as

$$\sigma = \frac{P_{\text{scat}}}{I_{\text{inc}}},$$  \hfill (3.40)
where $P_{\text{scat}}$ is the total scattered power and $I_{\text{inc}}$ is the incident power intensity. $\sigma$ therefore has units of area in 3D and length in 2D and can be seen as a measure of the effective ‘size’ of the scattering centre. The Mie efficiency $S$ is then defined as

$$ S = \frac{\sigma}{G}, $$

where $G$ is the geometrical cross section of the scattering centre. The Mie efficiency is dimensionless and characterises how ‘large’ the scatterer is relative to its geometrical cross section.

Rockstuhl calculated the Mie efficiency analytically. Here an FDTD method is employed. After Rockstuhl, we define an imaginary cylinder separation $a$ and choose the radius to be $R = 0.2a$. This enables frequencies to be mapped onto the photonic band structure normalised frequencies $af/c$. We set the permittivities $\varepsilon_1$ and $\varepsilon_2$ to 1 and 13 respectively. We make use of the FDTD method to build on Rockstuhl’s analysis in the following ways. First, we place a monitor in the incident plane to observe the interaction of the plane wave with the cylinder. Second, we centre a 1D transmission monitor of length $a$ on the cylinder; the monitor is oriented perpendicular to $k_0$ so as to measure the transmitted power in the vicinity of the cylinder.

Results for the Mie efficiency and transmitted power are shown in Figs. 3.12A & B respectively. The Mie efficiency shows three clear scattering resonances. We may associate two major transmission minima (around $af/c$ values of 0.3 and 0.62) with the frequency regions immediately above the first two of the Mie resonances. Three frequencies are highlighted, and characteristic snapshots of the $E_z$ field corresponding to each of these frequencies are shown in the right hand panels.

Frequency 1 lies below the resonance of the fundamental Mie coefficient $a^0$. Incident and scattered fields are in phase at the cylinder surface and the plane wave propagates (from right to left) without significant distortion (Fig. 3.12, panel 1).

Frequency 2 sits slightly above the first Mie resonance. The analytical solution shows that, at a Mie resonance, the phase of the resonant amplitude coefficient $a^m$ of the scattered field changes by $\pi$ with respect to the corresponding coefficient $i^m$ of the illuminating field. Around the first resonance, the only non-zero Mie coefficient is $a^0$. Just above this resonance, the scattered field is in anti-phase with the dominant component of the incident field. The fields interfere destructively at the cylinder surface to produce a stationary field node (Fig. 3.12, panel 2). This field node inhibits wave propagation in the vicinity of the cylinder which can be seen as a corresponding minimum of the transmission. As the frequency increases, non-resonant scattering contributions from the second Mie coefficient $a^1$ become significant. These provide a pathway for the transmission of radiation past the cylinder and the transmission begins to rise.

Frequency 3 sits slightly above the resonance of the second Mie coefficient $a^1$. At this point, $a^0$ is still out of phase with $i^0$. A narrow frequency region exists within which $a^1$ is also out of phase with $i^1$. Again we see a corresponding transmission drop as the incident and scattered fields interfere destructively. This interference produces two stationary field nodes (Fig. 3.12, panel 3) - one at the cylinder surface and one cutting through its centre. The third Mie resonance,
around $af/c = 0.8$, does not inhibit transmission significantly; the lower-order Mie coefficients are off-resonance and provide a transmission pathway for the incident radiation\(^{142}\).

Fig. 3.13 presents a detailed picture of the fields and Poynting vectors around the cylinder for the three frequencies highlighted in Fig. 3.12. At frequency 1 (Fig. 3.13 columns 1 & 2), the plane wave passes through the cylinder with little distortion. A small amount of back-scattering is evident in the Poynting vector.

At frequency 2 (Fig. 3.13 columns 3 & 4), a field node, associated with a propagating nodal plane of the plane wave, is strongly localised at the cylinder surface throughout the majority of a cycle. The node must eventually advance (phase $5\pi/6$ to $\pi$); in so doing, the field drops to zero across the cylinder and the next plane wave nodal plane slides into place. Strong back-scattering is evident in the Poynting vector throughout the cycle. The propagation is mediated by a zeroth-order resonance of the cylinder, in which the field within the cylinder is everywhere in phase. At frequency 3, propagation is mediated by a first-order resonance in which the fields on opposite sides of the cylinder interior are out of phase. Some back-scattering, although not as strong as around the first Mie resonance, is evident.
The fields propagate from left to right with increasing phase (shown in the leftmost column).
3.7.2 Aperiodic Cylinder Ensembles

Consider now a TM plane wave incident on a finite but not-necessarily periodic array of dielectric cylinders. In the limit of a well-designed infinitely thick array, we expect that the transmitted power should drop to exactly zero for frequencies just above the first cylinder Mie resonance; the array would therefore possess a photonic band gap. For this reason, quasicrystalline\textsuperscript{65,67}, hyperuniform\textsuperscript{62} and quasi-random\textsuperscript{141,142} (random with a minimum separation condition) cylinder arrays have all been observed to possess TM PBGs.

The structural characteristics necessary for an aperiodic array to possess a TM PBG may be summarised as follows\textsuperscript{61,142}. First, the cylinders should not be too close to one another; it is helpful to impose a minimum allowed inter-cylinder distance. This condition ensures that electromagnetic modes of adjacent cylinders are weakly interacting and that their response may be modelled by the single cylinder Mie theory. Second, the array should be homogeneous and without voids. Large regions without a cylinder can support localised field modes. These modes can appear as defect states within the gap. If chained together in space, they can provide a pathway for light propagation through the structure.

Rockstuhl\textsuperscript{142} showed that the normalised frequency range over which the TM gap occurs is similar for crystalline, quasicrystalline and quasi-random structures. Specifically, the frequency of the lower gap edge is identical, but the gap begins to narrow from above as the disorder is increased. From this evidence, we conclude that the dominant mechanism of TM PBG formation is, in all cases, the Mie mechanism.

A comparative study of PBG spectral range is a useful way to determine a common PBG formation mechanism\textsuperscript{61,142}. However, signatures of the Mie mechanism may also be identified from the $E_z$ component of the field eigenmodes around the PBG. I exemplify this by analysing the field distributions of two hyperuniform cylinder arrays. In both cases, eigenmodes were calculated for cylinders of permittivity $\varepsilon_r = 13$ using the MIT photonic bands package\textsuperscript{79}.

We consider first a cylinder array derived by decoration of a $\chi = 0.6$ hyperuniform point pattern. Two $E_z$ distributions below the PBG are shown in Fig. 3.14A & B. Panel A shows a mode a little below the gap, while panel B shows a mode at the lower gap edge. Both modes are characterised by wave propagation mediated by a zeroth-order Mie resonance; the field is strongly localised on the cylinders, and field nodes occur near the cylinder edge. The field distribution around each cylinder is therefore similar but not identical to that of frequency 2 in Fig. 3.12. The regime of strong field node localisation at the cylinder surface cannot be accessed in MPB as this would correspond to finding an eigenmode in the PBG.

Two $E_z$ distributions above the PBG are shown in Fig. 3.14C & D. Panel C is a little above the gap, while panel D is at the upper gap edge. Compared to the modes below the gap, we observe a distinct change in the localisation character of the electric field. Propagation is now clearly mediated by the first-order Mie resonance, in which fields on opposite sides of the cylinder are in antiphase.
Microwave transmission experiments have shown that, in a disordered PBG structure, photon transmission is highly diffusive around the PBG edge and photon mean free paths are correspondingly short. Transport is mediated by modes of finite spatial extent, and photons propagate by hopping diffusively between modes. Panels B and D, in which the field is localised within small regions of the structure, are therefore typical of field modes at the gap edges.

\( E_z \) field profiles around the gap edges in a second, more disordered, hyperuniform structure tell a similar story (Fig. 3.15). The structure comprises cylinders of permittivity \( \varepsilon_r = 13 \) located at the point positions of a \( \chi = 0.49 \) hyperuniform design. This design possesses a more diffuse total scattering structure function than the \( \chi = 0.6 \) structure; the positional correlations between cylinders are less well-defined and this is reflected in the reduced structure of the field profiles.

In spite of this increased disordered, the fingerprints of the Mie mechanism are clearly evident. As before, panels A and B show a delocalised and localised mode below and at the gap edge respectively. The field propagation just below the gap is clearly mediated by a zeroth-order Mie resonance of the cylinders. Panels C and D show a delocalised and localised mode above the gap.
A typical delocalised mode (somewhat below the gap, A) and localised mode (at the lower gap edge, B) show propagation mediated by the zeroth-order Mie resonance. A delocalised mode (a little above the gap, C) and a localised mode (at the upper gap edge, D) show a distinct change in field localisation character and a transition to propagation mediated by the first-order Mie resonance.

Here, field propagation is clearly mediated by the first-order Mie resonance channel, evident in the field node that passes through the cylinder centres.

### 3.8 The Generalised Resonant Scattering Mechanism

The Mie and Bragg mechanisms can account for photonic band gap formation in a wide variety of structures. The Bragg mechanism is relevant to structures of arbitrary dielectric configuration so long as they have delta function-like structure factors. The Mie mechanism explains the formation of TM PBGs in both periodic and aperiodic cylinder arrays as a result of Mie resonant scattering by the fundamental scattering centres.

PBGs in amorphous network architectures, however, pose a problem. Such structures have been produced in 2D by application of a Delaunay tessellation protocol to hyperuniform and quasicrystalline point patterns and have been shown to possess sizeable TE band gaps. In three dimensions, only a single truly amorphous complete PBG structure is known.
structure is called photonic amorphous diamond (PAD). PAD structures may be derived from continuous random network models of amorphous silicon by connecting neighbouring atoms with dielectric cylinders.

The problem is as follows. First, the total scattering structure functions of amorphous networks are relatively diffuse; the broad first Brillouin zone-like resonance does not provide the concentrated momentum transfer needed to favour standing wave formation. Second, the scattering centres correspond to low-symmetry vertices where the dielectric cylinders meet. They cannot be modelled by the Mie theory, which is applicable only to scatterers with spherical and circular symmetries, and no analytical solution for scattering centres of lower symmetry is known to exist.

In spite of this, compelling evidence exists to show that Mie-like resonant scattering processes occur when light interacts with the fundamental scattering centres of a connected network. By analogy to the 2D TM case, a TE PBG (in 2D) or a complete gap (in 3D) might be engineered in an amorphous network by connecting the fundamental scattering units to form a continuous random network. In the following section I explore resonant scattering in a fundamental network unit of the honeycomb photonic crystal using an FDTD method. Characteristic field profiles may be associated with this generalised resonant scattering, and these field profiles identified in amorphous TE PBG networks.

### 3.8.1 Resonant Scattering by Network Vertices

Consider a honeycomb network of dielectric walls. A sensible choice for the network’s fundamental scattering unit is the set of all walls and vertices within 2 edges of a given vertex. This unit, which I call a 2-tree, is shown in outline in panel 1 of Fig. 3.16. I define an imaginary unit cell length $a = \sqrt{3}L$, where $L$ is the length of each cylinder in the 2-tree; this allows frequencies to be compared with the normalised frequencies of existing honeycomb band structures. I set the 2-tree permittivity to $\varepsilon_r = 13$, the cylinder radius to the optimum value for a TE PBG as in Fig. 3.3B, and repeat the FDTD experiment of section 3.7.1 using a TE polarised plane wave source. In this case, the transmission monitor is centred on the 2-tree central vertex and has width $2a$.

The Mie efficiency of the 2-tree, which has geometrical cross-section $2a$, is shown in Fig. 3.16A. The corresponding transmitted power through the monitor is shown in Fig. 3.16B. Like the cylinder, the 2-tree shows several distinct peaks in its Mie efficiency which are associated with the tree’s scattering resonances. The transmission shows a pronounced dip around $af/c = 0.4$. Just as in the cylinder case, this appears to be associated with a frequency region which extends from the peak of the first scattering resonance (annotation 1) to the shoulder of the second scattering resonance (annotation 3). Representative snapshots of the $H_z$ field profiles are shown for the three annotated frequencies. These three frequencies are chosen to characterise the field modes at the edges and exact centre of the transmission minimum.

The $H_z$ field snapshot at the transmission dip lower edge (panel 1) is characterised by two well-defined nodes localised in the dielectric. These nodes follow precisely the zig-zag pattern of the dielectric distribution; these zig-zags form the (11)-type Miller planes of the honeycomb
network (as in Fig. 2.5B) and are hereafter called (11)-bands. I call the mode in panel 1 the ‘cell’ mode by the manner in which the 2-tree air cells are fully filled with field.

The field snapshot at the transmission minimum (panel 2) is similar to the cell mode, although the field fills the 2-tree air cells somewhat less effectively. The nodes are similarly located but are less well defined; they do not cleanly bisect the (11)-band as in the cell mode.

The $H_z$ field at the transmission dip upper edge (panel 3) preferentially localises in the dielectric (11)-band. The nodes cut perpendicularly through the dielectric walls which link adjacent and parallel (11)-bands. This mode is referred to as the ‘stripe’ mode by the manner in which the (11)-band is clearly highlighted by the field localised inside it.

These three field modes are visualised in detail in Fig. 3.17, which presents $H_z$ and the Poynting vector parallel to $k_0$ for a number of snapshots throughout half a field cycle. The nature of the cell and stripe modes is clear here. The cell mode consistently localises $H_z$ in the dielectric (11)-band (the node cleanly bisects the dielectric) and the air cells are generally completely filled with field. The stripe band generally illuminates the (11)-band in a single colour demonstrating consistent localisation of $H_z$ in the dielectric throughout a cycle. Both modes show clear back-scattering in their associated Poynting vectors.
The fields propagate from left to right with increasing phase (shown in the leftmost column). The mode at the centre of the transmission dip ($af/c = 0.4$, central two columns Fig. 3.17) is difficult to categorise by its field distribution. Its Poynting vector, however, is very distinctive. Strong back-scattering in the vicinity of the 2-tree is apparent throughout the cycle. Close inspection shows that, at a given point along the leading edge of the 2-tree, the Poynting vector oscillates smoothly between flux to the right (gold) and flux to the left (green). This indicates that a local standing wave has been formed. This standing wave inhibits propagation through the 2-tree and explains the significant transmission minimum at this frequency.

It must be stressed that the scattering resonances of the 2-tree are not Mie resonances. Rather,
they are a generalised type of resonant scattering in the Mie regime ($\lambda \approx$ scattering centre size). The behaviour of the two tree, however, is directly analogous to the single cylinder case. The frequency region immediately above the first scattering resonance is associated with a significant transmission minimum. The field mode at the centre of this dip is a standing wave localised in the vicinity of the 2-tree. Field profiles above and below the transmission minimum may be characterised as ‘cell’ modes and ‘stripe’ modes by their characteristic field localisation states.

Figure 3.18: Characteristic TE PBG-edge $H_z$ profiles for a $\chi = 0.6$ hyperuniform disordered honeycomb. A typical delocalised mode (somewhat below the gap, A) and localised mode (at the lower gap edge, B) show strong localisation of field nodes near cylinder edges. A delocalised mode (a little above the gap, C) and a localised mode (at the upper gap edge, D) show a distinct change in localisation character; field nodes now penetrate the cylinder centres.
3.8.2 Resonant Scattering in Continuous Random Networks

Just as in the case of aperiodic cylinder architectures, we may analyse the field modes around the TE PBG in random network architectures and identify fingerprints of the generalised resonant scattering mechanism. Here, I focus on the two $\chi = 0.6 & 0.49$ hyperuniform structures from section 3.7.2. Specifically, their centroidal tessellations are constructed to produce a continuous random network of trivalent scattering centres. I refer to networks of this type, be they hyperuniform, random or quasicrystalline, as disordered honeycombs. The eigenmodes of these structures were calculated for the TE polarisation using the MIT photonic bands package.

Fig. 3.18 shows a selection of $H_z$ field profiles below and above the TE PBG. Panels A and B show modes a little below and at the lower gap edge respectively. Both modes can be clearly identified as cell-type modes; the field is strongly localised in the honeycomb air cells and the field nodes perfectly bisect the dielectric (11)-bands. Panels C and D show modes a little above and at the upper gap edge respectively. Now both modes may be identified as stripe-type modes; the field is consistently localised in parallel stripes corresponding to the (11)-bands of dielectric.

In the spectral region between the cell and stripe modes of Fig. 3.18 lies the photonic band gap. No eigenmodes exist in this region and so plane wave expansion yields no fields to visualise. However, by analogy with the behaviour of an isolated 2-tree, I suggest that the PBG is formed as a result of simultaneous resonant scattering by all the component 2-trees of the network. Each 2-tree strongly inhibits the propagation of light by forming a localised standing wave. This resonant scattering behaviour spans a significant frequency range and opens a sizeable spectral gap between the two permitted propagation pathways.

The generalised resonant scattering mechanism of PBG formation is equally applicable as the level of network disorder increases. Fig. 3.19 shows characteristic PBG edge $H_z$ field profiles for the $\chi = 0.49$ hyperuniform disordered honeycomb. As before, the modes below the gap (panels A & B) are cell-type modes. The modes above the gap (panels C & D) are stripe-type modes. The field distributions are less well-ordered than in the $\chi = 0.6$ case, but they nonetheless show the characteristic field localisation properties of cell and stripe modes.

On cursory inspection, Figs. 3.18 & 3.19 could be interpreted as evidence that the dielectric and air band picture is not applicable to disordered honeycombs. The figures, however, present the $H_z$ field component while the electromagnetic energy functional is formulated in terms of the electric field energy density. Calculation of a field concentration factor for hyperuniform disordered honeycombs shows that, as for the crystalline honeycomb in Fig. 3.11, the dielectric and air band picture accounts for the spectral gap between cell-type and stripe-type modes.

To conclude, I have shown that the basic scattering unit of a honeycomb network - the 2-tree - possesses a number of scattering resonances for TE polarised light. The formation of a standing wave mode in the vicinity of the 2-tree occurs in the spectral region above the first scattering resonance. This local standing wave strongly inhibits the propagation of light in the neighbourhood of the scatterer. Structurally deformed 2-trees may be connected to form continuous random networks which possess sizeable TE photonic band gaps. The gap edge modes correspond to extended cell-type and stripe-type modes which stem from the modes of
Figure 3.19: Characteristic TE PBG-edge $H_z$ profiles for a $\chi = 0.49$ hyperuniform disordered honeycomb. Panel A shows a typical delocalised mode somewhat below the gap and panel B shows a localised mode at the lower gap edge. Panel C depicts a delocalised mode a little above the gap and panel D a localised mode at the upper gap edge.

an isolated 2-tree. Light propagation below the PBG is mediated by cell modes and propagation above the gap is mediated by stripe modes. These characteristics of the generalised scattering resonance mechanism parallel the Mie mechanism of PBG formation in aperiodic cylinder arrays.

### 3.9 Conclusions

This chapter has introduced a number of important theoretical concepts and approaches in the analysis of structured dielectric media and photonic band gaps. The Maxwell equations in systems comprising dielectric materials with real-valued permittivities were presented. In particular, the equations may be formulated as a Hermitian eigenvalue problem for the magnetic field $\mathbf{H}(r)$. From this, field eigenmodes are intimately linked to the electromagnetic energy functional (via the Rayleigh quotient). Specifically, when $\mathbf{H}(r)$ is an eigenmode, the functional is both stationary and takes the value $\omega^2/c^2$. From the form of the electromagnetic energy functional, low frequency eigenmodes are expected to concentrate their electric field energy density inside high-permittivity dielectric material while high frequency eigenmodes will leak electric field energy density into regions of lower permittivity.
Complete solution of the Maxwell equations is usually only possible computationally. Here, I presented overviews of numerical solution paradigms based on the plane wave expansion method (PWEM) and the finite difference time domain (FDTD) method. The PWEM is an indispensable frequency-domain approach to calculating the dispersion relations of periodic media. In the PWEM, the magnetic field is expanded as a truncated Fourier series; expansion coefficients may then be determined using standard linear algebra techniques or by minimisation of the Rayleigh quotient. The FDTD method, on the other hand, solves the Maxwell equations in the time domain and calculates spectral quantities via Fourier transform. FDTD is an extremely versatile method which can be used to calculate a multitude of observable quantities including electric and magnetic field profiles, transmission spectra and farfield radiation patterns. Both the PWEM and FDTD methods are used widely throughout this thesis.

In accordance with Bloch’s theorem, eigenmodes of a photonic crystal may be labelled with a Bloch wavevector \( \mathbf{k} \) that is drawn from the first Brillouin zone. For each Bloch wavevector, there exists a discrete energy ladder of eigenmodes which may be labelled with a band index \( n \). Continuous variation of an eigenmode’s \( \mathbf{k} \) gives rise to smooth variation in its eigenfrequency \( \omega_{k,n} \). By varying \( \mathbf{k} \), it is possible to construct a set of dispersion relations \( \omega_{k,n}(\mathbf{k}) \) and plot these curves as a band structure. Having constructed band structure for a \( \mathbf{k} \) space path around the BZ irreducible wedge, photonic band gaps may be identified as frequency regions within which no photonic bands exist. More rigorously, PBGs correspond to absolute zeros of the density of states.

PBGs were illustrated for three well-known photonic crystal architectures. A honeycomb architecture comprising dielectric cylinders, connected by thin dielectric walls, exhibits the largest complete PBG of all known two-dimensional structures. Further, distinct honeycomb architectures comprising only cylinders and only dielectric walls are known to exhibit sizeable PBGs for TM-polarised and TE-polarised radiation respectively. In three dimensions, no photonic crystals are known to possess a PBG larger than that of the rod-connected diamond architecture; diamond is therefore known as the champion structure. The rod-connected single network gyroid (SNG) structure exhibits a complete PBG that is almost as large as that of diamond; SNG is thus a near-champion structure.

Conventionally, PBGs in photonic crystals are understood to form as a result of standing wave formation due to Bragg scattering. This process is most easily understood in the nearly-free photon limit where dielectric contrasts are low and eigenstates are plane wave-like. At the Brillouin zone edge, plane wave states are scattered onto a counter-propagating equivalent. As a result, zero group velocity standing waves form. These standing waves have lattice periodicity and can exist in low and high energy states depending on their energetic interaction with the dielectric distribution; the spectral gap between the two states defines a PBG.

PBGs are also understood to form by a Mie scattering mechanism in the specific case of planar dielectric cylinder arrays. Analytical solution of the Maxwell equations shows that a single cylindrical scatterer exhibits a number of Mie resonances. Just above the first TM Mie resonance, scattered and incident fields are in anti-phase at the cylinder surface; a localised standing wavefront, which inhibits propagation through the scatterer, is thus formed. This behaviour was confirmed using an FDTD method. The PBG-edge electric field profiles of dielectric cylinder
arrays illustrate the significance of the Mie mechanism. Both above and below the gap, the propagation of light is mediated by eigenmodes which resemble a linear combination of the Mie modes of an isolated cylinder. The PBG marks a transition from zeroth- to first-Mie-resonant character and results from the suppression of propagation by localised standing wave formation at frequencies just above the first Mie resonance.

Further, I used an FDTD method to show that a primitive structural unit - a 2-tree - of a honeycomb network exhibits, for TE radiation, resonant scattering behaviour that is analogous to the Mie scattering of TM radiation by a single cylinder. This behaviour is characterised by the formation of a localised standing wavefront that inhibits propagation through the scatterer. Standing wave formation occurs for a range of frequencies just above the first scattering resonance of the 2-tree’s Mie efficiency. Crucially, the characteristic field distributions of an isolated 2-tree are observed in the PBG-edge magnetic field profiles of disordered honeycomb networks; these modes can be described as cell-type and stripe-type below and above the PBG respectively. The electromagnetic properties of isolated 2-trees thus appear to be preserved when they are coupled together in an extended network; in particular, localised standing waves will form at frequencies between the cell-type and stripe-type modes. In the absence of Bragg scattering, PBG formation in disordered honeycombs is thus attributable to generalised resonant scattering by the structural units of the network.
Chapter 4

Unfolding the Photonic Band Structure

4.1 Band Structure in Aperiodic Media

Band structure is an extremely useful means of characterising the dispersion of light in a complex periodic structure. Of foremost relevance to this thesis, calculation of a material’s dispersion relation $\omega(k)$ is an indispensable tool for investigating the existence of photonic band gaps. Beyond this, $\omega(k)$ can be employed to explain the anomalous interaction of light with photonic crystals\(^{145}\). Such effects include the superprism effect\(^{146}\) and negative refraction\(^{147}\), and may be harnessed to engineer devices with advanced optical processing functionalities.

The key assumption of band structure, however, is that the structure under consideration is translationally periodic. Band structure diagrams of $\omega$ versus $k$ require that a given mode may be characterised by its Bloch wavevector $k$. Specifically, the Bloch wavevector describes the phase acquired by an eigenstate when it is translated through a lattice vector $R$. Consider a translation operator $\hat{T}_R$ which translates a vector field through a lattice vector $R$. It can be shown (Appendix B) that the action of the translation operator on a Bloch state $H_{k,n}(r)$ may be written as

$$\hat{T}_R H_{k,n}(r) = e^{i k \cdot R} H_{k,n}(r). \quad (4.1)$$

A Bloch state is, therefore, an eigenstate of the translation operator. The eigenvalue $e^{i k \cdot R}$ describes the relative phase difference between the Bloch state at positions $r$ and $r + R$.

Consider now the magnetic field operator $\hat{\Theta}_H$ of Eqn. 3.11. It is easily shown (Appendix B) that the commutator $[\hat{\Theta}_H, \hat{T}_R] = 0$. The magnetic field and translation operators thus share the same set of eigenstates - the Bloch waves. The Bloch wavevector $k$ is therefore a constant of motion for a given Bloch wave; $k$ is a good quantum number with which a Bloch state may be labelled. Band structure, as applied to a periodic medium, must therefore be interpreted as a correlation...
Modelling complex aperiodic media, which inherently lack any true periodicity, appears therefore to render existing Bloch wave eigensolvers useless. However, such eigensolvers can nonetheless be applied to aperiodic media if an artificial periodicity is imposed. The method, called the supercell method, is based on the modelling of complex disordered media using large periodic unit cells. Such a unit cell, usually called the super cell, contains a complex material decoration that models the aperiodic material over some large finite lengthscale $L_{SC}$. The supercell is constructed using a periodic boundary condition such that the electromagnetic fields may be expressed in a plane wave basis (Eqn. 3.27). Supercells can be very effective models of aperiodic media in the limit of large $L_{SC}$. Specifically, any spurious electromagnetic modes associated with the artificial periodicity will have periods comparable to, or greater than, the supercell lengthscale $L_{SC}$. For large supercells, these spurious modes thus possess low normalised frequencies and exist below the typical energy scales of interest.

Once an effective supercell has been designed, Bloch wave eigensolvers can then easily be applied. The eigenmodes become Bloch waves of the form $e^{i k_{sc} \cdot r} \hat{H}_{k_{sc},n}(r)$, where the Bloch wavevector $k_{sc}$ is now restricted to the first Brillouin zone of the supercell. A major problem arises, however, due to the small size of the supercell first Brillouin zone; it occupies a region in $k$ space of characteristic lengthscale $2\pi/L_{SC}$. The dispersion relation $\omega(k_{sc})$ is compressed into a small region of the $k$ space and becomes highly ‘folded’ and difficult to interpret.

Fig. 4.1 illustrates how a band structure folds when the supercell method is applied. Consider representing a quarter-wave stack using an artificial supercell comprising 4 single unit cells, each of unit length. The irreducible BZ of the supercell thus spans the domain $0 < k_{sc} < \pi/4$, making it one quarter the size of the first BZ of the structure’s primitive cell. Fig. 4.1A shows the dispersion relation for the primitive cell, while Fig. 4.1B shows the folded supercell
relation. Interpretation of the folded relation, beyond establishing the frequencies of any photonic band gaps, is naturally difficult. Matters becomes progressively worse as larger supercells are employed. A typical supercell TE band structure for a hyperuniform disordered network is shown in Fig. 4.1C. The $k$ space path runs from the $\Gamma$ to $X$ points in the supercell Brillouin zone. The band structure is highly folded, and is impossible to interpret beyond reading off the PBG position.

Efforts have therefore been made to untangle the complex band structures of large supercells; this process is usually called ‘unfolding’. Unfolding of the dispersion relation of hyperuniform photonic structures has been attempted experimentally. The method applies a microwave transmission technique to establish the phase $\phi$ acquired by a wave propagating through the structure. Accounting for the sample size, this phase may then be related to a Bloch-like vector $k$ to produce unfolded dispersion relations. Unfolding has also been attempted in analogous electronic systems in which the objective is to determine the dispersion relation $E(k)$ for the energy levels of electrons in the material. The folded band structures may be unfolded into an arbitrarily chosen extended Brillouin zone (EBZ) by performing overlap integrals to determine the ‘Bloch character’ of a given mode of the supercell.

The unfolded band structures that result from these methods seek to preserve the infinitesimally thin bands of a quantum number correlation plot. Such an approach maintains a close connection with the idea that a single Bloch-like wavevector is an effective means of characterising an eigenmode in an aperiodic system. In reality, however, this is not strictly true.

Consider again a translation operator $\hat{T}_r$ which translates a vector field by a vector $r$. In a truly aperiodic structure, any given eigenmode will never be an eigenstate of the translation operator. The translation operator possesses no eigenmodes and no eigenvalues; accordingly, it is not possible to define a Bloch wavevector. Strictly speaking, the dispersion relation $\omega(k_B)$, where $k_B$ refers specifically to a Bloch wavevector, does not exist. Indeed, this reality has been acknowledged and is understood to lead to band broadening effects; a single wavevector $k$ no longer generates a discrete set of possible eigenfrequencies and instead produces a continuous distribution. Unfolding the band structure of complex media thus remains an outstanding problem which has not yet been satisfactorily addressed. A novel, useful unfolding method should aim to achieve several things. First, it should not rely heavily upon any notion of Bloch-like character. The unfolded dispersion relations must naturally deal with the band broadening associated with aperiodicity. Second, the method should not restrict the unfolding vector $k$ to an effective Brillouin zone. The EBZ implies a periodicity of the dispersion relation in the $k$ space which will, in the general case, never exist. The unfolding vector must instead be allowed to range freely throughout reciprocal space. Finally, the method should ideally be simple, requiring little complex data analysis to arrive at the desired dispersion relation.
4.2 Unfolding Preliminaries

In order to move to a generalised band structure for aperiodic materials, it is useful to understand in detail the nature of the Bloch wavevector $\mathbf{k}$. I now elucidate this.

It can be shown (see Appendix C) that the Maxwell equations may be written in a Hamiltonian form. Specifically, a position-dependent Hamiltonian operator $\hat{H}$ can be defined such that the Maxwell curl equations take the form

$$\hat{H}|\mathbf{E}, \mathbf{H}\rangle = \omega|\mathbf{E}, \mathbf{H}\rangle,$$

(4.2)

where $|\mathbf{E}, \mathbf{H}\rangle$ is a six component vector, time-harmonic with frequency $\omega$, which describes the state of the electromagnetic field at time $t$ and position $\mathbf{r}$. Eqn. 4.2 describes the time evolution of the electromagnetic field and is formally analogous to the Schrodinger equation ($\hat{H}|\psi\rangle = E|\psi\rangle$).

Consider now a photonic crystal described by a position dependent relative permittivity $\varepsilon_r(\mathbf{r})$ which is periodic under translation through the lattice vectors $\mathbf{R}$ of a Bravais lattice. We introduce also a translation operator $\hat{T}_\mathbf{R}$ whose action on a vector field is to translate it through a lattice vector $\mathbf{R}$.

It is easily shown (see Appendix C) that the translation operator commutes with the photonic crystal Hamiltonian. The translation operator and the Hamiltonian thus share a common set of eigenstates - these are the Bloch waves. Further, when operating on a Bloch wave, eigenvalues of the translation operator take the form $e^{i\mathbf{k}\cdot\mathbf{R}}$ (Eqn. 4.1). The translation operator’s zero commutator with the Hamiltonian ensures that these eigenvalues remain constant as the electromagnetic field evolves in time. The Bloch wavevector $\mathbf{k}$ is therefore a constant of motion; it is an effective quantity with which to label solutions to the Maxwell eigenvalue problem (Eqn. 4.2).

The Bloch wavevector, however, is more than just a label. A Bloch state of the magnetic field takes the form $e^{i\mathbf{k}\cdot\mathbf{r}}\hat{H}_{k,n}(\mathbf{r})$, where $\hat{H}_{k,n}(\mathbf{r})$ is a function which is periodic in the lattice vectors $\mathbf{R}$. We may thus expand the Bloch state as a Fourier series in the reciprocal lattice vectors $\mathbf{G}$. We may write

$$e^{i\mathbf{k}\cdot\mathbf{r}}\hat{H}_{k,n}(\mathbf{r}) = \sum_{\mathbf{G}_i} H_{k,n}(\mathbf{G}_i)e^{i(\mathbf{k}+\mathbf{G}_i)\cdot\mathbf{r}},$$

(4.3)

where the summation runs over all vectors $\mathbf{G}_i$ in the set of reciprocal lattice vectors $\{\mathbf{G}\}$. Note specifically that the term for which $\mathbf{G}_i = 0$ corresponds to a plane wave with wavevector $\mathbf{k}$.

We can expect that this low order term of the Fourier series expansion will be important in determining the properties of a Bloch mode. I illustrate this with an example.

Consider again the Bloch modes of a quarter wave stack comprising layers of air and dielectric material; this is depicted in Fig. 3.10. Panels A, B, C and D show the field eigenmodes for low index contrast stacks calculated using a Bloch wavevector of $k = \pi/L$. In the low index
contrast limit, where the stack comprises ‘layers’ of air, its Bloch states will be equivalent to the
eigenmodes of free space; the eigenmodes will thus be plane waves. We can expect that a small
increase in the index contrast should not greatly perturb these eigenstates. This is exactly what
we observe; the field profiles of a low index stack are approximately plane waves. The spatial
frequency of these waves is $\pi/L$; this is precisely equal to the Bloch wavevector.

At high index contrast (Panels E & F), it becomes clear that the Bloch waves are significantly
different to the eigenstates of free space. Consider, however, decomposition of these Bloch waves
into a Fourier series. The dominant plane wave component of the decomposition will again
have a spatial frequency precisely equal to the Bloch wavevector $\pi/L$; this is clear visually from
the field profiles, which complete a whole cycle over a distance $2L$. Across the three refractive
indices, it seems that the principal Fourier component of a Bloch wave is a plane wave with
spatial frequency precisely equal to the Bloch wavevector.

This analysis suggests a novel approach to calculating a generalised band structure, in which we
reject the concept of a Bloch wavevector almost entirely and move to a momentum representation
of the eigenmodes of a structured medium. Consider an eigenmode $H(r, \omega)$ of $\hat{\mathcal{H}}$ in an arbitrary
(not necessarily periodic) structure. In any real experiment, such a mode will typically comprise
a linear combination of all the modes of frequency $\omega$ which solve the Maxwell equations, and
will thus contain simultaneously all the possible momentum states of the magnetic field. The
momentum representation $H(k, \omega)$ can be accessed easily by performing an overlap integral of
$H(r, \omega)$ with the eigenstates of free space. We may write

$$H(k, \omega) = \int_{-\infty}^{\infty} H(r, \omega) e^{-ik \cdot r} d^3r, \quad (4.4)$$

where we note that the ‘overlap with the eigenstates of free space’ corresponds simply to a
Fourier transform of the field distribution. Intuitively, we expect maxima of the momentum
representation to pick out the Bloch-like character of the field. Beyond this, however, we obtain
knowledge of all the momentum states of the field. The distribution of these momentum states
provides a direct route to quantifying the way in which the structure scatters light (i.e. -
elastically changes its momentum state).

### 4.3 The Spectral Function

The relevant quantity in obtaining the generalised dispersion relation $\omega(k)$ is the spectral function
$M(k, \omega)$. The spectral function is itself not a totally novel concept$^{150-152}$. Recently, the spectral
function was employed to characterise the ability of a planar patterned slab to couple light from
free space into non-leaky guided modes$^{152}$. The spectral function was employed qualitatively,
demonstrating that patterned slabs support electromagnetic modes with a significant momentum
component within the light line. It was suggested that engineering of the $k$ space distribution of
the spectral function resonances could facilitate the design of efficient light-harvesting devices.
To the best of my knowledge, I am not aware of sources beyond these which discuss the spectral
function, and have found no work that has noted the potency of the spectral function as a means of calculating the generalised band structure of aperiodic media.

In the sections that follow, the spectral function is applied to 2D planar architectures, defined in the $xy$ plane, which naturally support independent transverse electric (TE) and transverse magnetic (TM) polarised electromagnetic excitations. With this in mind, I define the spectral function $M(k, \omega)$ after Vynck et al.\textsuperscript{152} as

$$M(k, \omega) = \begin{cases} |E_x(k, \omega)|^2 + |E_y(k, \omega)|^2 & \text{TE polarised} \\ |H_x(k, \omega)|^2 + |H_y(k, \omega)|^2 & \text{TM polarised} \end{cases} \quad (4.5)$$

The particular version of the spectral function employed will therefore depend on the polarisation state of the modes being studied. For the two dimensional systems considered here, the spectral function is a function of the three variables $k_x, k_y$ and $\omega$. Generalised dispersion relations may be obtained by slicing the spectral function in whatever way is desired in order to obtain an appropriate data subset. For instance, a cut $M(k; \omega_0)$ at some constant frequency $\omega_0$ describes the complete momentum distribution of the field modes with eigenfrequency $\omega_0$. Further, a cut $M(k_x, \omega; k_y = 0)$ would yield a dispersion relation $\omega(k_x)$, analogous to a Bloch band structure plotted along a single reciprocal space direction.

Computationally, the spectral function is accessed via finite difference time domain (FDTD) simulations. The general methodology requires a large periodic supercell of the structure of interest. This structure is simulated in the FDTD engine under a periodic boundary condition. Electromagnetic modes of the structure are excited by randomly (Poisson) distributed dipole sources, which inject a spectrally broad pulse of radiation. The FDTD engine is run and, after a short time has elapsed to allow pulse injection to occur and transient field states to pass, a monitor records the time domain fields across the whole simulation domain. On termination of the simulation, the FDTD engine naturally handles the frequency decomposition of the time domain fields into their eigenmodes $H(r, \omega)$ and $E(r, \omega)$, one for each frequency of interest. These eigenmodes are then post-processed to calculate their Fourier transforms and form the spectral function according to Eqn. 4.5.

It is clearly important to make sure that the calculated eigenmodes $H(r, \omega)$ and $E(r, \omega)$ comprise a ‘fair’ linear combination of all the possible eigenmodes of the system with frequency $\omega$. Unfortunately, there is no way to guarantee this using the FDTD method. The best solution is to make sure a large number of dipoles (typically at least $O(1000)$) are used to excite the modes of the system. In the limit where the number of dipoles becomes large, fields are excited at a large number of positions $r$ in the simulation domain; this guards against leaving troublesome strongly-localised modes unexcited. Further, by allowing transient field states to pass, the light is given time to scatter into an equilibrium distribution. Scattering helps to populate any eigenmodes left unexcited by the initial dipole pulse and drives the light to an equilibrium momentum distribution in which the scattering rate into any given plane wave state is matched by the scattering rate out of it.
4.4 Band Structure via the Spectral Function

4.4.1 A Homogeneous Medium

To begin, I consider a trivial material that is simply homogeneous dielectric of permittivity $\varepsilon_r = 13$. The spectral function may be formed according to the methodology of section 4.3. A cut of the spectral function of the form $M(k_x, \omega; k_y = 0)$ is shown in Fig. 4.2A. The wavevector and frequency axes are normalised using a fictitious ‘unit cell’ parameter $a$, such that the axes are dimensionless; the choice of $a$ has no effect on the results. Two cuts of the form $M(k; \omega_0)$ are shown in Fig.4.2B panels 1 & 2, each corresponding to the annotated frequency in the dispersion relation; I refer to such cuts as both the momentum distribution of an eigenmode and the dispersion relation in the plane.

We see immediately that the spectral function reproduces the dispersion relation of a homogeneous dielectric. The calculated dispersion relation (Fig. 4.2A) describes the straight line $\omega = c k / n$. From the dispersion relation, we see that the frequency eigenstates of free space are also momentum eigenstates; momentum may be mapped to frequency in a one-to-one manner and vice versa. The momentum distributions supply information regarding the directionality of the dispersion. In this case, we see that the dispersion is perfectly isotropic; all momentum states with magnitude $k$ are found with equal probability. The radius of the momentum distribution naturally increases as we probe the momenta at a higher frequency eigenmode.

![Figure 4.2:](image)

**Figure 4.2:** A cut of the spectral function $M(k, \omega)$ along a single direction in the $k$ space (A) for a homogeneous medium of permittivity $\varepsilon_r = 13$. Cuts of the spectral function at fixed frequency (B, panels 1 & 2) show the isotropy of the momentum distributions.
Note that the non-uniformity along the light line in Fig. 4.2A is likely to be an artefact of the periodic boundary condition applied to the FDTD domain. Specifically, a source emitting in a domain of characteristic lengthscale $L$, simulated under a periodic boundary condition, will interfere with itself; this interference can be either constructive ($L/\lambda \approx n$, for integer $n$) or destructive ($L/\lambda \approx (n+1)/2$). The total power emitted by the source thus varies with frequency, leading to an oscillation in the intensity of the light line.

### 4.4.2 A Honeycomb Network Photonic Crystal

I now apply the spectral function to calculate the band structure of a honeycomb network photonic crystal. I follow the methodology of section 4.3, this time choosing a large supercell of a honeycomb network of dielectric walls of permittivity $\varepsilon_r = 13$. The supercell is rectangular, comprising 256 honeycomb primitive cells along each of its edges. The wall width was chosen to maximise the width of the fundamental photonic band gap. A small section of the honeycomb structure is shown in Fig. 4.3A.

I probe specifically the TE modes of the structure, which are excited by randomly distributing a large number of magnetic dipoles, polarised in the $z$ direction, in the plane of the structure. The FDTD simulations employ a uniform mesh of size $\Delta$ such that $\lambda_{\text{min}}/n\Delta = 16$, where $\lambda_{\text{min}}$ is the shortest wavelength simulated and $n$ is the refractive index of the dielectric.

The spectral function, once calculated, is sliced in two orthogonal $k$ space directions; the two slice directions are shown superimposed on the honeycomb reciprocal lattice in Fig. 4.3B. The first slice is of the form $M(k_y, \omega; k_x = 0)$; it runs from the $\Gamma_1$ point, at the centre of the first Brillouin zone, and passes through a sequence of high symmetry points in subsequent BZs. The second slice is of the form $M(k_x, \omega; k_y = 0)$; it originates at the $\Gamma_1$ point, leaves the first BZ through the $K_1$ point and then passes through a sequence of $\Gamma$ and $K$ points of higher order BZs.

![Figure 4.3: The optimum honeycomb network structure (A) used in calculation of the spectral function. Once calculated, the spectral function is sliced along two orthogonal directions in the reciprocal space (B). These slices intersect a number of lattice points (solid circles) and high symmetry points (hollow circles) of the reciprocal lattice. A number of Brillouin zones are shaded for clarity; the first BZ is dark blue.](image-url)
4.4.2.1 Results

Fig. 4.4A & B show the two slices through the spectral function (right side of each figure) compared to band structures calculated, using the MIT photonic bands package\(^79\), along identical \( k \) space paths (left side of each panel). The spectral functions are normalised to their maximum value and plotted on a logarithmic colour scale. The bands appear pixellated, which is a result of the frequency resolution of the calculation. Due to the large memory requirements of the calculation, band structures were necessarily limited to approximately 100 frequency points over the frequency range of interest. The agreement between the usual plane wave expansion band structures and those calculated by the spectral function method is excellent.

Fig. 4.5 presents a number of momentum distributions for fixed frequency cuts through the spectral function; the labels correspond to the frequencies annotated in red in Fig. 4.4. Each momentum distribution is overlaid with the honeycomb reciprocal lattice points (white dots) and the first Brillouin zone (blue hexagon). Panel 1 shows also the directions of the two spectral function slices.

In contrast to the frequency resolution, the resolution in the \( k \) space is high. The use of a large supercell ensures a fine mesh size \( \Delta k \) in the resulting Fourier transforms. More importantly, large supercells delocalise the eigenmodes over a large region of the direct space. It is a well known result of Fourier analysis that uncertainties in position and momentum are conjugate variables. Greater delocalisation of the eigenmodes therefore decreases the size of the features that may be resolved in the field’s momentum representation.

Panel 1 shows the momentum states of light at a frequency well below the photonic band gap. The principal momentum ring is centred on the \( \Gamma_1 \) point and is fully isotropic. At this low frequency, the dispersion relation (low frequency band structure, Fig. 4.4) is linear. It can be
Figure 4.5: Momentum distributions for eigenmodes of a honeycomb photonic crystal corresponding to annotated frequencies in Fig. 4.4. Panel 1 is below the PBG, panels 2, 3 & 4 show momentum concentration at the BZ edge at the lower PBG edge. Panels 5 & 6 show momenta just above the PBG. Panels 7, 8 & 9 show example high frequency momentum states.

modelled by an effective (homogeneous) medium of relative permittivity given by the Maxwell-Garnett mixing rule. The corresponding momentum distribution thus resembles that of a homogeneous medium. 6 faint subsidiary rings can also be observed, each centred on one of the 6 nearest neighbour reciprocal lattice points.

Panels 2, 3, & 4 show momentum distributions in the vicinity of the photonic band gap lower edge. Scattering becomes significant at these higher frequencies; the dispersion relation (Fig. 4.4) is strongly perturbed, and the momentum distributions are no longer well-modelled by those of an effective medium. In panel 2, the principal momentum hexagon touches the BZ edge at the $K$ point. In panel 3, momentum states at the $K$ point are suppressed and a stop gap opens along the $\Gamma \rightarrow K$ direction; these momentum states re-appear above the gap in panel 5. The PBG occurs between panels 4 & 5, and panel 4 shows the momentum distribution immediately below the gap. Here, the momentum is strongly localised at the $M$ points of the BZ.
Panels 5 & 6 show the momentum states just above the PBG. In panel 5, momentum states in the vicinity of the $K$ point reappear. This closes the $\Gamma \rightarrow K$ stop gap but the $\Gamma \rightarrow M$ stop gap remains open. In panel 6, momentum states at the $M$ points reappear, but a complete ring of allowed momentum states inside the BZ has already closed the $\Gamma \rightarrow M$ stop gap.

Panels 7, 8 & 9 show momentum distributions at higher frequencies. These distributions rapidly become complex and difficult to interpret. They encode all the information concerning the allowed momentum states of the light field needed to reproduce the band structure (Fig. 4.4).

4.4.2.2 Discussion

Band structures calculated via the spectral function reflect exactly the accepted plane wave expansion band structures. To understand this, note that the natural eigenstates of the honeycomb network, the Bloch states, form a complete basis in which any general eigenmode $E(r, \omega)$ can be expressed. We may write

$$E(r, \omega) = \sum_n \sum_k \alpha_{k,n} E_{k,n}(r, \omega') \delta(\omega' - \omega),$$

(4.6)

where the double summation is performed over all possible Bloch states and the delta function picks out only those states with frequency $\omega$. Decomposition of a measured eigenmode $E(r, \omega)$ into its momentum representation picks out its principal momentum components. These principle momenta correspond to the Bloch wavevectors of all the modes present in its Bloch state decomposition (Eqn. 4.6). The spectral function thus captures the Bloch character of an eigen-mode $E(r, \omega)$ and accurately predicts the band structure.

Throughout the entire sequence (Panels 1-9), note that the fundamental momentum distribution in the first BZ is repeated, although less intensely, throughout the neighbouring BZs. This is naturally interpreted as a result of Bloch’s theorem, in which the eigenmodes of the system take the form $e^{i \mathbf{k} \cdot \mathbf{r}} \mathcal{H}_{k,n}(\mathbf{r})$, where $\mathcal{H}_{k,n}(\mathbf{r})$ is a periodic function under translation by a direct lattice vector $\mathbf{R}$. As a periodic function, we may expand the $\mathcal{H}_{k,n}(\mathbf{r})$ as a Fourier series in the reciprocal lattice vectors. Inserting an appropriate expansion into the Bloch form, we see that

$$H_{k,n}(\mathbf{r}) = e^{i \mathbf{k} \cdot \mathbf{r}} \mathcal{H}_{k,n}(\mathbf{r}) = \sum_G \mathcal{H}_{k,n}(G) e^{i(k+G) \cdot \mathbf{r}}.$$

(4.7)

Any Bloch state with wavevector $\mathbf{k}$ is thus decomposed into a superposition of plane waves with momenta $\mathbf{k} + \mathbf{G}$. The momentum representation of a single Bloch mode will appear as a fundamental bright spot at wavevector $\mathbf{k}$ and a number of higher-order momentum components at wavevectors $\mathbf{k} + \mathbf{G}$.

The Bloch theorem provides a natural interpretation of the reciprocal space periodicity of the momentum states of the light field. However, the Bloch theorem addresses the special case where the scattering medium is translationally periodic; its applicability is thus restricted. Instead, it is hugely advantageous to develop a framework with which the momentum distributions of aperiodic
media may be interpreted. I therefore propose an alternative interpretation of the overall form of the momentum distribution in which any two plane wave states may be coupled by a Bragg scattering process. Excitation of a state $k$ will naturally excite a variety of other momentum states to which the state $k$ is coupled by Bragg processes.

I define a Bragg process as an elastic photon scattering event in which the momentum of a plane wave photon with wavevector $k_i$ is scattered onto a plane wave photon with wavevector $k_s$ by a momentum transfer $q$. Crucially, in a Bragg process the momentum $q$ is acquired from the constructive interference of waves scattered by structural correlations of the medium through which the light is propagating. In a photonic crystal, these structural correlations are the Bragg planes, and the momentum transfer $q$ can take a number of discrete values corresponding to the reciprocal lattice vectors. In an aperiodic medium, the momentum transfer generally takes a continuum of possible values as measured by the structure factor.

Appendix C discusses in detail an analytical formulation of Bragg scattering, the main findings of which I now summarise. In the low index limit, the dielectric distribution of a scattering medium may be modelled as a small perturbation to a homogeneous (effective) medium. Plane wave states in the perturbed medium become coupled through the perturbation. In particular, the scattering rate from a plane wave state $i$ to state $j$ depends on the value of the structure factor $S(q)$ (Eqn. 2.5, Eqn. C.21) at the corresponding momentum transfer $q = k_s - k_i$. Any non-zero value of the structure factor can thus change the momentum of a photon. In the single scattering limit (the Born approximation), the momentum distributions of an eigenmode can be seen to arise from Bragg scattering of the momentum states of the corresponding homogeneous (effective) medium momenta.

In high index structures, such as the $\varepsilon_r = 13$ honeycomb network considered here, both multiple scattering processes and energetic interactions with the dielectric distribution become significant. The resulting spectral function no longer resembles the singly-scattered homogeneous medium momentum states. Nevertheless, the physical behaviour of strongly scattering systems will evolve smoothly as the scattering strength is increased. Even in the high index case, plane wave momentum states will be coupled through a structure-factor-like quantity, and the effects of Bragg processes will be evident in the eigenmode momentum distributions.

With this in mind, I now explore the significance of the BZ edge in PBG formation. Consider the schematic diagrams in Fig. 4.6; these show the reciprocal lattice (white dots), the first BZ (yellow hexagon) and a number of $k$ states of interest. Consider a pair of momentum states $k$ and $-k$ (panel A) which lie on the $\Gamma \rightarrow K$ axis. State $k$ is Bragg scattered onto state $-k'$ by the reciprocal lattice vector $G_{11}$, shown by the red arrow. These two states are resonant with one another, since $-k'$ can scatter back onto the original state $k$ by addition of $G_{11}$; this resonance is indicated by a cycle of red arrows. The states $k$ and $-k$ are, however, uncoupled. State $-k$ is itself Bragg resonant with state $k'$, as shown by the orange arrows.

Consider now increasing $k$ until it lies at the K point of the first BZ (Fig. 4.6B & Fig. 4.5 Panel 2). Here, the states $k$ and $k'$ are identical. State $k$ is thus scattered onto its own negative $-k$ and vice versa; the two states are resonant as indicated by the orange arrows. This direct coupling between a momentum state and its negative creates a standing wave. Since $k$ lies at
the BZ edge, the energy density of this standing wave has the periodicity of the lattice along the $\Gamma \rightarrow K$ direction. The standing wave can exist in a low energy and a high energy state subject to its localisation of electromagnetic energy with respect to the honeycomb dielectric distribution; these two states form the edge states of the photonic stop gap in the $K$ direction.

Further, note that the BZ K point is actually a double Bragg resonance. The two Bragg processes shown in panel A, which previously distributed radiation between 4 distinct $k$ states, now focus the same radiation into two precisely counter-propagating states $k$ and $-k'$. The BZ edge is thus a surface along which the momentum states of the light field naturally focus. This focussing of momentum magnifies the standing wave effect, and favours PBG formation.

Although the configuration of Panel A also contains two equal magnitude counter-propagating states $k$ and $-k$, this is not sufficient to create the standing waves associated with photonic band gaps. States $k$ and $-k$ could arise, for instance, from a single point source radiating in all directions. In this case, the two states will never exist at the same point in the structure and will not interfere. Instead, we require a scattering mechanism that couples the states $k$ and $-k$ together; this is possible only at the BZ edge.

Another case of interest concerns $k$ states that lie at the BZ M points (Fig. 4.6C & Fig. 4.5 Panel 3). Consider preparing the photonic crystal in the momentum state $k_1$ shown in Fig. 4.6C. The plane wave state will Bragg scatter. The dominant scattering mechanisms, corresponding to the strongest resonances of the structure factor, are illustrated with red arrows; $k_1$ is resonant with two other states, $k_2$ and $k_3$, both at a BZ M point. After some time has passed, the states $k_1$, $k_2$ and $k_3$ will form a scattering equilibrium in which each state is equally excited. By the symmetry of the BZ, the superposition of these plane waves creates a zero group velocity standing wave. The energy density of the standing wave has lattice periodicity and forms low and high energy states with a spectral gap between them.
4.4.2.3 Summary

To summarise, I have shown that the spectral function method provides a useful counterpoint to the regular numerical band structure calculation methods. The eigenmodes of a photonic crystal, as calculated by the FDTD approach, contain all the possible Bloch modes at that frequency. Decomposition of a set of eigenmodes into their momentum representation picks out their ‘Bloch character’ and can be used to build a band structure.

The spectral function yields the momentum states of the light field without confining the momentum to the first Brillouin zone. Momentum distributions may be approximated in the low index single scattering limit as the Bragg scattered momenta of an effective medium (Appendix C). Here, in the high index case, Bragg scattering may be observed as the repetition of an allowed momentum state \( \mathbf{k} \) at position \( \mathbf{k} + \mathbf{G} \). Momentum states that lie at the BZ edge experience a resonant Bragg scattering that can lead to standing wave formation. The disappearance, and reappearance at a higher frequency, of a momentum state at the BZ edge is the diagnostic signature of a spectral gap brought about by standing wave formation. This is direct evidence of the Bragg mechanism of PBG formation.

4.4.3 Hyperuniform Amorphous Networks

The major advantage of the spectral function method is that it can be applied, without modification, to aperiodic scattering distributions. In this section, I employ the spectral function method to calculate the generalised band structures of a hyperuniform disordered honeycomb.

I begin with a low index \( \varepsilon_r = 2.25 \) structure. This structure is weakly scattering, and I explore the idea that the dispersion results from Bragg scattering the momentum states of an effective

![Figure 4.7](image_url): Total scattering structure function of a \( \chi = 0.5 \) hyperuniform disordered honeycomb network (A), showing characteristic zero around the origin and a strong isotropic scattering resonance. The radially integrated structure factor (B) shows the breadth and magnitude of this resonance. Inset (B) shows the hyperuniform network.
medium in the single scattering approximation. Following this, the high index $\varepsilon_r = 13$ case is illustrated. At this index contrast, the dispersion relation is strongly modified compared to the effective medium case. Nevertheless, the characteristic ‘folding’ of the dispersion relation as a result of Bragg processes is clear.

The structure itself is a hyperuniform disordered honeycomb network, derived from a $\chi = 0.5$ hyperuniform point pattern by application of the Delaunay tessellation protocol. The width of the dielectric channels is set to $0.175a$, where $a$ is the mean inter-vertex separation of the undecorated hyperuniform point pattern. The resulting structure has a dielectric fill fraction of 55%. A small section of the structure is shown inset in Fig. 4.7B.

Fig. 4.7A shows the structure factor $S(k)$ of the hyperuniform network. The characteristic zero of the structure factor is visible around the origin. The primary feature of $S(k)$ is the strong isotropic scattering resonance around $ka/2\pi = 1.05$. The radially integrated structure factor $S(k_r)$ is shown in Fig. 4.7B; for reasons which will become apparent, I have annotated both the regions of peak momentum transfer (orange) and a region exactly halfway between $q = 0$ and the peak of the structure factor (pink).

As before, spectral functions are calculated using the FDTD method. I focus on the TE modes of the structure, and excite them using a Poisson-distributed array of $z$-polarised magnetic dipoles. We shall see that the momentum states of the light field possess an average rotational isotropy. As a result, the dispersion diagrams along all $k$ space directions are similar. Generalised band structures are therefore presented as an azimuthal average in the $k$ plane; this is written as

$$M(k, \omega) = \frac{1}{2\pi k} \int_0^{2\pi} M(k, \omega) \, k \, d\phi,$$

(4.8)

where $k = |k|$ is the radial coordinate in the $k$ plane and $k \, d\phi$ is the length element. Azimuthal averaging reduces noise and produces much better defined dispersion diagrams than those obtained by considering a single $k$ space direction only.

4.4.3.1 A Low Index Network

In the first case, I calculate the spectral function for a dielectric network of permittivity $\varepsilon = 2.25$. The generalised band structure is shown in Fig. 4.8 (left panel) together with a number of momentum distributions in the plane corresponding to the annotated frequencies (red).

The most striking feature of the dispersion diagram is the intense diagonal slash from bottom-left to top-right. This slash describes the dominant momentum states of the structure, which are well modelled by a linear dispersion relation of the form

$$\frac{af}{c} = \frac{1}{n_{eff} 2\pi} \frac{ka}{n_{eff} 2\pi},$$

(4.9)
where $n_{\text{eff}}$ is the refractive index of an effective homogeneous medium. The value of $n_{\text{eff}}$ can be predicted using the Maxwell-Garnett mixing rule\cite{152} or simply read off from the gradient of the dispersion diagram.

The momentum states of the effective medium are observed to dominate the total momentum distribution of the light field. All the momentum distributions (Fig. 4.8 Panels 1-4) exhibit an intense isotropic ring, similar to the homogeneous medium case (Fig. 4.2).

We also observe a subsidiary dispersion band approximately 2 orders of magnitude less intense than the effective medium band. This subsidiary band becomes apparent around $ka/2\pi = 0.55$ where the effective medium band is observed to branch into two. This subsidiary band can be resolved in the momentum distributions as momentum states within the principal effective medium ring (Fig. 4.8, Panels 2-4). In Fig. 4.8 Panel 4, it is clear that the subsidiary band is itself statistically isotropic in the momentum space.

The splitting of the effective medium band into two can be understood as a result of scattering the effective medium momentum states by Bragg processes. Following Appendix C, the low index hyperuniform structure may be formulated as a perturbation to a homogeneous medium. We write the position dependent relative permittivity as $\varepsilon_r[1 + \Delta(r)]$, where $\varepsilon_r$ is the effective medium permittivity and $\Delta(r)$ is a step-like function that gives the fractional variation of the permittivity with respect to the mean.

We prepare, at time zero, a radiation bath in a homogeneous medium of permittivity $\varepsilon_r$; the spectral function of this initial state is exactly that of Fig. 4.2. We then instantaneously turn on the perturbation by setting $\Delta(r)$ to a non-zero value. We seek a solution to the Maxwell equations by expanding the fields using the eigenmodes of the homogeneous medium. Specifically we seek a solution of the form
Figure 4.9: Generalised band diagram for the TE modes of an $\varepsilon_r = 2.25$ hyperuniform network calculated via the spectral function FDTD method (A). The dispersion may be qualitatively reproduced through scattering the momentum states of the effective medium by Bragg processes (B).

$$E(r, t) = \alpha_i(t) \sum_i E_i^{(0)} e^{i(k_i \cdot r - \omega_i t)}, \quad \text{(4.10)}$$

where $\omega_i = ck_i/\sqrt{\varepsilon_r}$ satisfies the homogeneous medium dispersion relation and $\alpha_i(t)$ is a time dependent coefficient. It can be shown (Appendix C) that, in the single scattering approximation, the state of the radiation field a short time $t$ after time zero is approximately described by

$$|\alpha_j(t)|^2 \propto |t \omega_j K \int \alpha_i(k_i ; t = 0) \left[ \int \Delta(r) e^{-i|k_j - k_i| \cdot r} d^2 r \right] d^2 k_i + \alpha_j(k_j ; t = 0)|^2, \quad \text{(4.11)}$$

where $K$ is a constant and $\alpha_i(k_i ; t = 0)$ is the initial state of the radiation field at time zero. The double integral may be interpreted as a convolution of the initial state of the radiation field with the structure factor, or structure factor-like quantity, $\int \Delta(r) e^{-i|k_j - k_i| \cdot r} d^2 r$. Scattering is thus mediated by the structure factor; the dominant Bragg processes correspond to momentum transfers for which the value of the structure factor is large.

Fig. 4.9 shows the result of a numerical implementation of Eqn. 4.11 compared to the spectral function as predicted by the exact FDTD solution. The FDTD experiment is characterised by $a = 270\text{nm}$ and $\omega_i \sim [0, 1.1] \times 10^{16} \text{ rad s}^{-1}$, and the constant $K$ was determined accordingly. The initial state of the radiation field was taken as $\alpha_i(k_i ; t = 0) = \delta(|k| - \sqrt{\varepsilon_r} \omega_i/c)$; this models the homogeneous medium case. The state of the field, as given by the coefficients $|\alpha_j(t)|^2$ of Eqn. 4.11, was then calculated at $t = 10\text{fs}$.

We observe that Fig. 4.9B is a good qualitative match to the exact form of the spectral function as calculated using the FDTD method (Fig. 4.9A). The fundamental features of the band diagram are thus well-modelled by scattering the effective medium momentum states with the momentum transfers of the structure factor.
The mechanism with which the effective medium splits into two around \(ka/2\pi = 0.55\) is now clear. Let the peak of the structure factor along a particular reciprocal space direction correspond to a momentum transfer of \(k_p\). The point \(k_p/2\) is a critical point analogous to the Brillouin zone edge in a photonic crystal. It is the point at which a plane wave state with momentum \(k_i = k_p/2\) will be strongly scattered onto the counter-propagating state \(k_s = -k_p/2\). When \(k_i < k_p/2\), the magnitude of the scattered wavevector satisfies \(|k_s| > |k_i|\). When \(k_i > k_p/2\), we observe that \(|k_s| < |k_i|\). The point \(k_p/2\) is thus the momentum at which the effective medium band and scattered band cross.

Note that the structure factor (Fig. 4.7A) is a diffuse quantity, and the point \(k_p/2\) is not well-defined in any particular direction. Instead, there is a critical annulus in the \(k\) space within which an incident momentum state will be approximately scattered onto a counter-propagating state. This critical region, shown in pink in Fig. 4.7B, is the natural generalisation of the concept of a Brillouin zone to an amorphous structure.

### 4.4.3.2 A High Index Network

I now consider a high refractive index realisation of the same hyperuniform network. I set the permittivity of the dielectric network to \(\varepsilon_r = 13\) and apply the FDTD method, without alteration, to calculate the spectral function \(M(k, \omega)\).

The generalised band diagram for the high index case is shown in Fig. 4.10. A number of momentum distributions, corresponding to the frequencies annotated in red, are shown in Fig. 4.10, Panel 1-4.

The band diagram of the high index structure is significantly different to the low index case. We observe that there is no longer an obvious continuous slash from bottom-left to top-right which would represent the momentum states of the effective medium. Instead, the main dispersion
The band is broken into a number of distinct sections, with each section displaying an approximately linear dispersion. Taken independently, the discrete linear sections of the main dispersion band resemble the dispersion of a homogeneous medium.

The major feature of the high index case is the sizeable photonic band gap which falls around $0.2 < \alpha f/c < 0.28$. Below the gap, the band appears to bend down until horizontal, suggesting a zero group velocity at the PBG edge. Immediately below the PBG, the momentum states are concentrated in the critical $k$ space annulus within which they may be scattered onto counter-propagating states. This alone is not sufficient to claim that the PBG results from an effective Bragg mechanism, but it suggests that the PBG likely arises from the cooperative action of Bragg processes and the generalised resonant scattering mechanism.

At this high refractive index, plane wave momentum states are strongly scattered. Further, energetic interactions between the plane wave states and the distribution of dielectric material are strong. When the plane waves possess a periodicity of approximately $2a$, as they do within the critical $k$ space annulus, the electromagnetic energy density has period $a$ and can align, at least at local length scales, with the distribution of dielectric material. The localisation of electromagnetic energy, either within, or outside, regions of high refractive index, constitutes a strong energetic interaction which perturbs the density of states and may open a spectral gap. The discrete sections of the main dispersion band may thus be interpreted as the evolution of the momentum states of the homogeneous medium, subject to a strong energetic interaction with the scattering structure.

The dispersion diagram shows clear signatures of scattering through Bragg processes. Above the gap, we observe the branching of the main band into two, just as in the low index case. This can be attributed to the strong momentum transfers of the structure factor, which ‘fold’ the principal dispersion band back in towards the origin. Multiple such branchings can be observed at higher frequencies, particularly at the second critical $k$ space annulus around $k = 1.05$ where the main dispersion band becomes discontinuous.

### 4.4.3.3 Summary

The spectral function may be used to predict the generalised band structures of aperiodic media. Here I have studied the TE modes in two realisations of a hyperuniform connected network of dielectric material.

In the low index case, the principal dispersion band is given by the momentum states of an effective medium. The band structure then arises from the scattering of the effective medium momentum states by Bragg processes. The significance of a particular Bragg process is determined by the value of the structure factor at the corresponding momentum transfer $q$. Momentum states that lie halfway between the origin and the principal structure factor resonance may thus be strongly scattered onto counter-propagating states. This suggests that a critical annulus, that lies halfway between the origin and the broad main resonance of the structure factor, is a natural generalisation of the Brillouin zone to amorphous media.
In the high index case, significant energetic interactions between the electromagnetic field and the distribution of dielectric material strongly perturb the main dispersion band. When the momentum states of the field lie in the critical $k$ space annulus, partial standing waves may form that can localise electromagnetic energy density, at a local level, either in regions of dielectric or air. A sizeable photonic band gap opens, which results from cooperative interplay of Bragg and generalised resonant scattering mechanisms. Although the main dispersion band is strongly perturbed, momentum states remain coupled through the possible momentum transfers of the structure factor.
4.5 PBG Formation in Penrose Quasicrystals

The spectral functions of periodic and amorphous materials demonstrate the intimate connection between optical dispersion and the possible momenta that may be passed to a photon through a Bragg process (as measured by the structure factor). Dispersion in photonic crystals is well-defined, on account of their Bragg-like structure factors, but highly anisotropic. Dispersion in amorphous materials, on the other hand, is statistically isotropic but diffuse and poorly defined.

Quasicrystals combine the best of both worlds. They possess structure factors that demonstrate crystallographically forbidden high-order rotational symmetries; they should thus interact with light more isotropically than photonic crystals. Simultaneously, their structure factors are described by rationally independent Z-modules which densely fill the momentum transfer space at all length scales. If the structure factor of a quasicrystal could be resolved with arbitrary precision, every peak would be observed to be Bragg-like, and may be expected to scatter plane wave states through a sharply-defined Bragg process. We therefore may expect dispersion in photonic quasicrystals to display a rich variety of features at all intensity scales.

Naturally, the possible application of quasicrystals in optics has fired much interest\textsuperscript{72}. In particular, it has been shown that both one and two-dimensional quasicrystals can exhibit multiple complete photonic band gaps, of significant normalised width, at distinct energy scales\textsuperscript{64,65,74,75,111}. The ability to confine and guide light of two or more distinct frequencies within the same material offers great flexibility in the design of quasicrystal-based optical components. A thorough characterisation of the optical properties of quasicrystal structures is thus highly desirable.

In this section, I apply the spectral function method to calculate the complete dispersion relations of a number of two-dimensional quasicrystalline photonic structures derived from Penrose tilings. First, I introduce the specific geometries of the photonic quasicrystals. I also discuss existing work, and its relevant conclusions as they apply to current understanding of PBG formation in Penrose-derived architectures. Then, I introduce the structure factors of the Penrose samples and index the principal reciprocal lattice vectors. Generalised band diagrams, as calculated by the spectral function method, are then presented for both TM and TE band gap structures. I focus in particular on the frequency region around the ‘sub-fundamental’ gap, and observe in great detail the momentum states of the light field above and below several complete PBGs.

4.5.1 Geometry and Background

The Penrose tiling is a well-known aperiodic tiling of the plane (Fig. 4.11A, purple tiling) whose fundamental building blocks are the Penrose rhombs. There are two types of rhomb, as shown in Fig. 4.11B. Both rhombs have side length $d_0$. The ‘fat’ rhomb has diagonals of length $d_2$ and $d_3$, while the ‘skinny’ rhomb has diagonals of length $d_1$ and $d_4$. Throughout this section, I normalise the dimensions of the Penrose patterns such that $d_0 = 1$.

The specific Penrose tiling that I employ here is a large rectangular periodic approximant structure that was constructed using the cut and project method\textsuperscript{106,108}. Such periodic approximants are produced by approximating the golden ratio $\tau = (1 + \sqrt{5})/2$ with a rational value. Here
\( \tau \) is approximated as 13/8. The resulting Penrose pattern is rectangular, with characteristic side lengths \( L_x = 34.132 \) and \( L_y = 89.721 \). In total, the pattern contains 3770 unique vertices, corresponding to points where the Penrose rhombs touch point-to-point. The periodic approximant is known to possess two structural defects where the Penrose rhomb matching rules are violated\(^{67}\). The periodic structure is, however, sufficiently large that it is an excellent model of a truly aperiodic tiling.

I employ two types of structure, both of which are derived from the Penrose 13-8 approximant. In the first case, a dielectric cylinder of permittivity \( \varepsilon_r = 13 \) and radius \( r/d_0 = 0.177 \) is placed at every vertex of the point pattern. The resulting structure, of which a small section is shown in Fig. 4.11C, has a dielectric fill fraction of 12.1%. I refer to this structure as the TM structure. TM structures are known to possess significant PBGs for TM polarised light\(^{67}\); spectral functions are thus calculated by exciting only the TM polarised field modes. This is achieved with a random distribution of electric dipoles with their dipole moments oriented along the \( \hat{z} \) direction.

In the second case, a Delaunay tessellation protocol\(^{62}\) is applied to the Penrose point pattern. The resulting structure is a trivalent connected network that possesses exactly \( 2N \) network vertices, where \( N \) is the number of points in the seed point pattern. Fig. 4.11B shows the relationship between the Penrose tiling (purple) and the connected network obtained by Delaunay tessellation (black).

Once tessellated, the network is decorated by connecting the vertices with dielectric walls of permittivity \( \varepsilon_r = 13 \) and perpendicular width \( w/d_0 = 0.204 \). The resulting structure, of which a small section is shown in Fig. 4.11D, has a dielectric fill fraction of 37.8%. I refer to this structure as the TE structure. Trivalent quasicrystalline networks of this type are known to exhibit large PBGs for TE polarised light\(^{67}\). The field modes are thus excited with a random distribution of magnetic dipoles, with dipole moments polarised along \( \hat{z} \).

Folded band structures for TM and TE-type structures, calculated using the MIT photonic bands package\(^{79}\), are shown in Fig. 4.12. Panel A shows the band structure for a TM-type architecture along the \( \Gamma \to X \) direction of the supercell BZ. Note that this particular TM
The largest gap, which I refer to as the fundamental gap, spans the approximate frequency region $0.395 < af/c < 0.54$. Just below the fundamental gap lower edge, a second small PBG can be observed; I refer to this as the sub-fundamental gap. A third significant gap exists above the fundamental PBG, although we shall find that this vanishes when the 12.1% dielectric fill TM structure is studied.

Fig. 4.12B shows an equivalent folded band structure for the TE architecture. Similar to the TM case, the TE structure displays both a large fundamental PBG and a smaller sub-fundamental gap. Fig. 4.12C shows detail from the TE band structure, focusing on the frequency region around the sub-fundamental gap. Having zoomed in, numerous other small but possibly complete PBGs can be resolved.

Without considering further $k$ points in the supercell BZ, it is hard to judge with certainty whether these mini spectral gaps are in fact absolute. To investigate this question, I consider the density of states $\rho(\omega)$ and compare this with the band structure (right panel Fig. 4.12C). The density of states was calculated using the $k$ space integration method of Busch and John\textsuperscript{134}. In total, the eigenfrequencies of 25 distinct $k$ points within the supercell BZ contributed to the DOS calculation.

The DOS calculation suggests that the photonic mini gaps correspond to true $\rho(\omega)$ zeros, and are thus absolute PBGs. Further, zooming in on the Penrose band structure (Fig. 4.12C) reveals yet further possible mini-gaps; the spectral distribution of the PBGs appears self-similar and

![Diagram](image-url)
fractal-like in character. This behaviour parallels the observation of fractal-like character in the modes of a Penrose-structured waveguide.\textsuperscript{153}

Florescu, Torquato and Steinhardt\textsuperscript{67} analysed the field distributions of the eigenmodes immediately below and above the fundamental Penrose PBG. In both the TE and TM cases, the localisation character of the fields is observed to change discretely on traversing the gap. Below the PBG, TM structures demonstrate propagation mediated by a zeroth-order Mie resonance. Above the gap, propagation is clearly mediated by a first-order Mie resonance. In light of recent progress in understanding the generalised resonant scattering mechanism (Section 3.8), the TE field distributions may now be re-analysed. Below the fundamental gap, the TE modes are characterised by ‘cell-type’ modes, while above the gap the modes are of the characteristic ‘stripe-type’. I conclude that the Mie and generalised resonant scattering mechanisms play an important role in the formation of the fundamental PBG in Penrose TM and TE structures respectively.

These observations raise an interesting question. If the fundamental TM PBG is related to the lowest frequency Mie resonance of a cylindrical scatterer, what mechanism is the key contributor to the formation of the sub-fundamental gap? This question may also be asked of the Penrose TE structures (although it is not as well-posed due to the lack of analytical solution for scattering by a network vertex). The lowest frequency generalised scattering resonance falls within the fundamental PBG; what, therefore, is causing the sub-fundamental gap for the TE structure?

To investigate these questions, we may examine the field distributions of the TM and TE structures’ eigenmodes in the vicinity of their sub-fundamental PBGs. Using a supercell method in

\textbf{Figure 4.13:} Electric energy concentration factor $C$ plotted against frequency for the Penrose TM structure. I highlight discontinuities in the TM concentration factor at a failed PBG (dashed green line, 1), the sub-fundamental PBG (shaded green, 2) and the fundamental PBG (shaded yellow, 3). $E_z$ field profiles either side of these discontinuities are shown to the right.
Unfolding the Photonic Band Structure

MPB\textsuperscript{79}, the eigenmodes of the TM and TE structures were determined and the evolution with frequency of the electric energy concentration factor\textsuperscript{80,143} was calculated. The electric energy concentration factor - $C$ - measures the proportion of the total energy of the electric field that is stored within the high index dielectric material\textsuperscript{143}. Step changes in the concentration factor are associated with spectral gaps via the denominator of the electromagnetic energy functional (Eqn. 3.19).

Fig. 4.13 presents the concentration factor for the Penrose TM structure. To the right of this, I plot electric field ($E_z$) distributions for eigenmodes just below and above any notable concentration factor discontinuities. To begin, the concentration factor increases steadily with frequency. Around $af/c = 0.28$, we reach the band index where, for cylinders of radius $r/d_0 = 0.116$, a small mini-gap can open; here we observe no gap and a jump in the concentration factor, which is annotated as a green dashed line and labelled as discontinuity 1. Just above this, we reach the position of the sub-fundamental PBG (shaded solid green); here there is another small discontinuity in $C$ which I label as discontinuity 2. The fundamental PBG (shaded yellow) is marked by a large change in $C$ which is labelled as discontinuity 3. It is clear from the field profiles either side of discontinuity 3 that the character of the eigenmodes changes from a zeroth Mie resonance-type to a first Mie resonance-type; the fundamental PBG is thus the usual Mie scattering-induced gap. However, no clear change in the character of the eigenmodes is evident across either the failed PBG or the sub-fundamental PBG (discontinuities 1 & 2 respectively).

Fig. 4.14 presents an identical analysis for the Penrose TE structure. As before, three notable

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure414}
\caption{Electric energy concentration factor $C$ plotted against frequency for the Penrose TE structure. Concentration factor discontinuities are highlighted at the sub-fundamental gap (shaded green, 1), mini-gap 1 (green dashed line, 2) and the fundamental PBG (shaded yellow, 3); $H_z$ field distributions for modes just below and just above these discontinuities are shown to the right.}
\end{figure}
concentration factor discontinuities are annotated. In order of increasing frequency, the first discontinuity corresponds to the sub-fundamental PBG (shaded green and labelled 1). The second discontinuity (green dashed line and labelled 2) corresponds to mini-gap 1 of Fig. 4.12C. The third discontinuity occurs across the fundamental PBG (shaded yellow, and labelled as discontinuity 3). To the right of the concentration factor, I plot magnetic field ($H_z$) distributions for the eigenmodes either side of these concentration factor discontinuities. As in the honeycomb photonic crystal and hyperuniform disordered honeycombs (Section 3.8), the fundamental PBG (discontinuity 3) is associated with a change from cell-type to stripe-type eigenmodes; the fundamental gap can thus be associated with the generalised resonant scattering mechanism. Across the sub-fundamental PBG and mini-gap 1 discontinuities, the $H_z$ distributions appear to change the nature of their localisation within the Penrose network. Both above and below these discontinuities, however, the modes are characteristically cell-type; this suggests that generalised resonant scattering does not influence the formation of these small PBGs.

Existing research has also attempted to identify the origin of the Penrose sub-fundamental gaps. Della Villa et al. used the local density of states (LDOS) to probe the relative characters of the fundamental and sub-fundamental TM PBGs. Specifically, the minimum value of the LDOS for the two PBGs was measured as a function of sample size. As the sample size increased, it was found that the LDOS within the fundamental PBG decreased at a much greater rate than the LDOS in the sub-fundamental gap. Comparison with equivalent data for a square lattice photonic crystal suggests that the fundamental Penrose gap and primary square lattice gap behave equivalently; they share a common origin mechanism, which, by analogy with the photonic crystal, suggests gap formation through the synergetic interplay of Mie and Bragg mechanisms. The sub-fundamental gap, on the other hand, displays a distinctly different character. This corroborates the suggestion that the fundamental and sub-fundamental gaps originate through different physical processes.

Wang attempted to estimate the unfolded $k$ vectors of Penrose TM mid-gap frequencies. He argued that the mid-gap frequencies should lie on the light-line $k = \sqrt{\varepsilon_r \omega/c}$ of an equivalent homogeneous medium of effective permittivity $\varepsilon_r$. The unfolded $k$ vectors of the fundamental and sub-fundamental mid-gap frequencies were found to map onto wavevectors equal to $0.5G$, where $G$ is an intense resonance of the structure factor. This suggests that the Bragg mechanism plays a role in the formation of the sub-fundamental gap. However, it was observed in Section 4.4.3.2 that the primary dispersion band of a high refractive index PBG structure is not well-modelled by the momentum states of an effective medium. Rather, the categorical association of an eigenmode with a particular momentum space localisation requires complete and accurate dispersion information. This information may now be accessed through the spectral function.

### 4.5.2 Indexed Structure Factors

An understanding of the dispersion of light in a material must begin by quantifying the possible ways in which radiation may be scattered. The structure factor provides a complete description of the momenta $q$ that the structure may transfer to a photon through a Bragg process. An
understanding of the key details of the Penrose TM and TE architecture structure factors will thus inform later analysis of the generalised band diagrams.

Fig. 4.15 presents the structure factor of the Penrose cylinder array. Here, structure factors are calculated using a fast Fourier transform based approach which, unlike calculation via the cut and project method, naturally reflects the way in which a material decoration may modify the intensity of the peaks of the underlying reciprocal quasi-lattice.

The complete two dimensional structure factor, shown in Fig. 4.15A, is calculated for a single supercell of the Penrose TM structure; this broadens the peaks and makes them visible when plotted on a heatmap. The azimuthally averaged structure factor, shown in Fig. 4.15B, is a high resolution calculation for a $16 \times 6$ rectangular supercell array. This calculation reflects the relative intensity and Bragg-like character of the momentum transfers more accurately, and is diagnostic of the dominant Bragg processes in the structure.

Any peak of the Penrose diffraction pattern may be indexed with integers $[h, k, l, m, n]$, where these integers specify a linear combination $hb_1 + kb_2 + lb_3 + mb_4 + nb_5$ of the $Z$-module basis vectors. The basis vectors themselves may be written as

$$b_i = 2\left(\hat{x} \cos \left[\frac{\pi(i-1)}{5}\right] + \hat{y} \sin \left[\frac{\pi(i-1)}{5}\right]\right).$$

(4.12)

A single vector $[h, k, l, m, n]$ is understood to represent a family of reciprocal quasi-lattice vectors. A family is a set of vectors, all of which have identical norm, whose members may be generated from a single vector in the family by the application of a suitable rotational symmetry operation. The principal decagonal rings of the Penrose structure factor thus result from all the vectors of a family of related reciprocal quasi-lattice vectors. The important characteristics of a number of important reciprocal quasi-lattice vector families are summarised in table 4.1.
The structure factor of the Penrose TE architecture is shown in Fig. 4.16. As before, panel A shows the two-dimensional structure factor of a single supercell of the sample, while panel B shows a high resolution azimuthally averaged structure factor.

It is clear that the structure factor is intimately related to the Penrose reciprocal quasi-lattice. The intensity of the peaks, however, is modulated as a result of the complex distribution of scattering material with which the Penrose point pattern is decorated. We observe that the peak of the \( G_2 \) family of reciprocal quasi-lattice vectors has been suppressed such that the peak of the \( G_1 \) family is now dominant. Further, the momentum transfers of the \([1, -1, -1, 1, 1]\) (\( G_3 \)) and \([1, -1, 1, 0, -1]\) (\( G_4 \)) families have been enhanced; they may be observed as significant peaks in the azimuthally averaged structure factor (Fig. 4.16B).

The Jones zones of the \( G_3 \) and \( G_4 \) families are overlaid, together with those of the \( G_1 \) and \( G_2 \) families, on Fig. 4.16A. The \( G_3 \) family has a ten-fold symmetry; its Jones zone is marked by the purple decagon. Note that the \( G_2 \) Jones zone \( N \) points and \( G_3 \) Jones zone \( X \) points

<table>
<thead>
<tr>
<th>Rec. Lat. Vec. Family</th>
<th>Symoblic Norm</th>
<th>Norm</th>
<th>Colour</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>( G_1 ) ([1, 0, 0, 0, 0])</td>
<td>( \frac{\sqrt{5}}{\pi} )</td>
<td>1.0515</td>
<td>Blue</td>
<td>1/2 skinny rhomb long diagonal</td>
</tr>
<tr>
<td>( G_2 ) ([1, 0, 0, 1, 0])</td>
<td>( \frac{\sqrt{6}}{\pi} )</td>
<td>1.2361</td>
<td>Orange</td>
<td>1/2 fat rhomb long diagonal</td>
</tr>
<tr>
<td>( G_3 ) ([1, -1, 1, 1, 1])</td>
<td>( \frac{\sqrt{5}}{\pi} (\tau - 1) )</td>
<td>1.2997</td>
<td>Purple</td>
<td>Significant in tessellated network</td>
</tr>
<tr>
<td>( G_4 ) ([1, -1, 1, 0, -1])</td>
<td>( \frac{\sqrt{5}}{\pi} \sqrt{5 - 2\tau} )</td>
<td>1.3965</td>
<td>Maroon</td>
<td>Significant in tessellated network</td>
</tr>
<tr>
<td>( G_5 ) ([1, 0, 1, 0, 0])</td>
<td>( \frac{2}{\pi} )</td>
<td>1.7013</td>
<td>Red</td>
<td>1/2 fat rhomb short diagonal</td>
</tr>
<tr>
<td>( G_6 ) ([1, 1, 0, 0, 0])</td>
<td>( \frac{\sqrt{5}}{\pi} )</td>
<td>2</td>
<td>Green</td>
<td>1/2 rhomb side length</td>
</tr>
<tr>
<td>( G_7 ) ([1, 1, 1, 1, 1])</td>
<td>( \frac{2}{\pi} )</td>
<td>3.2361</td>
<td>Yellow</td>
<td>1/2 skinny rhomb short diagonal</td>
</tr>
</tbody>
</table>

Table 4.1: Major reciprocal lattice vectors for the Penrose cylinder array and tessellated network systems.
are degenerate. The \( G_4 \) family of reciprocal quasi-lattice vectors describes a 20-fold ring. The associated Jones zone is thus a regular 20-sided polygon; it is marked in maroon on Fig. 4.16A.

Finally, we see that, compared to the structure factor of the TM architecture, the \( G_6 \)-type momentum transfers have been almost completely suppressed; the intensity of the peak of the azimuthally averaged structure factor (Fig. 4.16B) at \( ka/2\pi = 2 \) is much weaker.
4.5.3 Unfolded Band Structures

Spectral functions were calculated following the general form of the FDTD method described in section 4.3. However, for the Penrose structures studied here, it was found that an extremely large direct space FDTD domain was crucial to generating accurate spectral functions. This should be contrasted with the periodic (Section 4.4.2) and amorphous cases (Section 4.4.3), where relatively modest structures, comprising 4096 total honeycomb unit cells and a single 8000 vertex hyperuniform network supercell respectively, were found to yield good results.

Therefore, both the cylinder and network 13-8 periodic approximant samples were used to produce large super-supercell (S-SC) structures. S-SC structures were formed by tessellating a supercell with identical copies of itself. Specifically, an $n \times m$ S-SC comprised $n$ supercells along the horizontal axis and $m$ supercells along the vertical axis.

Here I employ mostly $6\times16$ S-SCs, which contain 361,920 cylinders and 723,840 network vertices for the TM and TE structures respectively. FDTD simulations are run using a uniform square mesh of cell size $\delta$ such that $\lambda_{\text{min}}/n\delta > 16$, where $n = \sqrt{13}$ is the refractive index of the dielectric material and $\lambda_{\text{min}}$ is the shortest wavelength for which data was recorded. The $\lambda_{\text{min}}/n\delta > 16$ criterion was treated as a hard limit, and no simulations were run with an FDTD accuracy less than this. Where memory requirements allowed, the FDTD mesh accuracy was increased.

FDTD simulation of the large super-supercell samples is extremely memory intensive. On available hardware, simulation was only possible with significant downsampling of the FDTD mesh. The Maxwell equations were solved on the uniform mesh of size $\delta$, but the field was sampled and recorded on a smaller mesh of size $D\delta$, where $D$ is an integer downsampling factor.

Downsampling must be implemented carefully to ensure that momenta of interest are not larger than the largest observable momentum state as dictated by the Nyquist criterion. Specifically, the Nyquist bound on the largest observable momentum state is given by $|k|/a/2\pi < a/2D\delta$.

More importantly, at any specific frequency, the Nyquist bound must be greater than the momentum $|k|$ of all momentum states which are significantly excited. Consider a momentum state $k'$ where $|k'| > a/2D\delta$. This state will be aliased by the Fourier transform, and mapped onto an incorrect wavevector $k'_{\text{FFT}} < a/2D\delta$. If the value of the spectral function $M(k',\omega)$ is large, this aliasing will introduce significant numerical errors and distort the resulting spectral function. Aliasing can be easily identified by broken symmetries in the spectral function. The FFT operates on a square or rectangular domain, and the artefacts of aliasing will possess either square or rectangular symmetries. These errors are easily identified in the momentum distributions of structures whose reciprocal space rotational symmetry is not four-fold.

Aliasing should be avoided at all costs, however this is not possible without prior knowledge of the spectral function $M(k,\omega)$. Calculation of the spectral function should first be performed for a modest sample supercell, for which the Nyquist bound can be made arbitrarily large. This rough estimate of the spectral function can then inform the choice of sample size and downsampling factor for a second high resolution calculation.
Once calculated, the spectral functions are sliced along two orthogonal $k$ space directions; these directions, which I refer to as ‘cut 1’ and ‘cut 2’, are overlaid on the structure factors as yellow arrows (Figs. 4.15 & 4.16).

First, I calculate generalised band diagrams for the frequency range $0 < af/c < 0.65$; this broad frequency range gives a holistic picture of dispersion in the structures. Fig. 4.17 shows the band structure of the TM sample along the cut 1 and cut 2 directions. The $k$ vectors at which the cut passes through a Jones zone edge are annotated as dotted vertical lines; these lines are colour-coded according to table 4.1 and Figs. 4.15 & 4.16 to represent the reciprocal quasi-lattice vector family with which the Jones zone is associated.

The fundamental gap is clearly visible as the broad dark region centred on $af/c = 0.38$. The sub-fundamental gap corresponds to the first narrow dark slash visible beneath the fundamental. As before, we observe a single clear band at low frequencies associated with the momentum states of the effective medium.

As the frequency increases, the effects of Bragg processes become apparent; the effective medium band is observed to fold back towards the origin at numerous distinct $k$ vectors. The dispersion becomes diffuse as the main band approaches the edges of the $G_1$ and $G_2$ Jones zones. As a result, the precise distribution of momenta in the vicinity of the sub-fundamental gap is not well resolved; a high resolution calculation is required to probe this region in greater detail. The

![Figure 4.17: Generalised band diagram of the Penrose TM architecture along the cut 1 and cut 2 directions. The vertical dotted lines represent the points where each cut passes through a Jones zone edge; the identity of the Jones zone is colour-coded. The fundamental gap is visible as the broad dark band while the sub-fundamental gap appears as the narrow dark slash around $af/c = 0.295$. At this frequency scale, the distribution of momenta around the sub-fundamental gap is not clearly resolved.](image)
dispersion is similarly diffuse above the fundamental gap. Here, a main band and its numerous foldings may be resolved.

The generalised band diagram of the Penrose TE architecture, shown in Fig. 4.18, presents a similar picture. As before, the dispersion appears linear at low frequencies and multiple foldings are visible as the numerous faint bands which cut through the effective medium band from bottom-right to top-left.

The dispersion around the sub-fundamental gap is more clearly resolved than the TM case. As the momentum states of the main band approach the $G_1$ Jones zone, the band begins to curve down. It is clear that, in both cuts, the main band is flat at the $G_1$ Jones zone edge; this marks the lower edge of the sub-fundamental PBG.

Above the sub-fundamental gap, the distribution of momentum states becomes diffuse and no fine structure can be resolved. As the frequency continues to increase, the large fundamental PBG occurs. The dispersion remains diffuse above the fundamental gap but we nonetheless resolve the main band as an intense streak from bottom left to top right. Here, the main light line appears to fold back as a result of Bragg processes, notably the $G_1$ and $G_2$ processes.

![Generalised band diagram of the Penrose TE architecture along the cut 1 and cut 2 directions.](image)

**Figure 4.18:** Generalised band diagram of the Penrose TE architecture along the cut 1 and cut 2 directions. The vertical dotted lines represent the points where each cut passes through a Jones zone edge; the identity of each Jones zone is colour-coded and $G_3$ and $G_4$ Jones zones are not marked for clarity. The fundamental and sub-fundamental gaps are clearly visible. At the lower edge of the sub-fundamental gap, momentum appears to localise at the $G_1$ Jones zone edge (blue).
4.5.4 Sub-Fundamental Gap - TE Architecture

I now calculate high resolution generalised band structures to investigate the dispersion around the sub-fundamental gap more closely. I begin with the Penrose TE structure which is found to display simpler and clearer dispersion than than TM case. I calculate a spectral function for the frequency range $0.20 < af/c < 0.28$. In this particular case, I employ an extremely large $12 \times 32$ super-supercell of the connected network structure. This large domain results in very fine feature resolution in the momentum space.

Fig. 4.19 shows band diagrams over the frequency range $0.20 < af/c < 0.28$ for the Penrose TE architecture along the cut 1 and cut 2 directions. The points at which a slice intersect the edge of a Jones zone are marked as colour-coded vertical dashed lines. The sub-fundamental gap is visible as the broad dark region between $0.232 < af/c < 0.244$. The fundamental gap begins around $af/c = 0.271$ and extends off the top of the figure.

At low frequencies, we observe an intense principal band and many more distinct and mutually intersecting bands at lower intensities. The overall dispersion appears fractal-like and self-similar. This behaviour likely results from the scattering of the principal band by the many distinct and sharply-defined Bragg processes of the structure factor (Fig. 4.16B).

As the frequency increases, the main band propagates towards the $G_1$ (blue) Jones zone edge. The zone edge marks the $k$ space surface where the corresponding Bragg process scatters plane

![Figure 4.19: Generalised band diagram for the Penrose TE architecture in the frequency region of the sub-fundamental gap. The sub-fundamental gap corresponds to the dark region centred on $af/c = 0.238$, while the fundamental gap extends off the top of the figure. Just below the sub-fundamental gap, momentum is strongly localised at the $G_1$ Jones zone edge (blue). Momenta are similarly localised at the $G_2$ Jones zone edge (orange) at the lower edge of the first mini-gap.](image-url)
waves onto counter-propagating states. We see, in both cuts, that the band turning points correspond to momentum localisation at the Jones zone edge.

The lower edge of the sub-fundamental gap is characterised by momentum localisation at the Jones zone $N$ points (cut 2). As the frequency is increased, these momentum states disappear and then re-appear at frequencies above the sub-fundamental gap. The band structures thus suggest that standing wave formation at the $G_1$ Jones zone edge plays a key role in opening the spectral gap.

Above the sub-fundamental gap, the dispersion becomes more diffuse. We nonetheless can resolve a number of bands whose turning points exhibit momentum localisation at a Jones zone edge. Note the two thin dark slashes across the band diagrams around $af/c = 0.258$ and $af/c = 0.261$. These dark slashes correspond to the mini-PBGs which are visible in the TE structure’s density of states (Fig. 4.12C); note that there is a small frequency offset between the band diagram and the DOS due to difficulties matching the dielectric fill fractions in the FDTD engine and the MIT photonic bands package.

Immediately below the first mini-PBG, momentum is localised at the $G_2$ Jones zone edge. This suggests that the mini-gap results from standing wave formation as a result of the $G_2$ Bragg process. This Bragg process is less intense than the $G_1$ process (Fig. 4.16B), and the resulting spectral gap appears smaller than the sub-fundamental PBG.

The dispersion becomes quite diffuse above the first mini-PBG. A number of bands appear to exist, but they are not well resolved. Note that the thin bright slash that stands alone at $af/c = 0.271$, just within the fundamental gap, was observed to be a defect mode; the true edge of the fundamental gap thus falls around $af/c = 0.269$. Here, a band is faintly visible in cut 1, while cut 2 shows no clear momentum localisation at the edge of the fundamental gap.

The complete momentum distributions of the light field corroborate my analysis of the band diagram; these distributions are shown in Figs. 4.20 & 4.21, where each panel corresponds to one of the frequencies annotated in red on Fig. 4.19. Colour-coded Jones zones of interest are overlaid on the momentum distributions, although note that the $G_2$ Jones zone is shown in black to contrast with the colourmap.

Fig. 4.20 Panel A shows the momenta at low frequency (generalised band structure, frequency 1). Here, the fractal-like character of the momentum states is rendered very clearly; features can be resolved at all momentum scales. The principal feature of the distribution is the central bright ring corresponding to the momentum states of the effective medium. The central ring is scattered by Bragg processes into offset momentum rings of varying intensity. The most intense set of scattered momenta comprises ten intersecting rings, each one centred at a $G_1$ reciprocal quasi-lattice point.

Panels B & C show momenta just below the sub-fundamental gap (generalised band structure, frequencies 2 & 3). In panel B, the central ring touches the $G_1$ Jones zone $X$ points; in moving from panel B to C, we see that these momenta disappear due to the spectral gap that opens between the two possible standing wave states. Panel C corresponds to the lower edge of the sub-fundamental gap. Here we observe momenta strongly localised at the Jones zone $N$ points.
which, in an analogous manner to the momentum states immediately below the honeycomb fundamental gap (Fig. 4.5, panel 4), form a global standing wave which exists in two non-degenerate states. Just above the sub-fundamental gap, shown in Panel D, we observe the re-appearance of momentum states at the Jones zone X points.

The sub-fundamental gap thus results from overlapping spectral gaps along all possible propagation directions in the structure. These gaps arise due to the coupling of momentum states to counter-propagating states at the $G_1$ Jones zone edge. When momenta lie at the zone edge, they are observed to disappear. The high energy forms of the standing wave states are then observed to reappear at higher frequencies. In particular, I note that the momentum distributions of Bragg-resonant states possess a different character to those of regular propagating states. Propagating states, as shown in panels A & B, are either extended (panel A) or diffuse (panel B). Standing wave states, on the other hand, appear to concentrate momenta at numerous high-symmetry points of the reciprocal quasi-lattice, as shown in panels C & D.

Fig. 4.21 Panels A & B show the momentum distributions immediately below and above the first mini-gap respectively (generalised dispersion plot, frequencies 5 & 6). Below the gap, momenta are strongly localised at the $N$ points of the $G_2$ Jones zone (black). Above the gap, momenta at the zone $N$ points are suppressed, but states re-appear at the zone $X$ points. In both panels, the momentum distribution has a point-like character, localising momenta at high symmetry points throughout the $k$ space. As with the sub-fundamental gap, this sequence is diagnostic of PBG formation by resonant Bragg scattering.
Figure 4.21: Momentum distributions around the mini-PBGs and fundamental PBG for the Penrose TE structure; panels correspond to frequencies annotated in red on Fig. 4.19 according to A → 5, B → 6, C → 7 & D → 8. Edge states of the first mini-PBG (A & B) exhibit Bragg resonant character and momentum localisation at the $G_2$ Jones zone edge (black). States at the lower edge of the fundamental gap (C & D) appear comparatively diffuse.

Fig. 4.21 Panels C & D show the momenta in the vicinity of the fundamental gap lower edge (generalised dispersion plot, frequencies 7 & 8). Here, neither panel exhibits momentum localisation at the high symmetry points of a Jones zone. Immediately below the fundamental (panel D), the momenta diffusely fill the $k$ space; the distribution does not have the clear Bragg-resonant character of the edge states of sub-fundamental and first mini gaps. This suggests, in accordance with Della Villa et al’s investigation of PBG character, that the mechanisms which generate the fundamental and sub-fundamental gaps are different.

Earlier, I analysed the field modes above and below the fundamental PBG and concluded that they show signatures of generalised resonant scattering. Given that the momentum distribution of the gap edge state exhibits no Bragg-resonant character, I suggest that the Bragg mechanism plays a minimal role in the formation of the Penrose TE structure’s fundamental gap. Rather, the formation of the gap is principally mediated by generalised resonant scattering.

### 4.5.5 Sub-Fundamental Gap - TM Architecture

I now calculate high resolution generalised band structures to investigate the dispersion around the sub-fundamental gap more closely. Fig. 4.22 shows band diagrams over the frequency range $0.24 < af/c < 0.32$ for the Penrose TM architecture along the cut 1 and cut 2 directions. The sub-fundamental gap is visible as the dark region between $0.294 < af/c < 0.30$. The fundamental PBG begins around $af/c = 0.31$ and extends off the top of the figures.
Figure 4.22: Generalised band structures around the sub-fundamental PBG for the Penrose TM architecture. The sub-fundamental gap appears as a dark band around $0.294 < a_f/c < 0.30$. The fundamental gap extends off the top of the figure. The dispersion is somewhat more complex than that of the TE architectures. Nonetheless, we observe that, immediately below the sub-fundamental, momentum states are localised at the $G_2$ Jones zone edge.

The dispersion is evidently complex. At low frequencies, the main band is clearly visible. As the frequency increases, the main band approaches the $G_1$ Jones zone edge. In both cuts, the main band appears flat where it intersects the $G_1$ Jones zone. The momentum states at the zone edge disappear as the frequency increases further; this suggests the formation of standing waves by resonant Bragg scattering. However, it appears that the Bragg-induced scattering is not strong enough to open a gap. Instead, a new distinct band emerges; this is a visible in cut 1 between $0.265 < a_f/c < 0.28$. Above this band, around $a_f/c = 0.28$, we observe the reappearance of momentum states at the $G_1$ Jones zone edges. This dispersion is similar to the band structure around the sub-fundamental gap of the Penrose TE architecture (Fig. 4.19). In the TM case, however, a new band emerges along the cut 1 direction which prevents gap formation.

The origin of this band is complex. It is evident from the azimuthally averaged structure factor (Fig. 4.15B) that $G_1$, $G_2$ and $G_6$-type Bragg processes should all play a significant role in the coupling of momentum states at a given frequency. I suggest that the absence of a PBG at the $G_1$ Jones zone edge is a result of scattering, by a combination of $G_2$ and $G_6$ Bragg processes, which creates a significant number momentum states which are not directly coupled to their counter-propagating equivalents.

As the frequency increases, the distribution of momentum states becomes more diffuse. Immediately below the sub-fundamental gap, we observe strong localisation of momentum at the $G_2$ Jones zone edge; this suggests that the sub-fundamental gap forms through standing wave formation as a result of $G_2$ Bragg processes. The dispersion above the sub-fundamental gap
Figure 4.23: Momentum distributions around the sub-fundamental PBG of the Penrose TM structure; panels correspond to frequencies annotated in red on Fig. 4.22 according to A → 1, B → 2, C → 3 & D → 4. In Panel A, the effective medium states are strongly scattered by $G_1$, $G_2$ and $G_6$ Bragg processes. Panels C-D show partial momentum localisation at a Jones zone edge, superimposed on a complex momentum distribution that arises from interaction of the three major Bragg processes.

appears diffuse, and no clear momentum localisation is observed at the edge of the fundamental PBG.

Figs. 4.23 & 4.24 show the full momentum distributions for each of the frequencies annotated in red on Fig. 4.22. In each panel, a Jones zone is overlaid; these Jones zones are colour-coded, although the $G_2$ Jones zone is plotted in black to stand out from the hot colormap.

Fig. 4.23 Panel A shows low frequency momentum states (Fig. 4.22, frequency 1). Here, it is clear that the effective medium band (central bright ring) is subject to scattering by three strong Bragg processes. The $G_1$ and $G_2$ Bragg processes generate two interlocking decagonal distributions of rings, while the $G_6$ Bragg process scatters the effective medium band into the outer decagon of momentum rings. Note the size of the $G_1$ Jones zone relative to the total extent of the momentum distribution. A single $G_6$ scattering event corresponds to a large momentum transfer; this launches the momentum states of the effective medium far from the $k$ space origin.

Fig. 4.23 Panels B & C, which correspond to Fig. 4.22 frequencies 2 & 3, demonstrate the hugely complex dispersion that results from the interaction of the TM structure’s dominant Bragg processes. We observe some localisation of momenta around the $G_1$ Jones zone; these momentum states are directly coupled to their inverses, and lend the eigenmodes a partial standing wave character. The eigenmodes are, however, not complete standing waves. Scattering through $G_2$ and $G_6$ Bragg processes distributes the momenta widely throughout the $k$ space.
These extended momentum states are likely not directly coupled to a counter-propagating state and thus no PBG is observed to form.

Fig. 4.23 Panel D tells a similar story. Momenta are localised at the $G_2$ Jones zone $N$ points; these states will interfere to form standing waves. The zone-edge states are, however, scattered throughout the $k$ space by non-$G_2$ Bragg processes. This scattering produces a diffuse momentum distribution comprising many states which are not directly coupled to their inverses. PBG formation is thus inhibited.

Fig. 4.24 Panel A marks the lower edge of the sub-fundamental PBG (Fig. 4.22, frequency 5). Like Fig. 4.23 Panel D, it also shows strong momentum localisation at the $G_2$ Jones zone $N$ points. However, the momentum distribution now appears resonant throughout the $k$ space; the distribution is not diffuse and momenta are strongly focussed into discrete high symmetry points. The character of this momentum distribution is similar to the Bragg-resonant momentum states at the edges of the sub-fundamental gap (Fig. 4.20, Panels C & D) and first mini-PBG (Fig. 4.21, Panels A & B) of the TE architecture. The formation of the TM architecture’s sub-fundamental gap is thus associated with standing wave formation that results from scattering by the $G_2$ Bragg process.

Momentum distributions above the sub-fundamental PBG are shown in Fig. 4.24 Panels B, C

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4_24.png}
\caption{Momentum distributions around the sub-fundamental PBG of the Penrose TM structure; panels correspond to frequencies annotated in red on Fig. 4.22 according to $A \to 5$, $B \to 6$, $C \to 7$ & $D \to 8$. Panel A shows the lower edge of the sub-fundamental gap. Here, the momenta show Bragg resonant character and localisation at the $G_2$ Jones zone (black) is clear. No Bragg resonant character is obvious just below the fundamental PBG, shown in panel D.}
\end{figure}
Unfolding the Photonic Band Structure

& D; these correspond to Fig. 4.22 frequencies 6, 7 & 8 respectively. The momentum distributions are structured but diffuse. Panel D describes the light field just below the fundamental gap. Here, the momentum distribution remains diffuse and we observe no clear Bragg resonant character. Momenta are focussed in the region of the $G_2$ Jones zone (black) but this localisation is not pronounced. This behaviour is analogous to the momentum distribution just below the fundamental PBG of the TE architecture (Fig. 4.21 Panel D).

It is clear from the field distributions at the edges of the fundamental PBG (Fig. 4.13) that the Mie resonant modes of the dielectric cylinders play a key role in formation of the gap. Given the absence of clear Bragg-resonant character in the momentum distributions around the lower gap edge, I conclude that Bragg-induced scattering plays a minimal role in the formation of the fundamental PBG. Formation of the fundamental PBG is thus mediated primarily by the Mie mechanism, while the sub-fundamental gap results from scattering by $G_2$ Bragg processes.

4.5.6 Summary

Spectral functions have been successfully employed to produce generalised band structures for a cylinder array (TM) and connected network (TE) derived from a $13-8$ periodic approximant to the Penrose tiling. The dispersion diagrams of both TM and TE architectures exhibit a rich variety of features across a spectrum of intensity scales. Here, I have analysed the principal features of the band diagrams. In particular, I have elucidated the mechanisms through which the fundamental, sub-fundamental and other mini-PBGs form.

At low frequencies, the TE architecture exhibited a fractal-like band diagram due to scattering of the effective medium band by the numerous Bragg-like peaks of its structure factor. At the edge states of the sub-fundamental PBG, momenta were localised at the edges of the $G_1$ Jones zone. In the vicinity of the first mini-PBG, momenta were similarly localised at the edges of the $G_2$ Jones zone. Formation of these two gaps may thus be linked to standing wave formation resulting from the coupling of momentum states to their counter-propagating equivalents through a strong Bragg process. The momentum distributions associated with standing wave formation appeared resonant; they possessed a fractal-like character, and momentum was focussed into high-symmetry-like points of the $k$ space. In contrast, the lower edge of the fundamental PBG was characterised by a diffuse momentum distribution; Bragg processes thus appeared to play a minimal role in its formation. Rather, the fundamental resulted primarily from generalised resonant scattering by the network vertices.

Interpretation of the TM architecture’s dispersion diagrams was more challenging. At low frequencies, dispersion was clearly mediated by the scattering of effective medium states by the $G_1$, $G_2$ and $G_6$ Bragg processes; these three processes were all associated with significant peaks of the architecture’s structure factor. The sub-fundamental gap was associated with localisation of momentum at the edges of $G_2$ Jones zone and thus resulted from standing wave formation via Bragg scattering. Dispersion diagrams showed no clear Bragg resonant character at the lower edge of the fundamental PBG. Rather, the fundamental gap resulted primarily from scattering by the Mie resonances of the dielectric cylinders; this mechanism has been observed to open
sizeable PBGs in the absence of Bragg scattering. In general, the dispersion of the TM architecture exhibited many complex features, including states of partial standing wave character that did not enclose a PBG.

In both the TM and TE architectures the sub-fundamental gap was observed to result from Bragg scattering-induced standing wave formation. The fundamental gap, on the other hand, forms principally via the Mie and generalised resonant scattering mechanisms in the TM and TE architectures respectively. These observations clarify the relationship between the Bragg and Mie mechanisms of gap formation.

Specifically, the extent to which Bragg scattering contributes to gap formation in two and three-dimensional structures is not well understood. Gap formation in photonic crystals results from synergetic interplay of the Bragg and Mie/generalised resonant scattering mechanisms. It has been noted, however, that sizeable PBGs can form by Mie scattering and generalised resonant scattering (Section 3.8) in the absence of Bragg-like structure factor peaks. Here, for the first time, I have observed the converse. Field profiles of the TM architecture exhibit similar Mie resonant character at the upper and lower edges of the sub-fundamental gap; Mie scattering is thus not responsible for its formation. Instead, the sub-fundamental gap is associated with momentum localisation at a Jones zone edge, and thus appears to form through Bragg scattering alone. A similar argument applies to the sub-fundamental gap of the TE architecture.

4.6 Conclusions

In this chapter, I have introduced a novel approach to calculating the photonic band structure of an arbitrarily structured medium. This approach, called the spectral function method, is based on the projection of a structured medium’s electromagnetic modes into a momentum representation. Calculation of spectral functions is a two step process. Firstly, an FDTD method is used to determine the structure’s eigenmodes $E(r, \omega)$ or $H(r, \omega)$ for some frequency range of interest. Secondly, the eigenmodes are projected into their momentum representations $E(k, \omega)$ or $H(k, \omega)$ by fast Fourier transform. The norm of the momentum representation then defines the spectral function.

I have developed also a novel perspective with which to view the dispersion of light in a structured medium. A Hamiltonian formulation of Bragg scattering suggests that the momentum distributions of low index contrast architectures result, to first order, from scattering the momentum states of an effective medium by Bragg processes. The rate with which a particular Bragg process scatters a plane wave state, wavevector $k_i$, into a scattered state, wavevector $k_s$, is proportional to the value of the architecture’s structure factor $S(q)$ at the corresponding momentum transfer $q = k_s - k_i$.

I demonstrated that the spectral function method accurately predicts the band structure for the TE modes of a honeycomb photonic crystal. Further, Bragg scattering was observed to play a key role in the formation of the honeycomb photonic crystal PBG. The momentum distributions $E(k, \omega)$ of the PBG edge states exhibited localisation of momenta at the edges of the crystal’s Brillouin zone. At the Brillouin zone edge, plane wave states are scattered
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onto counter-propagating states and standing waves are formed. These standing waves have lattice periodicity; they thus exist in high and low energy states depending on the localisation of their electromagnetic energy density with respect to the underlying dielectric distribution. The spectral gap between these states defined the PBG.

After this proof of concept, I used the spectral function method to calculate generalised band structures for the TE modes of a pair of hyperuniform connected networks. In the low index case, I observed that the generalised band diagram comprised an effective medium band which split into two within the critical $k$ space region that exists halfway between the $k$ space origin and the peak of the architecture’s structure factor. The overall form of the band diagram was well predicted by the scattering of effective medium states via Bragg processes. In the high index case, the generalised band diagram was strongly perturbed by energetic interactions between the electromagnetic field and the dielectric material. Multiple distinct foldings of the main band by Bragg processes were nonetheless visible.

I then applied the spectral function method to probe the rich dispersion relations of structures derived from a Penrose quasicrystal. I studied the TM modes of a Penrose cylinder array and the TE modes of a connected dielectric network derived from a Penrose point pattern. For each architecture I studied the structure factor and indexed its main peaks.

Spectral functions revealed intricate fractal-like generalised band diagrams. In the TE case, several PBGs - a fundamental, a sub-fundamental, and two mini-PBGs - were all observed. Momentum distributions at the edges of the sub-fundamental and mini-PBGs showed Bragg-resonant character, with localisation of momenta at the edges of Jones zones associated with major structure factor peaks. Momentum distributions at the edge of the fundamental gap showed little Bragg resonant character. I concluded that the sub-fundamental and mini-PBGs resulted from standing wave formation due to Bragg scattering. The fundamental gap, on the other hand, was primarily a result of the generalised resonant scattering mechanism.

Dispersion in the TM case was observed to be complex. The TM architecture structure factor exhibited three major peaks. Scattering by the Bragg processes associated with these peaks distributed momenta widely throughout the $k$ space. The TM architecture displayed both a large fundamental PBG and a smaller sub-fundamental gap. As in the TE structure case, momentum distributions at the edges of the sub-fundamental gap exhibited localisation at the edges of a Jones zone. Just below the fundamental gap, momentum distributions were observed to be diffuse and without clear Bragg resonant character. I concluded that the sub-fundamental PBG forms due to the Bragg mechanism while the fundamental gap is principally a result of the Mie mechanism.
Chapter 5

Reciprocal Space Engineering
With Hyperuniform Gold Metasurfaces

Optical metasurfaces are artificial structures that are tailor-made to control the amplitude, phase and polarisation state of a light signal. They typically comprise an ultra-thin planar array of sub-wavelength scale nano-antennae mounted on a transparent substrate. The design, fabrication and application of metasurfaces is an active and high impact field of research. Specifically, metasurfaces can achieve advanced optical control using components that are only a fraction the size of conventional phase-accumulation-based lenses and wave-plates. Metasurfaces are thus likely to be crucial in the development of integrated optical circuits\(^{154-156}\), compact aberration-free imaging systems\(^{154,155,157}\) and holography and flat display technologies\(^{158}\). Further, since they are based on planar or multilayer architectures, their manufacture is compatible with existing nano-fabrication paradigms.

The most common form of metasurface exploits the localised surface plasmons of metallic nano-antennae to abruptly alter the phase of an incident light signal\(^{154,159}\). The phase shift acquired by interaction with a single antenna is controlled by its size, shape and orientation\(^{159}\). Arbitrary phase envelopes can thus be applied to an incident wavefront by engineering complex patterns of non-identical antennae at sub-wavelength scales. Engineering these phase envelopes is the primary means through which light is controlled by a metasurface. For instance, phase gradients can be used for beam steering (explained by a reformulation of Snell's law in the presence of a phase gradient\(^{159}\)) and to design ultra-thin lenses\(^{157,160}\), beam splitters\(^{161}\) and vortex beam generators\(^{162}\).

In this chapter, my collaborators and I approach the design of metasurfaces from a perspective of reciprocal space engineering. Specifically, we seek to investigate the extent to which manipulation...
of a metasurface’s reciprocal space can be used to engineer useful light-controlling behaviours. To achieve this, we employ a metasurface design derived from a hyperuniform point pattern and fabricate gold samples using e-beam lithography. The structure factor of these metasurfaces is dominated by a single, broad scattering resonance, whose impact we characterise through light scattering and fluorescence emission experiments.

The chapter is structured as follows. First, I discuss the design and manufacture of the hyperuniform gold metasurfaces. Second, I outline the experimental and theoretical methods employed to characterise the samples. Third, I present the results of our characterisation through light scattering of a selection of gold metasurfaces across a spectrum of sizes. Scattered light is decomposed into its component momenta by observation in the farfield, and I discuss the origins of the various scattering peaks. Specifically, we find that scattering from the metasurfaces is principally diffractive. Fourth, we investigate directional emission from our metasurfaces. Slab modes are directly excited by fluorescent molecules, and their dispersion relation is measured by decomposition of detected light into its frequency and momentum components. Comparison of the slab dispersion with spectral function calculations suggests that directional emission results from the folding by Bragg processes of an effective medium band back into the light cone. The directional emission is thus a direct result of the reciprocal space properties of the hyperuniform network.
5.1 Design and Fabrication

We employ a $\chi = 0.49$ hyperuniform pattern, comprising 4000 points and generated under a periodic boundary condition, as a seed for the gold metasurfaces. The pattern is defined inside a square box of side length $\sqrt{4000}$ such that the point density is unity. Designs of any required size are then produced by scaling the unit density pattern through multiplication by a scaling parameter $a$. A section of the point pattern, decorated by discs of radius $0.3a$, is shown in Fig. 5.1A. As a hyperuniform pattern characterised by a sizeable $\chi$ value, the point distribution exhibits significant local structural correlations. The structure factor of the point pattern is shown in Fig. 5.1B; the primary panel shows the azimuthally averaged structure factor, while the inset presents the complete diffraction spectrum. The structure factor exhibits the typical exclusion region around $k = 0$ which characterises stealthy hyperuniform patterns. Beyond this, the structure factor rises to a broad isotropic diffraction maximum with a peak around $\alpha k/2\pi = 1.03$.

As a next step, the point pattern was tessellated according to the Delaunay tessellation protocol of Section 2.4.2.3. Tessellation of a pattern comprising $N$ points generates a strictly trivalent network topology comprising $2N$ vertices, $3N$ unique edges and $N$ cells. We decorated the edges of the network with dielectric walls of thickness $0.35a$. A section of the tessellated design is shown in Fig. 5.1C; it is characterised by a continuous network (black) which encloses a number of deformed pentagonal, hexagonal and heptagonal islands (white). The structure factor of the network is presented in Fig. 5.1D. We observe that the stealthiness of the architecture has been significantly reduced; the diffraction spectrum (inset) exhibits low intensity diffuse scattering around $k = 0$, in contrast to the sharp exclusion zone of the simple point pattern. Nonetheless,

![Figure 5.1](image.png)

**Figure 5.1:** Engineering hyperuniform gold metasurfaces. We start with a $\chi = 0.49$ hyperuniform point pattern (A) whose structure factor (B) possesses a typical zero around $k = 0$ and a broad isotropic diffraction maximum. Delaunay tessellation forms a connected network (C) which broadly preserves the $k$ space characteristics of the point pattern (D). Pillar-type (E, left) and network-type (E, right) metasurfaces were then fabricated via e-beam lithography. SEMs of the resulting pillar-type (left) and network-type (right) metasurfaces (F).
the general form of the point pattern structure factor is reproduced by the network. Specifically, the momentum transfer space is dominated by a single broad and isotropic resonance with a peak around \( ak/2\pi = 1.09 \).

Metasurfaces were fabricated via electron beam lithography employing PMMA as a positive tone resist. Two types of sample were fabricated: these were pillar-type and network-type (both derived from the hyperuniform connected network of Fig. 5.1C). Pillar-type samples comprise a connected network of air enclosing isolated pentagonal, hexagonal and heptagonal gold pillars; this is illustrated schematically in the left-hand panel of Fig. 5.1E. Network-type designs are identical but inverted; they comprises a connected network of gold enclosing isolated air pillars, as illustrated on the right side of Fig. 5.1E.

To fabricate the pillar samples, we spin coat PMMA on top of a 10nm thin layer of ITO on a glass substrate. The islands of the hyperuniform network were patterned into the PMMA by e-beam exposure and the exposed areas were removed by development. Following this, 45nm of gold was deposited by thermal evaporation and the remaining PMMA lifted-off with acetone. To fabricate network samples, we spin coat PMMA directly onto a 45nm layer of Au on a glass substrate. As before, the network islands were patterned via e-beam and the PMMA developed. The sample was then UV plasma etched prior to lift-off of the remaining PMMA. Fig. 5.1F shows SEMs of the resulting pillar-type (left) and network-type (right) metasurfaces.

We fabricated a collection of pillar and network metasurfaces for a spectrum of scaling parameters \( a \). In all cases, metasurfaces were 40\( \mu \)m square. For large scaling parameters, it was thus necessary to fabricate only a sub-section of the total design. For small scaling parameters, designs were periodically repeated to fill the 40\( \mu \)m square build region. We name samples according to the side length of the hyperuniform network design when scaled by \( a \). For instance, a pillar sample defined by \( a = 790.6 \) has a side length of \( 790.6 \times \sqrt{4000} = 50 \mu \)m and is thus known as \( L_p50 \). Table 5.1 summarises the pillar-type metasurfaces fabricated and documents their scaling parameters.

### Table 5.1: List of named pillar-type metasurfaces and their associated scaling parameters \( a \).

<table>
<thead>
<tr>
<th>Design name ( L_p )</th>
<th>( a ) [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L_p50 )</td>
<td>790.6</td>
</tr>
<tr>
<td>( L_p45 )</td>
<td>711.5</td>
</tr>
<tr>
<td>( L_p40 )</td>
<td>632.5</td>
</tr>
<tr>
<td>( L_p35 )</td>
<td>553.4</td>
</tr>
<tr>
<td>( L_p30 )</td>
<td>474.3</td>
</tr>
<tr>
<td>( L_p25 )</td>
<td>395.3</td>
</tr>
<tr>
<td>( L_p20 )</td>
<td>316.2</td>
</tr>
</tbody>
</table>

5.2 Methods

#### 5.2.1 Experimental Set-Up

Metasurfaces were optically characterised using a leakage radiation microscopy method; this process is illustrated schematically in Fig. 5.2A. Samples were mounted inside an optical microscope directly onto a glass substrate (refractive index \( n_g = 1.52 \), not shown). Samples were illuminated at normal incidence, defined as the \( z \) axis, either from above or below as applicable (Fig. 5.2A shows illumination from above). At a given frequency \( \omega \), wavevectors \( 0 < k < n_g \omega /c \)
can leak into the glass where they may be observed in the farfield. The use of a glass substrate over air thus increases the range of observable momentum states, and facilitates the observation of surface plasmon polaritons whose dispersion relation lies outside the free space light line.

Farfield light is a natural Fourier transform of the nearfield; it is decomposed into transverse momentum components \([k_x, k_y]\) according to the angle of observation. The observation angle \(\theta\), measured from the normal, is related to the magnitude \(k\) of the transverse momentum according to \(k/k_0 = n_g \sin \theta\), where \(k_0\) is the free space wavevector at the frequency of observation. Light was analysed in the farfield beneath the sample (within the glass) by an objective with a maximum collection angle of \(\theta_{\text{max}} \approx 72.5^\circ\). Given the use of a glass substrate, the overall numerical aperture (NA) of the collection optics was \(NA = n_g \sin \theta_{\text{max}} = 1.45\). The numerical aperture controls the maximum observable farfield momenta which are, for a given wavevector of illumination \(k_0\), not greater than \(k_0 NA\).

Where applicable, farfield light was further manipulated prior to observation. Fig. 5.2A shows how the light was spectrally decomposed. Momentum components of the farfield were selected by a narrow slit. This light was then passed through a diffraction grating which splits the light into its component frequencies. A planar detector then records a complete momentum and frequency decomposition of the collected light.
5.2.2 FDTD Set-Up

Experimental observations were corroborated by finite difference time domain (FDTD) electromagnetic simulations implemented in Lumerical FDTD solutions\textsuperscript{130}. Figs. 5.2B & C show the FDTD region configuration; panel B shows a view of the FDTD region in the xz plane while panel C shows a view in the plane of the samples (looking down the z axis).

Metasurface designs were imported as images and centred at the origin of the FDTD region. In order to render the computations tractable, I simulate only sub-regions of the total 40\(\mu\)m designs. For a given metasurface, this region was chosen to be square of side length 22\(a\). The thickness of the samples was set to 45nm. The size of the FDTD region was set to \((\Delta x, \Delta y, \Delta z) = (22a + 5, 22a + 5, 1)\mu m\), and this region was surrounded on all sides by perfectly matched layers (PMLs, orange Fig. 5.2B & C). The volume beneath the sample \((z < -22.5nm)\) was filled with glass, modelled as a homogeneous dielectric material of refractive index \(n_g\). The background index of the FDTD region was set to \(n = 1\) such that any regions with unspecified geometry were modelled as air.

Samples were illuminated with a total field scattered field (TFSF) source. The TFSF source, shown as a red box in Fig. 5.2B, produced plane wave-type illumination in a finite spatial region. The TFSF source was used to illuminate the sample from either above or below as applicable (the red arrow in Fig. 5.2B indicates illumination from below). I positioned a large planar detector underneath the samples to record the nearfield electric and magnetic fields. This monitor spanned the complete \(xy\) plane of the FDTD region and was positioned 30nm from the metasurface/glass interface. The nearfield data recorded by this monitor was transformed to the farfield, using Lumerical’s in-built algorithm, for comparison with experimental results.

The metasurfaces themselves were modelled as a binary mixture of gold and air. For this, I employ reference experimental data\textsuperscript{163} for the refractive index \(n(\omega)\) and extinction coefficient \(\kappa(\omega)\) of gold at optical wavelengths; this data is shown as points in Figs. 5.2D & E respectively. Lumerical fits this index data to produce the continuous quantities needed for the FDTD method; the Lumerical index and extinction coefficient fits are shown as solid lines in Figs. 5.2D & E respectively.

5.2.3 Surface Plasmons

Consider a planar interface between two bulk media, each characterised by a complex frequency dependent permittivity. It can be shown that the homogeneous Maxwell equations permit the existence of eigenmodes which are bound to the interface. These modes are travelling waves which propagate along the interface and decay exponentially with distance from it. Specifically, modes can exist subject to the condition that the real component of the relative permittivity changes sign across the interface\textsuperscript{164}.

At optical frequencies, the relative permittivity of a conductor can be strongly negative. In simple terms, this results from the response of the conductor’s free electrons to a time-varying electromagnetic field. Because these electrons have mass, their oscillation is not necessarily in
phase with high frequency applied fields. Bound surface modes, referred to as surface plasmon polaritons, can thus exist at the interface between a dielectric and a metal.

Surface plasmons comprise propagating waves of conduction electron density, characterised by a wavevector $k_{sp}$, coupled with evanescent electromagnetic fields that decay with distance from the interface. The dispersion relation of these modes can be readily calculated and may be written as

$$k_{sp} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}},$$

(5.1)

where $\omega$ is the frequency of the surface plasmon oscillation, $\varepsilon_m$ is the complex frequency-dependent permittivity of the metal and $\varepsilon_d$ is the permittivity of the dielectric. Using Eqn. 5.1, surface plasmon dispersion relations can be readily calculated from reference refractive index data. Fig. 5.2F shows the calculated dispersion relation of a surface plasmon at the interface between gold and air. The plasmon wavevector lies outside the free space light line; this increase in momentum is associated with the confinement of the wave to the interface.

### 5.3 Scattering Characterisation

We performed light scattering experiments to investigate the optical properties of the gold metasurfaces. We focus specifically on the pillar-type metasurfaces listed in Table 5.1. Fig. 5.3A shows micrographs of all these samples. It is clear that the size and separation of gold pillars decreases with decreasing scaling parameter $a$.

Samples were illuminated from below with a laser, wavelength 532nm, and back-scattered light was observed in the farfield. The farfield intensity distribution of each pillar metasurface is shown in Fig. 5.3B. The maximum observable momentum, as imposed by the numerical aperture and wavelength of illumination, is overlaid as a coloured dashed circle. $L_p$50-30 samples all exhibit broad and statistically isotropic scattering rings which resemble the primary resonance of the design’s structure factor, as shown in Fig. 5.1D. The momentum associated with the scattering resonance peak increases with decreasing $a$. As $a$ falls below 400nm, the scattering ring passes beyond the observable momentum limit and becomes unresolvable. The bright spot at the centre of each farfield results from specular reflection back along the axis of incidence.

Farfield intensity distributions were azimuthally averaged (Eqn. 2.6) to better resolve any fine features. Fig. 5.3C presents the average detected intensity as a function of in-plane momentum (normalised to the incident wavevector $k_0$). As the pillar separation decreases (red→black→green→blue→cyan→purple), the momentum of the primary scattering peak increases and the total detected intensity decreases. $L_p$50-$L_p$35 structures are all characterised by a single large scattering peak; each peak contains some fine structure that varies from sample to sample. Interestingly, the $L_p$30 sample exhibits a clear double peak, while the $L_p$25 sample shows only a single peak.
We compare these scattering observations with the results of FDTD simulations. FDTD was performed according to Section 5.2.2. Nearfield data was recorded for 532nm plane wave illumination. This data was transformed to the farfield and the scattering pattern was azimuthally averaged. The results of these FDTD simulations are shown in Fig. 5.3D. We observe that the experimental results are well modelled by my FDTD simulations; the general shape and fine features of the scattering peaks are captured by the FDTD simulations. In particular, FDTD predicts the signature double peak of the \( L_p30 \) sample, suggesting that this feature is a genuine property of the sample. We note a small systematic offset between the experimental and FDTD-predicted peak centres. We attribute this to either a systematic manufacturing error (samples uniformly too large) or a minor mis-calibration of the detection equipment; we consider the FDTD results to be more accurate, and peak positions are hereafter measured using the FDTD data.

\[
\begin{array}{ccccccccc}
\text{Design name} & L_p50 & L_p45 & L_p40 & L_p35 & L_p30 & L_p25 & L_p20 \\
\hline
k_{\text{peak}}/k_0 & 0.734 & 0.815 & 0.916 & 1.048 & 1.223 & 1.467 & 1.834 \\
\end{array}
\]

Table 5.2: Expected scattering peaks positions \( k_{\text{peak}}/k_0 \) for purely diffractive scattering, calculated for 532nm laser light.
Comparison with Fig. 5.3D suggests scattering arising from purely diffractive processes should peak around $ak_{\text{peak}}/2\pi = 1.08$. Inversion of this relationship permits calculation of the peak position as a function of $a$; the predicted peak positions $k_{\text{peak}}/k_0$ are presented in table 5.2. We observe that the $L_p$50-35 peak centres, as calculated by FDTD, lie directly where the diffraction peak is expected to occur. The insets of Figs. 5.3C & D show plots of each sample’s scattering peak position plotted against the reciprocal of the scaling parameter. This relationship should be linear if the peaks result from diffractive scattering; this is exactly what we observe. In the case of the $L_p$30 structure, it is the second peak, located around $k = 1.21$, that is attributable to diffraction.

To explain the origin of the scattering peak around $k = 1.10$, we appeal to the dispersion relation of a surface plasmon confined to an air/gold interface. This dispersion relation is shown in Fig. 5.2F where a single point has been highlighted in black. This point describes the surface plasmon dispersion at a free space wavelength of 532nm and corresponds to $(k_{\text{sp}}, \omega) = (12.9 \mu m^{-1}, 3.54 \text{fs}^{-1})$. When plotted on the farfield scattering plot (Fig. 5.3D), a surface plasmon resonance should manifest as a peak around $k/k_0 = 1.09$. This plasmon momentum is in good agreement with the observed position of the first peak of the $L_p$30 design, located around $k/k_0 = 1.10$. Further, the significant shoulder of the $L_p$35 pattern’s peak around this momentum is likely also a surface plasmon effect.

It is not apparent why this surface plasmon resonance is significant only for the $L_p$30 design. We suggest that the the gold pillars of the $L_p$30 sample are an appropriate size to support a high order surface plasmon resonance, possibly a quadrupole or hexapole-type mode. As the gold pillars become smaller, lower order surface plasmon modes come on resonance. This increases the extinction cross section of the metasurface and explains the reduction in total scattered intensity with decreasing scaling parameter.

We also performed a broadband scattering characterisation of the $L_p$50 design. The sample was illuminated from above by white light, and transmitted light was spectrally decomposed into its frequency and momentum components (as shown in Fig. 5.2A). The experimental scattering spectrum is shown in Fig. 5.4C. Wavelength is recorded along the horizontal axis while the vertical axis measures $k/k_0$ - the momentum normalised to the free space wavevector at the frequency of observation; note that $k/k_0 = n_g \sin(\theta)$ and thus the vertical axis records the sine of the farfield observation angle.

Experimental results display a bold diagonal slash, from low scattering angle to high scattering angle, that shows the evolution of the primary scattering peak with increasing wavelength. We know from Fig. 5.3C & D that this scattering is diffractive at 532nm. Further, simple diffraction suggests that the peak position should scale linearly with wavelength; specifically $k_{\text{peak}}/k_0 = 1.09\lambda/a$. The experimental results (Fig. 5.4C) exhibit this linear relationship, and we conclude that the scattering for the $L_p$50 sample is diffractive across the range of wavelengths studied.

FDTD simulations of white light scattering by the $L_p$50 sample corroborate these observations. Samples were illuminated from above with a spectrally broad plane wave pulse and 80 farfield transforms distributed uniformly on the wavelength range [390, 910]nm were calculated from the
nearfield data. Scattering farfields were azimuthally averaged and then stacked to form Fig. 5.4A. We observe that FDTD predicts diffractive scattering that is in good agreement with the experimental results.

We emphasise that the hyperuniform metasurfaces exhibit statistically isotropic scattering characteristics. Figs. 5.4B & D show simulated and experimental farfield scattering distributions at a wavelength of 634nm (highlighted as a white stripe in Figs. 5.4A & C). Hyperuniform slabs make use of the broad and isotropic peak in momentum transfer space (Fig. 5.1) to scatter normally incident light into a cone of farfield intensity.

### 5.4 Directional Emission

So far, we have investigated the ability of the gold metasurfaces to mediate the coupling between incident and scattered plane waves. Although some fine structure was observed, the scattering was principally diffractive and may be regarded as a probe of the momentum transfers of the slab’s structure factor. Incident plane wave states with wavevectors of the form $k_i = (0, 0, k_z)$ were scattered onto outgoing plane wave states with wavevectors $k_s = (k_x, k_y, k'_z)$. Photons thus acquired a transverse momentum kick, the magnitude and direction of which was established by measuring their scattering angle in the farfield (as in Fig. 5.3B).

We now change our approach and seek to characterise the electromagnetic modes that the metasurface slabs support. To achieve this, we directly excite the metasurface’s modes by embedding fluorescent dye molecules on its surface. The dye molecules emit photons directly into the slab modes. These modes then leak into the glass where they may be observed. Specifically, slab modes couple, subject to a conservation of momentum criterion, to the plane wave states of the homogeneous glass substrate. These plane waves then propagate to the farfield where they are
naturally separated by the magnitude and direction of their transverse momentum components. The fluorescence emission method is thus a direct probe of the momentum distribution of the metasurface’s electromagnetic modes.

Samples were spin coated with a 50nm layer of PMMA polymer within which fluorescent DCM dye molecules were dispersed. Dye molecules were thus distributed across the sample surface and infiltrated any air cells or channels of the metasurface. Fig. 5.5 schematically illustrates the dispersion of dye molecules (red) in and around the gold metasurface. Dye molecules were excited by a circularly polarised green laser of wavelength 532nm. Emission from the molecules was broadband across red wavelengths. Emitted light was spectrally decomposed in the farfield according to Fig. 5.2A.

Fig. 5.6A presents the frequency momentum distribution of light emitted from the $L_{50}$ structure, hereafter referred to as the dispersion plot. As before, the horizontal and vertical axes present wavelength and normalised momentum $k/k_0$ (a proxy for $n_g \sin(\theta)$). The light line, that is the dispersion relation of free space light, is a key point of reference; it is described by the horizontal thin white dashed lines at $k/k_0 = \pm 1$.

The dispersion plot exhibits two striking features. First, we observe a pair of broad and intense emission bands just outside the light lines. These emission bands result from the characteristic radiation profile of a dipole near a material interface\textsuperscript{165}. Specifically, consider a dipole emitter in vacuum. When this emitter is placed close to, typically around one wavelength away from, an interface with a material of higher refractive index, evanescent fields can couple directly to the propagating modes of the high index medium. This direct coupling swamps the region outside the free space light line with emitted radiation, exactly as we see in Fig. 5.6A.

Second, we observe fine features inside the light cone which describe the decomposition of the metasurface slab modes into their in-plane momentum components. These may be viewed as the generalised dispersion relation $\omega(k)$ of the slab modes, as discussed in Section 4.4.3. These features inside the light cone were observed to be statistically isotropic over the wavelength range probed.

Attempts were made to corroborate the observed dispersion relations by direct FDTD simulation of the fluorescence emission. First, I randomly generated a position inside an air channel of the $L_{50}$ structure. Second, an electric dipole source, polarised along the $z$ direction, was located at
Figure 5.6: Observed dispersion relation of the $L_p50$ slab modes measured by fluorescence emission. The dispersion plot (A) shows the generalised dispersion relation $\omega(k)$ for the eigen-modes of the metasurface slab. Direct FDTD simulation of the fluorescence emission (B) can replicate the experimental observations.

We observe that the experimental and FDTD predicted dispersion plots are in good agreement. We note, however, that the FDTD method was computationally expensive and very time-consuming. 48 separate FDTD simulations were run to generate the dispersion plot of Fig. 5.6C. Even then, the convergence to the experimental results was relatively weak.

Using the fluorescence emission method, dispersion diagrams were measured for the $L_p50$, $L_p45$, $L_p40$, $L_p35$ and $L_p30$ metasurfaces. For each dispersion plot, we convert the emission wavelength and in-slab momentum to the dimensionless quantities $af/c$ and $ka/2\pi$ respectively. Experimental dispersion diagrams were then stacked to probe the dispersion over a large normalised frequency range. This stack of dispersion diagrams is shown as the left hand panel of Fig. 5.7A. Note that the dispersion diagram of the $L_p50$ structure (Fig. 5.6A) corresponds to the highest frequency slice in the stack of dispersion diagrams.

Naturally, the dispersion diagram exhibits some discontinuities where experimental datasets have been stitched together. Looking past this, we observe an interesting trend. As the normalised
frequency increases from $af/c = 0.63$, the dominant momentum of the slab modes first decreases, reaching a diffuse zero in the region of $af/c = 0.9$, before increasing linearly. This is easily visualised in the farfield. At low frequency, the slab emits light isotropically into a cone. As frequency increases, the opening angle of the emission cone decreases to zero, at which point light is emitted normal to the slab plane, before gradually opening back out into a second cone.

To explain this behaviour, we look beyond direct simulation by FDTD and appeal to the spectral function (introduced in Chapter 4). Consider an arbitrarily structured planar material whose electromagnetic modes $E(r, \omega)$ and $H(r, \omega)$ have been determined by an FDTD calculation. As discussed in Chapter 4, the spectral function is the norm of the projection of either $E(r, \omega)$ or $H(r, \omega)$ into a plane wave basis. The spectral function is thus a scalar field in frequency and momentum ($\omega$ and $k$) space, the value of which specifies the extent to which a plane wave $e^{-ik \cdot r}$ contributes to the overall slab mode eigenmode at frequency $\omega$. It is thus sensible to suggest that the spectral function plays an essential role in determining the coupling between the modes of a slab and the plane wave eigenstates of free space.

Consider a metasurface network structure (Fig. 5.1E) comprising a connected network of dielectric material, refractive index $n = 1.5$, enclosing isolated air cells. I calculated the spectral function associated with the transverse electric (TE) modes of this structure according to the methodology of Section 4.3. Specifically, a two-dimensional FDTD simulation was employed to calculate the structure’s eigenmodes. A large number of magnetic dipoles were randomly distributed within the structure, each polarised normal to the slab plane. Radiation was injected and the slab eigenmodes $E(r, \omega)$ and $H(r, \omega)$ were determined. The spectral function $M(k, \omega)$ was then calculated according to Eqn. 4.5.

Note that $M(k, \omega)$ was treated as a statistically isotropic quantity in the $k$ space; I thus take the azimuthal average and present the spectral function as a planar figure. Fig. 5.7B shows
the spectral function of the connected dielectric network structure together with the light line, marked as the dotted white line. We observe that, at low frequencies, the slab modes are well modelled by the dispersion relation of an effective medium. According to the mechanism outlined in Sections 4.4.2 & 4.4.3, plane wave states are coupled together via the non-zero momentum transfers of the structure factor. The effective medium band crosses the scattered band at $ak/2\pi \approx 0.55$; this is the region around halfway to the dominant momentum transfer of the structure factor (Fig. 5.1D), located at $ak/2\pi = 1.09$. The effective medium band thus appears to branch into two, with the less intense scattered branch folding back in towards the origin.

I highlight this scattered band in particular. With increasing frequency, the scattered band behaves identically to the gold metasurface dispersion relation of Fig. 5.7A. First, the band slopes in towards the origin, reaching a diffuse zero around $(ak/2\pi, a/f/c) = (0,0.9)$. At this point, two scattered bands pass through each other and the dispersion relation appears to change direction.

I calculated a high resolution spectral function in the region $a/f/c [0.63, 1.42]$ for direct comparison with the observed slab dispersion relation. Fig. 5.7A compares the experimental observations (left panel) with the generalised band structure as predicted by the spectral function (right panel). Although a gold metasurface and a simple connected dielectric network are distinctly different systems, the agreement between the experimentally observed and FDTD-predicted dispersion is striking. This agreement may be rationalised as follows.

The electromagnetic response of an architecture is determined by many properties. Foremost amongst these properties is the architecture’s structure factor. Non-zero values of the structure factor scatter light by providing the momentum transfers through which plane wave states may couple (so-called Bragg processes, Eqn. C.21). For a low refractive index architecture, we observe that the generalised dispersion relation is well-modelled by first order Bragg processes alone (Fig. 4.9).

Generalised dispersion relations are also influenced by resonant scattering processes. For instance, photonic band gaps in dielectric cylinder arrays can be traced to the Mie resonances of their scattering centres (Section 3.7.1). However, even when generalised band structures are perturbed by PBGs, for instance the high index hyperuniform network of Fig. 4.10, their overall form is still dictated by band folding resulting from Bragg processes. Similarly, we expect that other material-dependent effects, such as surface plasmon resonant scattering, will act as localised perturbations to a generalised band structure that is primarily determined by Bragg processes.

With this in mind, the similarities between the gold metasurface and connected dielectric network generalised dispersion relations, as shown in Fig. 5.7A, can be understood. Both architectures are identically structured and possess similar structure factors. In both cases, the overall dispersion is well modelled by the scattering of an effective medium band by Bragg processes. In the case of the gold metasurfaces, material-specific effects lead to some fine structure in the dispersion relation that is stamped onto the main scattered band. These perturbations are small, particularly since our gold pillars are slightly too large to exhibit significant surface plasmon resonances.
Finally, we note that Fig. 5.7A is an experimental demonstration of the utility of generalised band structure, as predicted by the spectral function method. Specifically, decomposition of a slab’s eigenmodes into a plane wave basis can directly predict the farfield angular profile of its directional emission. Consider a slab, located in the $xy$ plane, on which a plane wave with wavevector $(k_x, k_y, k_z)$ and frequency $\omega$ is incident. For the plane wave to couple to the slab, there must exist modes whose electric or magnetic fields vary with spatial frequency $(k_x, k_y)$. FDTD can generate slab eigenmodes $E(r, \omega)$ and $H(r, \omega)$ which, if carefully simulated, should be a fair sum of all the slab modes with frequency $\omega$. The norm of the projection of these modes into a plane wave basis, evaluated at the point $(k_x, k_y)$, measures the extent to which all eigenmodes at frequency $\omega$ possess the required spatial frequency for coupling. The value of the spectral function at $(k_x, k_y)$, normalised to the maximum value of the spectral function, is thus a measure of the ability of the plane wave to couple in and out of the slab relative to all other possible plane waves.

5.5 Conclusions

In this chapter, my collaborators and I designed, fabricated and characterised gold metasurfaces derived from hyperuniform connected networks. We studied hyperuniform networks as an exercise in sculpting the scattering characteristics of a metasurface by reciprocal space engineering. Specifically, the structure factor of our hyperuniform networks was dominated by a single, broad scattering resonance centred around $ak/2\pi = 1.09$. This scattering resonance was observed to dictate both the farfield light scattering and directional emission properties of the metasurfaces.

Metasurfaces were designed by tessellation of a hyperuniform point pattern to form a trivalent connected network. Both network-type and pillar-type metasurfaces were successfully fabricated in gold using an e-beam lithography method. Samples were characterised using a leakage radiation microscopy method. Specifically, light from the samples was observed in the farfield where a complete spectral analysis was possible.

We investigated the scattering of 532nm laser light by a variety of pillar-type metasurfaces, each with a different scaling parameter. Scattering patterns were found, in the most part, to be entirely diffractive, resulting from a single scattering of the incident plane wave states by the dominant momentum transfers of the structure factor. One metasurface, the $L_p30$ sample, was observed to exhibit an extra distinct scattering resonance. This resonance was thought to be plasmonic in nature; it fell at the precise wavevector associated with a surface plasmon, excited by 532nm light and confined to an air/gold interface. Experimental observations agreed well with, and were thus corroborated by, the results of FDTD simulations of the scattering.

We also performed a broadband scattering characterisation of a single metasurface (the $L_p50$ sample). Again, the scattering was observed to be primarily diffractive; white light was scattered isotropically into a cone whose opening angle increased with increasing wavelength of illumination. White light scattering results were in good agreement with the predictions of FDTD simulations.
Following this, the eigenmodes of the metasurface slabs were directly probed using a fluorescence emission technique. Metasurfaces were spin coated with dye molecule-doped PMMA. These dye molecules were excited by laser light and fluoresced, emitting photons directly into the electromagnetic modes of the slab. These modes leaked into the microscope where the emitted light was spectrally decomposed. Emitted light was thus separated into its component momentum and frequency components, allowing the dispersion relation of the slab modes to be visualised.

We observed that the metasurfaces possess interesting directional emission properties. At low frequencies, light was emitted into a conical ring in the farfield. With increasing frequency, the cone opening angle decreased to zero, thus focussing the light to a point, before opening back out again.

Efforts were made to simulate the fluorescence emission results by direct three-dimensional FDTD simulation. This method was found to generate plausible results, but with limited reliability due to the significant computational cost. Instead, the dispersion relation of the slab was modelled by the generalised band structure of a hyperuniform connected dielectric network, calculated via the spectral function method. Agreement between the observed and predicted dispersion relations was striking. The observed dispersion of the metasurfaces corresponded to an effective medium band that had been back-folded by Bragg processes. The directional emission of the metasurfaces was thus found to be fundamentally controlled by their corresponding structure factors. Further, these experimental results demonstrate a clear application of the generalised band structure predicted by the spectral function method; it can be used to predict the farfield intensity profile of directional emission from a slab.
Chapter 6

Local Self-Uniformity

The diamond structure was the first known photonic crystal design\textsuperscript{21,135}; although nearly thirty have passed since its discovery, its complete photonic band gap (PBG) remains the largest known\textsuperscript{61,92}. In some respects, this is natural; its maximally spherical Brillouin zone ensures maximal spectral overlap between Bragg scattering-induced stop gaps. On closer inspection, however, the Bragg mechanism alone cannot account for the various PBG sizes observed in the known complete gap architectures. In spite of its FCC crystal system, the inverse opal gap is only 1/5th that of diamond’s\textsuperscript{80}. Further, sizeable PBGs are known to exist in photonic amorphous diamond\textsuperscript{63,90} (PAD) and disordered honeycomb networks\textsuperscript{62} (Section 3.8). Because of their diffuse structure factors, these amorphous materials cannot provide the required intense momentum transfers to create zero group velocity states through a Bragg mechanism\textsuperscript{61}.

Since the discovery of the diamond gap, a diverse collection of high-index photonic crystal structures has been proposed, fabricated and observed to possess sizeable PBGs\textsuperscript{61,80,92,166}. From a device engineering perspective, the existence of a sizeable band gap is sufficient to engineer technologically significant optical and electro-optical components\textsuperscript{56,58,60,89}. Outstanding problems regarding the nature and formation of the photonic band gap have thus fallen by the wayside. From a physical perspective, however, the question of why specific photonic crystal designs succeed, while others possess no significant PBG, addresses important unresolved issues about light scattering in complex structures. I objective, therefore, is to determine the optimal structural characteristics of PBG-forming materials and to engineer a measure with which these characteristics can be controlled.

A successful formulation of ideal PBG-forming structural characteristics would have broad impact. Most obviously, it would allow rational design of novel ordered and disordered PBG structures\textsuperscript{167}. Perhaps more significantly, the question of PBG formation is one of a number of related problems concerning the multiple scattering of light. For instance, the ultra-bright white scales of the cyphochilus beetle are structurally optimised to maximise their broadband reflectance\textsuperscript{11–13}. However, given a more complete understanding of generalised resonant scattering, the precise nature of this structural optimisation may yet prove to be more subtle than current research suggests. Similarly, observation of Anderson localised light - light localised by strong multiple scattering in a disordered structure - has been a research goal for thirty
years\textsuperscript{25,37,168}. A variety of structures have been investigated\textsuperscript{38,40,169} but definitive observation of Anderson states in three-dimensions remains a contentious issue\textsuperscript{170}. The design of a successful Anderson-localising structure may be seen as a parallel problem to engineering a PBG material; it is a question of engineering the electromagnetic resonances and interactions of an ensemble of scattering centres.

In this chapter, and those that follow, I make the case that geometrical and topological uniformity at local length-scales is the key property that leads to the formation of sizeable PBGs in the high refractive index regime. It is important to qualify that my arguments pertain to the fundamental PBG of high refractive index structures. Specifically, it has been observed\textsuperscript{61,171} that Bragg processes are the dominant mechanism of PBG formation in low index materials. The origin of the large fundamental gap in high index structures, however, is not purely due to the Bragg mechanism\textsuperscript{61}. Analysis of field profiles in two-dimensional high index photonic crystals\textsuperscript{80}, quasicrystals\textsuperscript{67} and amorphous materials (Section 3.8.2) clearly demonstrates the significance of spatially-localised resonant scattering as a formation mechanism of the fundamental gap. It is expected, and evidence suggests\textsuperscript{61}, that generalised resonant scattering is equally key to the formation of the fundamental PBGs of high-index three-dimensional structures. It is in this regime, where generalised resonant scattering is the dominant PBG formation mechanism, that I focus my efforts.

I begin with a survey of the major classes of photonic crystal architectures in which I seek to establish the common characteristics of structures with large fundamental PBGs. I focus mainly on three-dimensional structures, but also briefly address network structures in the two-dimensional case. I establish that the common factor amongst the sizeable PBG networks is uniform vertex connectivity, and that highly symmetric vertex configurations favour the formation of large gaps. Informed by this, I attempt to develop a measure that reflects the extent to which a network possesses the abstract characteristic of symmetry. I propose the ‘tree overlap’ method, illustrating how it may be used to measure the symmetry of fragments drawn from a connected network. The method is then extended to disordered network fragments as a means of quantifying a network’s structural homogeneity. Following this, the tree overlap method is described formally, and the local self-uniformity distributions of a network are defined. Finally, a number of example local self-uniformity distributions are presented and their interpretation is discussed.

### 6.1 The Champion Structure Problem

Remarkably, after thirty years of photonic crystals research, only a small number of distinct three-dimensional architectures are known to possess a complete PBG.

Foremost, all known sizeable PBG structures are connected networks. Recall that the existence of a spectral gap implies a discrete change in the spatial localisation of the electromagnetic energy density (Eqn. 3.19). In the regular theoretical treatment of photonic crystals (Section 3.1), it is clear from the Maxwell equations that the quantity $\varepsilon_r(r)E(r)$ must be divergenceless. As a result, the electric field must form a circulating current without sources and sinks\textsuperscript{61}. Connected
network structures are thus advantageous. In a connected network, the continuous electric field lines may be accommodated in one type of material (either high or low index) without passing into the other. A network geometry thus maximises the potential for a large spectral gap by allowing dielectric and air-band modes to form.

The largest known complete PBG is that of the rod-connected diamond network (Section 3.5.2); colloquially it has been called the ‘champion’ structure. I calculate that an optimal rod-connected diamond structure possesses a complete PBG of width 31.4% for a permittivity contrast of 13 : 1. Every vertex in the diamond network sits at the centre of a tetrahedral coordination shell (Fig. 6.1A). Vertices are connected to their four nearest neighbours by dielectric cylinders and the shortest non-zero path that starts and ends at a given vertex has length 6 (Fig. 6.1A, orange path).

Maldovan and Thomas’s thorough review of diamond structured photonic crystals concluded that structures which are topologically related to diamond tend to show significant complete PBGs. For example, Maldovan et al. employed a level-set method to construct characteristic structures for each of the 11 FCC space groups. All but one of the complete gap structures they found were characterised by tetrahedral network centres and a diamond-like topology.

Further, numerous well-known PBG architectures may be viewed as low-symmetry embeddings of the diamond topology. The famous woodpile structure, for instance, is a topological diamond. Woodpile, shown in Fig. 6.1B, is formed by stacking layers of uniformly spaced parallel dielectric rods; each new layer is rotated by 90° with respect to the previous layer, and is offset by half a rod spacing. The points at which the dielectric layers touch may be viewed as vertices at which 4 lobes of dielectric material meet. Connecting these vertices, shown as the orange path in Fig. 6.1B, shows that the shortest-path rings have length 6. Although woodpile has neither the symmetry group of diamond nor its tetrahedral vertex configuration, its topology is equivalent to that of diamond and it could thus be produced by continuous deformation of the vertex positions in a diamond network.

Further evidence of the special character of diamond-like topologies has since come to light. Edagawa et al. discovered, for a permittivity contrast of 13 : 1, a complete PBG of width 18% in a rod-connected continuous random network model of amorphous silicon. The structure, dubbed ‘photonic amorphous diamond’ (PAD), comprises a connected dielectric network in which every vertex is strictly four-valent and the distribution of dielectric material about each vertex is approximately tetrahedral. Analysis of the PAD gap, as compared to the PBG in rod-connected diamond, suggests that both gaps share a common origin mechanism. Fig. 6.1E shows a typical amorphous silicon CRN, shown as a ball-and-stick model for clarity, from which PAD is derived; PAD is formed by connecting all bonded vertices with a dielectric cylinder.

Photonic amorphous diamond bears out Maldovan and Thomas’s observation that “a structure without strict diamond symmetry but having a connected diamond-like network morphology will show a diamond gap”. They concluded that “all the known periodic dielectric structures with large photonic band gaps (that is, those having complete gaps greater than 17% for an index contrast of about 3.6:1) are based on the diamond morphology”. Diamond and diamond-like structures thus dominate the set of known sizeable complete PBG
Figure 6.1: A schematic of the diamond network geometry (A) with a 6-fold ring annotated (orange). Woodpile (B) may be viewed as a topological diamond with diamond-like vertices and 6-fold rings (orange annotation). Cubic-close-packed spheres (C) with tetrahedral (orange) and octahedral (yellow) interstices. Inverse opal network (D). Amorphous silicon CRN from which PAD is derived (E). Singe network gyroid viewed just off the [111] axis (F). (Sources: panel B reproduced from Ref. [173], panel D from Ref. [36].)

Structures; overall, it is clear that the diamond structure possesses a local topological and geometrical order which strongly favours PBG formation. However, diamond-like structures do not have a monopoly on complete PBGs in three dimensions; there exists a small number of other distinct architectures.

One such distinct structure is inverse opal. Opal, named for the microstructure of the precious gem, is formed by arranging equal-sized spheres in a cubic-close-packed pattern. To form an inverse opal network, the sphere array is infiltrated with a high-index dielectric material and then the spheres are dissolved, leaving spherical air voids. A view down the [111] axis of a cubic-close-packed structure is shown in Fig. 6.1C. The colours blue, purple and green represent the A, B and C-type layers respectively. There are two-type of interstices (voids) in the sphere packing. The first, shaded orange in Fig. 6.1C, is enclosed by four spheres located at the corners of a tetrahedron. The second, centred at the yellow marker in Fig. 6.1C, is octahedrally coordinated by 6 spheres (4 in the indicated plane, and 2 normal).

Infiltration of the sphere array with material fills its interstices. Dissolution of the spheres thus leaves a network, shown in Fig. 6.1D, formed from interconnected tetrahedral and octahedral interstices. These two centres form the vertices of the network and give rise to 4-fold and 8-fold connected centres respectively. Unlike diamond, the resulting network is not topologically uniform; not all network vertices are equivalently connected. For a dielectric contrast of 13 : 1, inverse opal is found to possess a complete PBG of width $6\%^{80}$, significantly smaller than that of the diamond network.
Another distinct PBG architecture is the simple cubic scaffold. The photonic crystal is formed by connecting the vertices of a simple cubic lattice with dielectric rods. Like diamond, the resulting network possesses a uniform topology in which every vertex is connected to exactly 6 others. Rod-connected simple cubic structures are known to possess complete PBGs; I have calculated that an optimal rod-decorated simple cubic network possesses a PBG of width $8.4\%$ for a permittivity contrast of $13 : 1$. However, optimisation of the distribution of dielectric material about the fundamental vertex can create simple cubic structures with PBGs as large as $16.3\%$. The vertices of the resulting structures, although not decorated with simple shapes such as spheres and cylinders, retain the uniform local topology of the rod-connected photonic crystal.

Recently, a further uniformly co-ordinated network has been discovered to possess a sizeable PBG. The network, dubbed FCC8, is formed by connecting the lattice points of a simple FCC lattice to all of their nearest neighbours. The resulting network comprises vertices which are uniformly connected to 12 other identical vertices. I calculate that an optimal rod-decorated FCC lattice possesses a PBG of width $6.1\%$ for a permittivity contrast of $13 : 1$. It should be noted, however, that complex decorations can endow FCC8 with a PBG as large as $17.4\%$.

The final major class of PBG-forming architecture is single network gyroid (SNG, Section 3.5.3). Fig. 6.1F shows a ball-and-stick model of the SNG structure; it is a connected network with BCC symmetry in which every vertex is connected to its three nearest neighbour vertices. It was first proposed as a photonic crystal which might be self-assembled on account of its intimate connection to the gyroid minimal surface. Every vertex sits at the centre of an equilateral triangle whose points are its three nearest neighbours; connection of a point to its neighbours forms a trihedral unit (like the tetrahedral unit of the diamond network).

Adjacent trihedral units share a common connection, but are rotated around this connection by a dihedral angle of $\cos^{-1}(1/3)$. The topology of single network gyroid is complex; the shortest path rings starting at a given point have length 10. Like the simple cubic and diamond networks, however, its topology is uniform. Any two neighbouring vertices, although crystallographically distinguishable, are identically connected both geometrically and topologically. I have calculated

<table>
<thead>
<tr>
<th>Structure</th>
<th>Lattice</th>
<th>Gap Width</th>
<th>Co-ordination</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single Network Gyroid</td>
<td>BCC</td>
<td>28.1%</td>
<td>3</td>
<td>Near-champion</td>
</tr>
<tr>
<td>Diamond Network</td>
<td>FCC</td>
<td>31.4%</td>
<td>4</td>
<td>Champion</td>
</tr>
<tr>
<td>Topological Diamonds</td>
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<td>Sizeable</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>Amorphous Diamond</td>
<td>None</td>
<td>18%</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>Inverse Opal</td>
<td>FCC</td>
<td>6%</td>
<td>Mixed 4 &amp; 8</td>
<td>-</td>
</tr>
<tr>
<td>Opal</td>
<td>FCC</td>
<td>None</td>
<td>Isolated spheres</td>
<td>-</td>
</tr>
<tr>
<td>Simple Cubic</td>
<td>PC</td>
<td>8.4%</td>
<td>6</td>
<td>Larger gap when not rod-decorated</td>
</tr>
<tr>
<td>FCC8</td>
<td>FCC</td>
<td>6.1%</td>
<td>12</td>
<td>Larger gap when not rod-decorated</td>
</tr>
</tbody>
</table>

Table 6.1: The major types of three-dimensional photonic crystal architecture and their PBG sizes for a permittivity contrast of $13 : 1$. 
that an optimal rod-decorated SNG structure possesses a complete PBG of width 28.1%. The gap in SNG is thus comparable to that of the diamond network; I refer to SNG as ‘near-champion’.

Table 6.1 summarises the major types of photonic crystal architecture, ordered from top to bottom by the coordination number of a given vertex in the structure. We first note that PBG size does not correlate with the conventional isotropy of a network’s crystal system. If PBG formation was driven by the Bragg mechanism, we would expect the largest PBGs to form in crystals whose Brillouin zone is maximally isotropic; FCC-based structures would thus be champion, with lower symmetry structures performing less well. Rather, the opal and inverse opal structures categorically demonstrate that isotropic Bragg scattering is not the sole determinant of a champion PBG.

Instead, we observe that structures with a sizeable PBG are clustered towards the top of the table; a low coordination number appears to favour gap formation. Further, simple cubic, in spite of its high coordination number, displays a significant PBG. Inverse opal, on the other hand, possesses a very small PBG. The two networks are distinguished by their topologies; every vertex in the simple cubic structure is identically connected while the inverse opal network comprises a mixture of 4-fold and 8-fold connected vertices. We thus note that a mixed coordination number seem to disfavour PBG formation.

I now consider briefly to a selection of high index ($\varepsilon_r = 13$) two-dimensional photonic crystals. PBGs have been observed in two-dimensional structures for both arrays of dielectric cylinders (TM polarisation) and connected dielectric networks (TE polarisation). I consider only the TE PBGs in network structures; networks are the most obvious analogue to the major classes of three-dimensional complete PBG architectures and we should expect the generalised resonant scattering mechanism to play a significant role in forming their PBGs.

Subject to these constraints, the champion structure amongst the two-dimensional photonic crystals is the honeycomb network\textsuperscript{27}. I calculate that an optimum rod-decorated honeycomb network, as shown in Fig. 6.2A, possesses a TE gap of width 56.0%. Other two dimensional photonic crystals include the square and hexagonal networks. The square network, shown in Fig. 6.2B, is the two-dimensional analogue of the simple cubic network; it is formed by connecting the lattice points of a square lattice to their four nearest neighbours with dielectric rods. I calculate that an optimum square structure has a 32.1% gap. Analogously, a hexagonal network (Fig.
Table 6.2 summarises the discussion of two-dimensional photonic crystal architectures. We observe, just as in the three-dimensional case, that a low-coordination number favours the formation of sizeable PBGs. Amongst the three crystalline structures, PBG size decreases monotonically with increasing coordination number. The aperiodic structures all have a low coordination number and exhibit sizeable TE PBGs. Amongst the three-coordinated structures, we note that PBG size appears to decrease with decreasing structural order. The perfectly ordered honeycomb is champion, while the Penrose disordered honeycomb, which possesses a finite number of local vertex configurations, has a comparably large PBG. The hyperuniform structures are characterised by a continuum of local vertex configurations and are thus more disordered than the Penrose network. The mean PBG for the more ordered $\chi = 0.6$ network set is larger than that of the $\chi = 0.5$ set.

### 6.2 Taking Stock

An interesting picture is beginning to emerge. In both two and three dimensions, the common property of large PBG networks is the low coordination number of their network vertices. Further, all but one of the sizeable PBG networks discussed are characterised by locally (and globally) uniform vertex connectivities. Non-uniform local connectivity, like that of the inverse opal network, appears to disfavour gap formation. This suggestion is corroborated by the set of
optimal PBG networks found by an unconstrained topological optimisation method; the study produced a number of optimal network structures, all of which comprise uniformly connected vertices. Overall, it can be said that topological uniformity favours gap formation.

Within a particular class of network, as defined by the network’s dimensionality and coordination number, PBG size increases with increasing local structural order. The champion and near-champion gaps are found in structures whose local geometries are, given the specific connectivity of the structure, maximally symmetric. These local geometries are planar trihedral for honeycomb and single network gyroid structures, and tetrahedral for the diamond network. Breaking this local symmetry, as in trivalent and tetravalent random network structures, reduces the PBG width.

I thus ask, is it possible to develop an order metric which measures simultaneously the various ideal PBG-forming structural characteristics? Naturally, we may try to quantify the various geometrical environments in a random network using an order parameter which is sensitive to a known ideal vertex configuration, say tetrahedral. This type of approach has been employed to probe structural order and phase transitions in molecular dynamics simulations. There is, however, a major drawback to this type of approach; the order parameters select for only a single local geometry of interest.

By using an order parameter which is uniquely sensitive to a particular vertex configuration, one geometry is naturally favoured over others. It is clear, however, that the champion and near-champion PBG structures possess structurally distinct architectures which, from the point of view of PBG formation, are comparable. An appropriate order metric should thus be sensitive to all the champion and near-champion geometries without intrinsically favouring any. Further, comparison of a structure’s geometry to a number of known optimum configurations does not address the question of why a particular geometry is optimum. A successful order metric should elucidate this, measuring, in a simplified way, some structural property of direct optical significance.

Symmetry provides the key to the problem. In section 6.1 it was observed that, for a given vertex connectivity, it is the maximally symmetric vertex configurations which appear to yield the largest PBGs. The order metric must thus measure symmetry in an abstract sense; it should be sensitive to the existence of symmetry in general without explicitly looking for a specific symmetric configuration.

### 6.3 Measuring Symmetry Through Tree Overlap

What is a symmetry? The symmetries of a physical object are the rigid body transformations of the object that leave it invariant. A rigid body transformation is understood to be defined as an operation which preserves the distance between any two points within a Euclidean metric space. In a Euclidean space of dimension three the possible rigid body transformations are the familiar translation, rotation and reflection operations. Any arbitrary rigid body transformation can be represented as a combination of a single translation, rotation and reflection.
Throughout this work, the terms rigid body transformation and congruent transformation are used interchangeably.

Consider, for example, the symmetries of an equilateral triangle. The triangle is invariant under a number of congruent transformations. It may be rotated through 120°, 240° and 360° angles about an axis, normal to the plane of the triangle, passing through its centroid (Fig. 6.3A). Further, the triangle may be reflected in any mirror plane that passes through a vertex and cuts through the opposite edge normally (Fig. 6.3A). In total, there are 6 rigid body transformations, 3 rotations and 3 reflections which leave the triangle invariant.

Should we choose to, we may label the vertices of the triangle with unique identifying numbers 1, 2 and 3. Application of a symmetry operation to the triangle then produces a new distinguishable state in which the vertex labels have been permuted; I refer to the specific vertex permutation that results from a given symmetry operation as the ‘signature’ of the operation.

Reflection in a mirror plane, for example, permutes two vertex labels while leaving the third unchanged. Fig. 6.3B shows a reflection operation in which the labels of vertices 1 and 2 are swapped. I write the signature of the reflection as [2, 1, 3], which is understood to mean that vertex 2 occupies the former position of vertex 1, vertex 1 occupies the former position of vertex 2 and the position of vertex 3 is unchanged. Rotation about the centroid cyclically permutes the vertex labels. Fig. 6.3C shows an example rotation with a signature of [3, 1, 2].

In the case of the equilateral triangle, we may show that each symmetry operation has a unique signature. Further, the number of symmetry operations (6) is equal to the number of possible vertex permutations (3!). The symmetry operations are found to form a closed mathematical group under sequential application; in this case, the 6 transformations form the dihedral group of order 3 ($D_3$).

Figure 6.3: The symmetry operations of an equilateral triangle (Panel A) comprise reflections in three mirror planes (top) and three rotations about the centroid (bottom). Application of a symmetry operation permutes the vertices of the triangle. Reflection in a mirror plane (panel B) swaps two vertex labels while leaving the other invariant. Panel C shows a cyclic permutation through rotation by 120°.
I now introduce a general method, which I refer to as the ‘tree overlap method’, for measuring the symmetry of elements of a connected network. Tree overlap can be applied to any connected network of uniform valency, in which all vertices possesses an identical number of connections $\gamma$ to nearby vertices. It is based on an inversion of the relationship between a symmetry operation and its signature. Rather than calculating the signatures of a known set of symmetry operations, I specify a set of signatures and attempt to establish the congruent transformations that produce the required vertex permutations. Once a congruent transformation is identified, I measure the extent to which it reflects a true symmetry of the network element by overlapping the original and congruently transformed trees. The method appears complex, and so, for now, I give an overview of the overall process as it applies to a planar trivalent connected network. Detailed technical points are discussed later in the formal presentation of ‘tree overlap’ in section 6.5.

Consider again the honeycomb network. We choose a root vertex, and form the network fragment for which all vertices are within 2 edges of the root vertex; let us call this structure a 2-tree. Fig. 6.4A shows the 2-tree based on the root vertex $A$ as a fragment within the total honeycomb network.

I propose to use congruent transformations of the 2-tree as a means of ranking the extent of the local symmetry around vertex $A$. To achieve this, we separate the tree from the honeycomb network and consider it in isolation. We then duplicate the tree, producing two distinct identical trees $A$ and $A'$; these trees are shown in the first column of Fig. 6.4B. We label the root edges of each tree, that is the edges directly connected to the root vertex, with unique numerical identifiers $[1, 2, 3]$ and $[1', 2', 3']$. I suggest that the magnitude of the symmetry may then be measured as the extent to which the two trees $A$ and $A'$ overlap subject to a set of congruent transformations. The set of transformations is chosen such that each of its members probes one of the $3!$ signatures of the $D_3$ group; that is, each transformation generates 1 of the 6 possible alignment permutations of the two trees’ root edges.
I explore this idea with an example. To align the two trees, we first fix tree $A$ in space. We then select a particular alignment permutation to probe. For instance, let us try to transform tree $A'$ such that edge 1 aligns with edge $2'$, edge 2 with edge $3'$ and edge 3 with edge $1'$. We thus seek a transformation with a signature of $[2', 3', 1']$, where the entry in the first position indicates the edge of tree $A'$ with which edge 1 of Tree $A$ will be aligned, and so on. This process is shown in Fig. 6.4B, column 1.

Next, we identify the congruent transformation of tree $A'$ such that the root edges are maximally overlapped according to the signature. Although the required transformation is, in this highly symmetrical example, obvious, this will not generally be the case. Instead, we imagine for the moment that we have a means of calculating the required congruent transformation. Then, having found the transformation, we apply it to tree $A'$. In this case, the transformation is shown by the orange arrows in Fig. 6.4, column 2; we rotate tree $A'$ by $120°$ and translate it such that its root vertex overlaps that of tree $A$. Once transformed, we say that the two trees are maximally aligned in the permutation $[2', 3', 1']$. This maximally aligned configuration is shown in Fig. 6.4B, column 3; note that the two trees are drawn offset for clarity.

Once maximally aligned, we quantify the symmetry of the two trees by measuring the ‘quality’ of their overlap. To achieve this, we design some function which operates on the two trees and returns a scalar. If the two trees are perfectly aligned, we have found a symmetry of the structure and the function returns a value of unity. If the two trees do not perfectly overlap, our function returns a value strictly smaller than unity; we design the function such that its value decreases with decreasing overlap quality. Here, trees $A$ and $A'$ are identical and both possess the symmetries of the dihedral group. It is clear that we will be able to find a congruent transformation that maps tree $A'$ onto tree $A$ according to the specified signature. Our function will return unity, demonstrating that the permutation $[2', 3', 1']$ is indeed a symmetry operation of the tree.

We then repeat this process for each of the $3!$ characteristic root edge alignments. We specify in turn all of the $3!$ permutations of the alignment vector $[1', 2', 3']$, find a congruent transformation such that the two trees maximally align as specified, and then rate the quality of the resulting overlap with our similarity function. Applied to the example trees $A$ and $A'$, each alignment vector will correspond to a unique congruent transformation applied, non-cumulatively, to $A'$ which achieves perfectly the specified root edge alignment. Our overlap quality function will return unity for each alignment permutation, thus demonstrating that tree $A$ possesses the six symmetries of the $D_3$ group.

### 6.4 Generalisation to Non-Identical Trees

The ability to measure the quality of broken symmetries is already built into the tree overlap method. Consider a single asymmetric 2-tree; Fig. 6.5A shows an example of this type of tree, highlighted in orange, grown from from a root vertex in a disordered honeycomb network. The ‘symmetry’ of the deformed tree is understood to mean the extent to which it resembles the ideal symmetric configuration as measured by the tree overlap quality function. A nearly-symmetric
tree will overlap strongly with its duplicate for all root edge alignment permutations. The strength of this overlap will be reflected in the near-unit values returned by the overlap quality function. A strongly asymmetric tree, on the other hand, will overlap weakly with its duplicate and the overlap quality function will return a set of values significantly smaller than unity.

Given that a single asymmetric tree may be compared with itself using the tree overlap method, it is simple to compare two distinct non-identical trees using the same process. I illustrate this with an example.

Consider a disordered honeycomb type network, shown in Fig. 6.5A. As before, we may define trees by forming a network fragment grown from a particular root vertex. A 1-tree is formed by taking the set of edges and vertices within 1 edge of the root vertex; Fig. 6.5 highlights an example 1-tree, green, within the disordered network. Consider specifically two non-identical 1-trees $B$ and $C$. As before, we label the root edges of the trees with the unique numerical identifiers $[1_b, 2_b, 3_b]$ and $[1_c, 2_c, 3_c]$. These two trees are shown in Fig. 6.5B, left column.

We seek again to maximally overlap our two trees subject to a particular root edge alignment. First, we fix tree $B$ in space. Next we specify a root edge alignment permutation. Let us say that edge $1_b$ should overlap with edge $1_c$, edge $2_b$ with edge $3_c$ and edge $3_b$ with edge $2_c$; we thus seek a congruent transformation with a signature of $[1_c, 3_c, 2_c]$. We then invoke our method for finding the unknown congruent transformation which maximally overlaps the two trees as required. We see intuitively that this transformation will involve a translation to overlap the central vertices of trees $B$ and $C$, a small rotation and a reflection along the edge $1_c$ axis (equivalent to a $180^\circ$ rotation around the edge $1_c$ axis); these steps are indicated in Fig. 6.5B as orange arrows. Once maximally aligned, we then measure the quality of the overlap using the similarity function. Here, the function will return a value less than one indicating imperfect overlap.

As before, we then repeat the tree comparison process for the remaining 5 possible permutations of the alignment vector $[1_c, 2_c, 3_c]$, in each case maximally aligning trees $B$ and $C$ before measuring the quality of their overlap with the tree similarity function. Overall, we produce 6

![Figure 6.5: Example 1-tree (green) and 2-tree (orange) in a disordered honeycomb network (coloured highlights, panel A). Two non-identical trees may be compared in a similar way to identical ones (panel B). First, the tree root edges are labelled and an overlap permutation is specified. Next, the two trees are `maximally overlapped' according to the specified permutation. The extent to which the trees overlap is then measured.](image-url)
numbers which now describe the extent to which they are mutually superimposable. A set of
tree overlaps near unity suggests that the two trees are both near-symmetric and structurally
similar, while a set of values significantly less than one implies low symmetries and structural
dissimilarity.

I now develop the key concept of a local self-uniformity distribution; this is a collection of num-
bers describing the extent to which a network’s component trees may be overlapped. Consider
an arbitrarily structured connected network in which every vertex is connected to exactly $\gamma$
others. The extent to which it possesses ideal PBG-forming structural characteristics may then
be quantified by assembling some large set of its component trees and measuring their overlap
qualities. This process will produce a large set of numbers - the local self-uniformity distribu-
tion - whose values reflect the nature of the network’s structure. A set of unit overlap qualities implies
that every network element possesses the maximum symmetry of the $\gamma$-valent configuration. A
distribution of overlap qualities clustered just below one suggests amorphous character; the frag-
ments of the network are nearly symmetric and structurally similar. A set of overlap qualities
much less than one indicates strong tree dissimilarity and suggests that the network is chaotic
and unstructured.

6.5 Definitions and Methods

In this section, I revisit the qualitative description of the tree overlap method more formally.
I define the concept of a tree, the process through which two trees may be compared, and the
local self-uniformity distributions of a network. I then discuss the twin problems of finding a
congruent transformation that maximally overlaps two trees and of measuring the quality of
their overlap once aligned; my solutions to these two problems are described in detail.

I consider throughout a continuous random network (CRN) $C$. The CRN comprises a number
of labelled, distinguishable vertices, with known positions, which are interconnected via edges.
Let the CRN be regular such that every vertex is connected, via an edge, to $\gamma$ distinct vertices.
Computationally, a $d$-dimensional CRN may be stored as a set of vertex coordinates of size $|C|d$
and an adjacency matrix of size $|C|\gamma$. For a given vertex, the adjacency matrix records the labels
of the vertices to which it is connected.

6.5.1 Definition of an $n$-tree

An $n$-tree $T^n_a$ on a root vertex $a$ of a CRN is the set of edges and vertices that can be reached
from vertex $a$ by traversing no more than $n$ edges. I label all the vertices of $T^n_a$ with an index,
say $j$, subject to the constraint that indices $\{1, 2, ..., \gamma\}$ represent the tree’s root edges. The
tree’s root edges are understood to mean the $\gamma$ edges which are directly connected to vertex $a$;
formally, the root edges of $T^n_a$ may be defined as all the edges of the tree $T^n_1$.

An $n$-tree $T^n_a$ may be constructed by performing a breadth first search to depth $n$ starting at
vertex $a^{179}$. The branches of the tree are defined by its edge vectors. For $T^n_a$ I denote these as
$r_j^a$, which defines the vector to vertex $j$ from its parent vertex, where the parent is the vertex from which $j$ is reached when performing the breadth first search.

### 6.5.2 Definition of the spatial similarity statistic

Consider now two $n$-trees $T_a^n$ and $T_b^n$. Comparison of the two trees using the tree overlap method generates the spatial similarity statistic $\phi_{ab}$. I define the spatial similarity statistic as

$$\phi_{ab} = \frac{1}{\gamma!} \sum_{i=1}^{\gamma!} f(T_a^n, T_b^n; \sigma_i), \quad (6.1)$$

where $f$ is a similarity measure which grades the overlap of $T_a^n$ and $T_b^n$ when they are maximally aligned in a root edge permutation $\sigma_i$. $f$ returns a maximum value of unity for perfectly overlapping trees, and values less than unity for imperfect overlap. A permutation $\sigma_i$ is a specific permutation of the numbers $[1, 2, ..., \gamma]$; it is specified as a vector $[\sigma_i(1), \sigma_i(2), ..., \sigma_i(\gamma)]$, where the entry in position one indicates the root edge of tree $b$ which will be overlapped with root edge 1 of tree $a$, and so on. I sum the similarities for all $\gamma!$ overlap permutations of the trees’ root edges and then take the average. The spatial similarity statistic $\phi_{ab}$ thus represents the average quality of the overlap between trees $T_a^n$ and $T_b^n$.

The value of the spatial similarity statistic will depend both on the form that the measure $f$ takes and the method that is used to maximally align the two trees for each root edge alignment permutation. Descriptions of the $f$ used here, and the alignment procedure that is employed, will follow shortly.

### 6.5.3 Definition of the local self-uniformity distributions $\Phi_{nl}$

The LSU distributions of a CRN are particular sets of spatial similarity statistics obtained by overlapping its component trees. Consider a new tree $T_l^a$ with depth $l$ on vertex $a$. The set of vertices in $T_l^a$ is called the local neighbourhood of $a$ to depth $l$. The LSU distribution $\Phi_{nl}$ can then be written as

$$\Phi_{nl} = \{\phi_{ab}\} : b \in T_l^a, a \in C. \quad (6.2)$$

$\Phi_{nl}$ is thus the set of spatial similarity statistics for all trees of depth $n$ whose root vertices are within $l$ edges of one another.

Self-uniformity is thus understood to mean the extent to which a CRN’s component $n$-trees are structurally homogeneous and mutually superimposable. The qualifier ‘local’ specifies that a given $n$-tree is compared only to nearby $n$-trees in the network. In the limit where $l$ tends to infinity, the local neighbourhood of $a$ includes all vertices of the CRN. The LSU distribution associated with this limit, which describes the spatial similarities of all possible $n$-trees in the network, is called the global self-uniformity distribution.
6.5.4 Achieving a Maximal Tree Alignment

The spatial similarity statistic measures the average extent to which two trees $T^a_n$ and $T^b_n$ are mutually superimposable. For each root edge alignment permutation, the similarity measure $f$ operates on the two trees and determines the quality of their overlap. To align the two trees, however, it is necessary to determine a congruent transformation which maximally aligns $T^b_n$ with $T^a_n$ according to the specified permutation.

Maximal alignment is understood to mean that, given the specified root edge alignment permutation, the value returned by the similarity measure $f$ cannot be increased by further congruent transformation of $T^b_n$. Determination of the congruent transformation that yields maximal alignment is a complex problem. Here, I offer an approximate solution through a process of sequential edge alignment. I outline this process below, after which I discuss the advantages and disadvantages of the sequential edge alignment method.

The process of sequential edge alignment, as applied to a specific edge alignment of two tetrahedral 1-trees, is shown in Fig. 6.6. To begin, we translate $T^a_n$ such that its root vertex overlaps the root vertex of $T^a_n$ (this step is shown last in Fig. 6.6). Next, we attempt to align the root edges according to the specified permutation $[\sigma_i(1), \sigma_i(2), ..., \sigma_i(\gamma)]$. First, we align edge 1 of $T^a_n$ with edge $\sigma_i(1)$ of $T^b_n$ as best we can; $T^b_n$ is rotated about an axis which passes through its root vertex until the vectors $r^b_{\sigma_i(1)}$ and $r^a_1$ are parallel. Secondly, we attempt to align edge 2 of $T^a_n$ with edge $\sigma_i(2)$ of $T^b_n$ without diminishing the existing alignment. To achieve this, we rotate $T^b_n$ about the $r^a_2$ axis until the vectors $r^b_{\sigma_i(2)}$ and $r^a_2$ are maximally parallel; maximally parallel is understood to mean that the angle between the two vectors is minimised.

At this point, I consider trees of degree $\gamma = 3$ to be ‘maximally aligned’ since any further rotation* of $T^b_n$, although it may improve the alignment overall, necessarily reduces the alignment between edge 1 of $T^a_n$ and edge $\sigma_i(1)$ of $T^b_n$. I thus choose to apply no further transformations to $T^b_n$. The overlap for the maximally aligned trees is then calculated using the similarity measure $f$.

For trees of degree $\gamma > 3$ it is necessary to introduce a further alignment step. In this case $T^b_n$ is reflected in the plane defined by $r^a_1$ and $r^a_2$ so as to bring $r^a_3$ into maximal alignment with $r^b_{\sigma_i(3)}$ and $r^a_4$ with $r^b_{\sigma_i(4)}$. This step is performed only if the alignment between $T^a_n$ and $T^b_n$ is improved, as measured by an increase in the value of $r^a_3 \cdot r^b_{\sigma_i(3)} + r^a_4 \cdot r^b_{\sigma_i(4)}$. After this step, I consider the two trees to be maximally aligned; their overlap quality is then measured by the similarity measure $f$.

The sequential edge alignment process, described above, is easily coded and rapidly executed. It determines congruent transformations of $T^b_n$ that achieve good alignment between the required root edge pairings. It should be noted, though, that sequential edge alignment is not guaranteed to align the two trees such that the value returned by the similarity measure $f$ is maximised; the process will thus systematically underestimate the true value of the spatial similarity statistic $\phi_{ab}$. However, I suggest that sequential edge alignment broadly reflects the extent to which two

*Note that for a $\gamma = 3$ tree in three-dimensions, we may find that alignment can be further improved by reflection of $T^b_n$ in the plane defined by $r^a_1$ and $r^a_2$. This leaves the edges $\sigma_i(1)$ and $\sigma_i(2)$ of $T^a_n$ unchanged, while possibly increasing the alignment between the edge vectors $r^a_1$ and $r^b_{\sigma_i(3)}$. This was not implemented in my three-dimensional LSU calculations, and need not be implemented for a two-dimensional network.
Figure 6.6: Sequential edge alignment applied to two tetrahedral 1-trees. We fix tree $A$ in space and attempt to align tree $B$ in the edge alignment permutation $[1,4,3,2]$; edges are colour-coded to reflect the target edge alignment. First, edges $1_a$ and $1_b$ are aligned by rotation. Next edges $2_a$ and $4_b$ are aligned by rotation. We then reflect tree $B$ to simultaneously align edges $3_a$ and $3_b$, and $4_a$ and $2_b$.

trees can be overlapped, and that it is a good approximate solution to the maximal alignment problem. A more complex solution could employ a conjugate gradient optimisation method, using the similarity measure $f$ as its objective function, to determine the congruent transformation of $T_b^n$ that maximises the overlap quality with $T_a^n$.

6.5.5 The Choice of Similarity Measure

Once two trees $T_a^n$ and $T_b^n$ are maximally aligned, their overlap quality is determined with a similarity measure $f$. The similarity measure is an important user-controllable degree of freedom. $f$ should possess a number of general properties. Specifically, the measure should return a value that increases as the extent to which the two trees overlap increases. There should exist a maximum value that the measure can return; this value should only be returned when two identical trees are overlapped in a root edge alignment permutation that perfectly superimposes them. Beyond these requirements, we are free to consider how $f$ may best be formulated to suit the application.

Here, overlap quality is measured through the alignment of ‘natural’ edge pairs. A ‘natural’ edge pair comprises two edges, one from $T_a^n$ and the other from $T_b^n$, whose alignment will be considered because there is a sense that they ‘ought to overlap’. This concept is illustrated in Fig. 6.7A, where two distinct low symmetry 2-trees, $A$ and $B$, are overlapped. Tree $B$ has already been congruently transformed by sequential edge alignment such that its root edges align with tree $A$ as required. Once superimposed, we see that particular edge pairs naturally align; these edge pairs are colour-coded. My implementation of the similarity measure $f$ considers only the alignment between these pairs of edges.

With this in mind, I write the similarity measure $f$ as
\[ f(T_n^a, r^b_n; \sigma_i) = \frac{1}{|T_n^a| - 1} \sum_{j \in T_n^a} \frac{r^a_j \cdot r^b_{k(j)}}{\frac{1}{2}(|r^a_j| + |r^b_{k(j)}|)^2}. \] (6.3)

Overlap is calculated between edge pairs by taking their scalar product and normalising it with the square of their mean norm; overlap of a single pairing is thus distributed on \([-1, 1]\]. Specifically, we consider the natural edge pairs \(r^a_j\) and \(r^b_{k(j)}\); the index \(k(j)\) signifies that we do not know a-priori which edge vector of \(T_n^b\) forms the natural edge pairing with \(r^a_j\). A total of \(|T_n^a| - 1\) edge pair comparisons are performed; these are summed and then averaged such that \(f\) yields a maximum value of unity for perfectly overlapping trees.

Algorithmically, the evaluation of \(f\) is performed recursively in a depth-first sense; this simplifies the determination of the index \(k(j)\). At a particular point in the algorithm’s execution, it has reached some vertex pair \(j\) and \(k(j)\) by comparison of the natural edge pair \(r^a_j\) with \(r^b_{k(j)}\). At this point there exist \((\gamma - 1)!\) possible combinations in which the remaining \(\gamma - 1\) edge pairs around vertices \(j\) and \(k(j)\) may be overlapped. All possible combinations are considered, and the set that maximises the sum of edge pair scalar products is chosen as the set of natural pairings. This set of natural pairings is accepted, the edge overlap is calculated, and the algorithm proceeds to calculate overlap for the edges around each of the \((\gamma - 1)\) child vertices.

### 6.6 Local Self-Uniformity Distributions

Using Eqns. 6.1 & 6.2, we may now calculate the local self-uniformity distributions \(\Phi_{nl}\) for any CRN of fixed degree \(\gamma\). In this section, I present a number of example LSU distributions for common crystalline and amorphous networks. I demonstrate also the effect of tree depth \(n\) and locality \(l\) on the form of the LSU distribution. Importantly, I connect local self-uniformity to the concept of strong isotropy\(^{180}\). The champion and near-champion PBG networks - honeycomb,

**Figure 6.7:** Illustration of natural edge overlap pairings (A). When two distinct 2-trees are maximally aligned, we see that edge pairs, one from each tree, naturally overlap; natural edge pairs are colour-coded. Overlap quality is calculated considering the alignment of these natural pairings. Visualisation of the overlap of two maximally aligned 3-trees (orange and blue) in three-dimensions (B).
diamond and single network gyroid - are the only networks that are strongly isotropic. I remark on the significance of this, but delay discussion of the optical significance of strong isotropy until section 7.5.

6.6.1 Honeycomb and Disordered Honeycomb

To begin, I consider a selection of $\Phi_{nl}$ sets of the honeycomb network and its amorphous derivatives. I plot LSU distributions as histograms, in which the $x$ axis specifies the value of the spatial similarity statistic $\phi_{ab}$, and the $y$ axis records the frequency with which that spatial similarity occurs within the set $\Phi_{nl}$. The histogram frequencies are normalised such that they sum to unity; this allows comparison between $\Phi_{nl}$ sets of different size.

Fig. 6.8 panels A & B show characteristic LSU distributions for the honeycomb network. Panel A compares the sets $\Phi_{n,2}$ for $n = 1, 2 & 3$. The three results thus describe the extent to which trees of size $n$ can be made to overlap with similar trees drawn from their local area of depth 2. For all $n$, we see that the LSU distributions comprise a single peak at unity; all tree pairings in the set were thus found to overlap perfectly for all possible root edge alignment permutations.

This result serves as a useful sanity check of the LSU calculation framework. As we saw in section 6.3, it is clear that all vertex permutations of an equilateral triangle can be generated by...
congruent transformation. The root edges of a honeycomb $n$-tree are analogous to the vertices of the triangle, and all trees drawn from a honeycomb network possess the symmetries of $D_3$. We expect that any two $n$-trees, drawn from a perfect honeycomb network, should be superimposable in all $3!$ root edge alignment permutations. The size of the tree does not affect this; trees are grown symmetrically from the root vertex, and thus any two $n$-trees, of arbitrary but equal size, will possess a spatial similarity statistic of unity.

Panel B compares the sets $\Phi_{2,l}$ for $l = 1, 2, & 3$. These results describe the extent to which trees of size 2 are mutually superimposable with similar trees drawn from a local neighbourhood of depth $l$. As before, all tree pairs are perfectly superimposable and possess unit spatial similarity statistics. Together, the LSU distributions of honeycomb demonstrate that the network is structurally homogeneous, comprising only a single type of vertex.

Fig. 6.8 panels C & D show the same characteristic LSU distributions for a paracrystalline graphene glass. This glass is presented in Fig. 6.9; to highlight its paracrystallinity, I have shaded its cells according to their area. Specifically, cells with areas within $\pm 20\%$ of the typical 6-sided cell area are white. Cells with areas larger than this are shaded blue, and smaller cells are shaded red. It is clear that the glass contains substantial crystallites within which the network adopts a near-perfect honeycomb structure; these network regions appear predominantly white. Crystallites are then interconnected with regions of disordered random network; these regions appear blue and red. The paracrystalline graphene glass, along with Delaunay tessellated hyperuniform and quasicrystalline networks, falls into the broad class of ‘disordered honeycombs’.

Figure 6.9: A paracrystalline disordered honeycomb. The cells have been shaded according to their area; cells with areas within $\pm 20\%$ of the mean 6-sided cell area are white, while cells larger than this are blue, and smaller cells red. Crystallites and small locally crystalline regions comprise clusters of 6-sided cells; they thus tend to appear white, while amorphous network regions appear red and blue.
Panel C compares the sets $\Phi_{n,2}$ for $n = 1, 2 & 3$. Immediately we observe that the low symmetry trees of a disordered honeycomb cannot always be perfectly superimposed. The spatial similarity statistics display a range of values in the vicinity of unity, suggesting that the trees are structurally similar, but not identical and symmetric. 1-trees (orange line) are found to overlap most strongly, and the quality of the tree overlap, as measured by the mean and spread of the distribution, decreases with increasing tree size. This result indicates the amorphous character of the network; structural correlations are significant at short lengthscales, as probed by $\Phi_{1,2}$, and are found to decay as the LSU distributions probe the tree similarities at longer lengthscales.

Panel D shows the effect of locality $l$ on the sets $\Phi_{2,l}$. The characteristic double peak of the $\Phi_{21}$ distribution (orange) reflects the paracrystallinity of the network. 2-trees drawn from a crystallite can be made to overlap near-perfectly; this registers as a significant peak in the LSU distribution around unity. 2-trees drawn from glassy network regions are significantly less symmetric, overlap less effectively and register as a subsidiary peak around $0.95$. The double peak thus suggests structural inhomogeneity and the existence of two distinct network environments. As the locality of the $\Phi_{nl}$ set increases, trees from crystallites and random network regions will be overlapped; the two peaks becomes less sharp and begin to merge.

### 6.6.2 Diamond and Amorphous Diamond

So far, discussion of local self-uniformity has been grounded in two-dimensions where the processes of tree alignment and overlap are most easily visualised. As formulated, however, LSU calculations can be directly implemented for three-dimensional connected networks. Fig. 6.7B shows an example tree overlap in three dimension. In the figure, two 3-trees have been maximally aligned by sequential edge alignment; their spatial similarity is then determined through Eqn. 6.3, just as in the 2D case.

Fig. 6.10 shows a selection of LSU distributions for a diamond and amorphous diamond network. Panels A & B focus on the diamond network; they show, as before, the effects of tree depth $n$ and locality $l$ on the LSU distributions. We observe that, in all cases, the LSU distributions comprise a single peak at unity. The tetrahedrally-symmetric trees of the diamond network are thus perfectly superimposable for all $4!$ alignment permutations of their root edges.

For a tetrahedral 1-tree, this result is to be expected. It is easy to show that the $4!$ vertex permutations of a regular tetrahedron may all be generated by an appropriate congruent transformation. A pair of 1-trees may thus be aligned perfectly for all possible root edge alignment permutations and will share a unit spatial similarity statistic. The LSU distributions demonstrate that two $n$-trees of any size also share this property, although this is less easy to visualise.

Fig. 6.10 panels C & D show the same LSU distributions for an amorphous diamond network. The amorphous diamond network is a 1000-vertex CRN model of amorphous silicon, kindly provided by N. Mousseau. If decorated with dielectric cylinders of an appropriate radius, the structure is exactly that of photonic amorphous diamond. Unlike the two-dimensional graphene glass, the amorphous diamond CRN is not paracrystalline. It contains no substantial regions within which the network is a perfect topological diamond.
LSU distributions $\Phi_{n2}$ for various tree depths are shown in Fig. 6.10C. The spatial similarity is highest for 1-trees and is found to decrease with increasing tree size. As before, we conclude that the network possesses strong short range correlations which fade with increasing distance from our point of observation (the root vertex of the tree).

Fig. 6.10D shows LSU distributions $\Phi_{2l}$ for various localities. In contrast to the paracrystalline graphene glass, the LSU distributions are mostly insensitive to an increase in the locality of the tree comparisons. We conclude that the amorphous diamond network, although it is structurally disordered, is homogeneous in the sense that it contains no crystallites and its component trees are all mutually superimposable to a similar degree.

Given that they are both glassy networks, it is surprising that the paracrystalline honeycomb LSU distributions can display two peaks, while amorphous diamond distributions exhibit one. The two-dimensional glass (which was simulated by a two-dimensional implementation of the annealing protocol of section 7.1) contains both crystallites and amorphous network regions, while the three-dimensional glass is structurally homogeneous. This suggests that amorphous diamond contains a greater proportion of topological defects than the two-dimensional glass. Further, these defects appear to distribute homogeneously throughout the network, rather than separating into distinct crystallites and disordered regions.

Fig. 6.11 presents distributions of shortest path (SP) rings for the two glasses. The $x$-axis records the ring length, while the $y$-axis shows the relative frequency $f$ with which each ring length is observed. The two-dimensional glassy network (Fig. 6.11A) is dominated by
Figure 6.11: SP ring distributions for a paracrystalline graphene glass and an amorphous diamond network. The graphene glass topology (A) is dominated by 6-membered rings; the formation of 5-sided and 7-sided rings is strongly suppressed. The amorphous diamond topology (B) is more complex; a significant proportion of rings are not 6-sided. These topological defect states are more readily accommodated in three-dimensions.

6-membered rings; 66% of all SP rings are 6-sided, while nearly all the remaining rings are either 5-sided or 7-sided. In two dimensions, I suggest that the creation of topological defects is energetically costly; since the glass is confined to the plane, bond angles and bond lengths must change significantly to accommodate any defect. The three-dimensional glass (Fig. 6.11B) exhibits a broader distribution of SP ring lengths. Here, only 46% of rings are observed to be 6-membered; the network contains a significant proportion of 5-sided, 7-sided and even 8-sided rings. The three-dimensional glass is thus more topologically complex. I suggest that, in three-dimensions, topological defects are more readily accommodated by the network; the extra co-ordinate degree of freedom permits partial relaxation of topological defects, and facilitates their dispersion throughout the network.

6.7 Strong Isotropy

For the honeycomb and diamond networks, the $\Phi_{nl}$ sets presented above were found to consist exclusively of unit spatial similarity statistics. It is guaranteed\(^1\) that this will remain true in the limit where $n$ and $l$ tend to infinity; all the possible LSU distributions of the diamond and honeycomb networks will comprise a single peak at unity. This property has been dubbed ‘strong isotropy’.

Strong isotropy, introduced by Toshikazu Sunada, is a particularly stringent type of symmetry described as “the strongest amongst all possible meanings of isotropy”\(^2\). It arises from pioneering work to reformulate crystallography from an abstract mathematical perspective. Sunada’s work describes crystals as energy-minimising realisations of topological crystals - abstract graphs derived from forming the maximal covering graph of a chosen finite graph\(^2\). Strong isotropy may be defined as follows\(^1\).

**Definition of Strong Isotropy:** Consider a connected network, or mathematical graph, $C$ of degree $\gamma$. Let $x$ and $y$ be two vertices in $C$ whose edges are labelled $\{e_i\} = [e_1, e_2, ..., e_\gamma]$ and $\{f_i\} = [f_1, f_2, ..., f_\gamma]$ respectively. The network $C$ is said to be strongly isotropic if, for any $x \& y \in C$ and for any permutation $\sigma$ of $[1, 2, ..., \gamma]$, there exists a congruent transformation $g \in \text{Aut}(C)$ such that $gx = y$ and $ge_i = f_{\sigma(i)}$. 

A congruent transformation \( g \in \text{Aut}(C) \) is some combination of a translation, a rotation and a reflection operation which is also an automorphism of the network \( C \). An automorphism is understood to be a transformation which maps the network onto an indistinguishable realisation of itself (every symmetry operation of the equilateral triangle of Section 6.3 is thus an automorphism).

The implications of strong isotropy on the LSU distributions are thus clear. Any two 1-trees drawn from a strongly isotropic network of degree \( \gamma \) can, by a congruent transformation, be made to overlap perfectly for any choice of the \( \gamma! \) permutations of their root edge alignment. Further, this congruent transformation extends to an automorphism of the network, such that a pair of trees of any size are guaranteed to overlap perfectly and share a spatial similarity statistic of unity.

It has been proved that only three strongly isotropic networks exist in three dimensions or less; these are the honeycomb, diamond and single gyroid networks. Amongst these, honeycomb is a planar structure while the diamond and single network gyroid architectures are fully three-dimensional. Strong isotropy thus defines an exclusive set of structures.

All other known networks are not strongly isotropic. Consider, for instance, the simple cubic scaffold. Let us take two 1-trees from the simple cubic scaffold, tree \( A \) and tree \( B \), and label their root edges as shown in Fig. 6.12. Consider now trying to superimpose the two trees in the root edge alignment permutation \([1, 2, 3, 5, 4, 6]\). Fig. 6.12 shows that sequential edge alignment cannot align the root edges as required. Reflecting tree \( B \) to align the mismatched yellow and purple edges will cause misalignment of the orange and blue edge pairs. More generally, it is clear that there is a significant set of alignment permutations that are inaccessible by congruent
transformation of tree $B$. Consider the 6 vertices which coordinate the central vertex of the 1-tree. These vertices form a regular octahedron and are thus not all mutually equidistant. As a result, the vertices of an octahedron may not be permuted arbitrarily by any distance-preserving rigid body transformation\textsuperscript{178}.

In this way, we see that LSU naturally favours simple vertices with low coordination numbers. LSU measures a tree’s symmetry under permutation; trees are overlapped with themselves, or others, for all possible $\gamma!$ permutations of their root edge alignment. As the vertex complexity increases, a larger proportion of root-edge alignment permutations will become inaccessible; this leads to imperfect edge alignment, and a reduction in the LSU. As required, LSU thus reflects the decrease in PBG size with increasing coordination number, as shown in table 6.1.

The definition of strong isotropy provides an alternative perspective on local self-uniformity; we may view LSU as a continuous measure of the extent to which a network is strongly isotropic. By measuring the possible overlap qualities of distinct $n$-trees, the tree overlap method determines if a network exhibits the set of automorphisms required by strong isotropy. In any practical case, we compare finite-sized $n$-trees such that the automorphisms we probe are defined only for local regions of the network. As we move from perfect strong isotropy to a disordered network configuration, tree overlap quantifies the extent to which the network retains this particular set of ‘local automorphisms’. The paracrystalline graphene glass and amorphous diamond networks (Figs. 6.8 & 6.10 respectively) exemplify glassy network configurations with short range order. Their significant, although imperfect, tree spatial similarity statistics demonstrate that these networks retain a locally automorphic character.

I note that two of the strongly isotropic networks - honeycomb and diamond - correspond to the champion photonic band gap architectures in two and three-dimensions respectively. The rod-decorated photonic crystal derived from single network gyroid, the only other strongly isotropic network, possesses a large near-champion PBG. Further, amorphous derivatives of both the honeycomb and diamond networks both exhibit sizeable, although non-champion, gaps. Overall, these observations suggest that, in the high index limit, the property of strong isotropy may be associated with the formation of particularly large PBGs. Further, the quality of a network’s local automorphisms, as measured by LSU, appears to play an important role in gap formation in aperiodic materials.

Current evidence can only take us so far in adequately substantiating the suggestion that photonic band gaps are connected to the quality of a network’s ‘local automorphisms’. Beyond disordered honeycombs and amorphous diamond, few disordered networks of fixed degree have been designed and studied. In two dimensions, disordered honeycombs may be generated by Delaunay tessellation of an appropriate seed point pattern\textsuperscript{62,67}. This tessellation protocol has been generalised to three dimensions, where random networks with short range structural order have been engineered by tessellation of maximally-jammed random sphere packings\textsuperscript{81,82}. The tessellation protocol tiles the seed point pattern with deformed tetrahedra, and the resulting networks are strictly 4-coordinated. As a result, the networks are similar to amorphous diamond and fall into the broad category of diamond-like architectures. Given that a complete PBG is already known to exist in the amorphous diamond structure, further study of tetrahedrally tessellated three-dimensional point patterns is unlikely to clarify, beyond the current analysis, the
role of ‘local automorphisms’ in PBG formation. Instead, the study of novel network structures is likely to be more rewarding.

So far as I can establish, no amorphous derivative of the single network gyroid structure has yet been studied, designed or observed. By analogy with disordered honeycomb and amorphous diamond, an amorphous single network gyroid would be a three-dimensional random network of degree 3, characterised by local vertex geometries which approximate the high symmetry vertex arrangement in its crystalline precursor. Further, we might expect an appropriately-designed amorphous gyroid to possess, like disordered honeycomb and amorphous diamond, significant locally automorphic character, as measured by its LSU distributions.

The hypothetical amorphous gyroid network is thus of significant optical interest. Its realisation and study offer an opportunity to test the intuitions, developed in Sections 6.1 & 6.2, concerning ideal PBG-forming structural characteristics. Specifically, amorphous gyroid networks could be used to investigate further the possible connection between local self-uniformity and the formation of sizeable PBGs in high index aperiodic architectures.

6.8 Conclusions

I have introduced local self-uniformity as a means of measuring the ability of a connected network to support a complete photonic band gap. To achieve this, I analysed the known types of photonic crystal and PBG-forming architectures and, for rod-decorated structures at a refractive index contrast of 3.6 : 1, tabulated their PBG sizes. I concluded that sizeable PBGs are principally associated with two characteristics: vertex simplicity and vertex symmetry. Simple vertices have low coordination numbers. Networks which comprise simple vertices exhibit the champion and near-champion PBGs, and PBG size tends to decrease with increasing vertex complexity. Amongst the possible realisations of a network with a fixed vertex coordination, it is vertex symmetry which determines PBG size. The largest PBGs are associated with the maximally symmetric vertex coordination, and PBG size was observed to decrease with decreasing structural order.

To encapsulate these observations, I developed local self-uniformity as a measure of structural order in networks comprising vertices with a fixed coordination number $\gamma$. I defined an $n$-tree as the set of vertices that can be accessed by traversing no more than $n$ edges from a given root vertex. Two $n$-trees $T_a^n$ and $T_b^n$ may then be compared using the tree overlap method. To begin, I maximally align the two trees according to a prescribed root-edge alignment permutation; I achieve this through sequential root-edge alignment. Once aligned, I quantify the extent to which the two trees overlap using a similarity measure. The spatial similarity statistic $\phi_{ab}$ of the two trees is then defined as their average overlap across their $\gamma!$ root-edge alignment permutations. In particular, the similarity measure was defined such that two trees which overlap perfectly possess a spatial similarity statistic of unity; this value then exclusively decreases with decreasing overlap quality.

I defined the LSU distributions $\Phi_{nl}$ as particular sets of a network’s spatial similarity statistics. Specifically, $\Phi_{nl}$ contains the spatial similarities of all $n$-trees whose root vertices are separated
by no greater than \( l \) edges. A particular LSU distribution thus describes the extent to which a network’s trees are mutually superimposable over a length-scale \( n \) and within local regions of size \( l \).

I presented LSU distributions for the champion photonic crystals - the diamond and honeycomb networks - and their amorphous derivatives. The LSU distributions for diamond and honeycomb were found, for all \( n \) and \( l \), to comprise single peaks at unity. I demonstrated that amorphous honeycomb, specifically a paracrystalline graphene glass, and amorphous diamond both exhibit significant but imperfect LSU. By controlling the locality \( l \) of the LSU distributions, I observed that LSU diagnosed the existence of crystallites within the paracrystalline glass, but suggested that the amorphous diamond network was structurally homogeneous.

Any network whose LSU distributions, for all \( n \) and \( l \), comprise a single peak at unity is either a diamond, a single network gyroid or a honeycomb. These three structures constitute the complete set of strongly isotropic networks; LSU may thus be viewed as a continuous measure of the extent to which a network is strongly isotropic. A characteristic of strong isotropy is that any permutation of the edge labels about a given point extends to a congruent transformation that is an automorphism of the network\(^\dagger\). In this way, LSU measures the quality of a network’s locally automorphic character. The three strongly isotropic networks are either a champion photonic crystal design or, in the case of single network gyroid, near-champion. Further, locally self-uniform amorphous derivatives of honeycomb and diamond both exhibit sizeable PBGs. This suggests that a hypothetical amorphous gyroid should possess significant LSU and may exhibit a complete PBG.

In summary, LSU is a novel approach to classifying the structure of networked matter. In particular, it adopts an innovative perspective on the concept of symmetry. Specifically, by adopting a continuous measure of the extent to which two trees are mutually superimposable, LSU avoids classification through a simple binary (i.e. symmetrical, or non-symmetrical with respect to a particular symmetry operation). As a purely geometrical tool, LSU can be used to classify and analyse the structure of connected networks of fixed valency, and could be generalised to mixed-valency networks through a redefinition of the spatial similarity statistic. Further, LSU provides a unique perspective on the structure of glasses which may prove useful in continuing efforts to understand the nature of the glass transition.

\(^\dagger\)Note that this characteristic follows naturally from the definition of strong isotropy. It is, however, not sufficient to define strong isotropy.
Chapter 7

Locally Self-Uniform Amorphous Gyroid

The hypothetical amorphous gyroid network is of significant interest for photonic applications. Amorphous gyroid is a three-dimensional continuous random network (CRN) characterised by 3-fold connected vertices and short range structural correlations whose strength decays with distance. By analogy with the well-known glassy disordered honeycomb and amorphous diamond networks, the network structure about a given vertex in amorphous gyroid should be a low symmetry realisation of its structure in crystalline single network gyroid. We can expect that an amorphous gyroid structure possessing these properties should, like other glassy networks, exhibit substantial local self-uniformity. The realisation and study of amorphous gyroid thus presents an opportunity to investigate the possible connection between local self-uniformity and the formation of sizeable photonic band gaps (PBGs) in high refractive index disordered structures.

In this chapter, I explore the design, fabrication and optical characterisation of amorphous gyroid structures. I begin with a general discussion of the Wooten-Winer-Weaire (WWW) method with which high quality CRN models of amorphous silicon have been successfully generated. Here, I apply the method to generate amorphous gyroid models, and discuss the ways in which the WWW procedure must be modified to achieve this. Employing the modified WWW process, I generate amorphous gyroid networks and characterise their geometry, topology, structure factors and LSU. I find that high quality amorphous gyroid networks possess sizeable PBGs; specifically, the best 1000-vertex models have PBGs of width 16% for a relative permittivity contrast of 13 : 1.

Following this, I fabricate centimetre-scale prototypes of amorphous gyroid in high refractive index ($\varepsilon_r = 9.5 \pm 0.3$) aluminium oxide using an advanced ceramic 3D printing process. My collaborators and I verify the predicted photonic properties of the prototypes using a microwave transmission method. Specifically, we detect a sizeable PBG that accords well with our theoretical predictions, and demonstrate the isotropy of the gap as a function of microwave incident angle.
To close, I investigate the connection between local self-uniformity and PBG-forming ability. Specifically, I demonstrate the striking correlation between LSU and PBG size in both amorphous gyroid and hyperuniform disordered honeycomb systems. I discuss at length the physical connection between LSU and PBGs, arguing that the electromagnetic properties of a high index network arise from coupling the modes of its trees in a tight-binding-like regime. I employ an FDTD method to demonstrate how LSU measures the extent to which a network’s trees possess PBG-forming resonant properties. Further, I suggest that perfect symmetry under permutation limits the number of electromagnetic resonances that a scattering unit supports; this suggestion explains the origin of the champion and near-champion PBGs in strongly isotropic photonic crystals.

7.1 The WWW Algorithm

In this section, I introduce the Wooten-Winer-Weaire (WWW) algorithm for the generation of glassy networks. The method was introduced in 1985 by Wooten, Winer and Weaire\textsuperscript{117}, who used it to create computer models of the proposed continuous random network structure of amorphous silicon. The WWW method has since been iteratively refined to allow efficient generation of large high-quality amorphous silicon networks\textsuperscript{83,118,183}; it is a well documented computational protocol and thus an ideal method to adapt to the generation of amorphous gyroid networks.

7.1.1 Overview

The generation of a glassy CRN is a complex computational challenge. Consider a three-dimensional CRN comprising \(N\) vertices. For a given network topology, there exist \(3N\) degrees of freedom (the cartesian coordinate positions) which must be explored to find the optimum glassy realisation. The number of possible topologies, however, is combinatorially complex; choosing an appropriate topology presents a problem which cannot be solved through computational ‘brute force’. The WWW algorithm solves this problem by providing a method with which the massive configuration space of the structure may be efficiently explored; this is made possible by a simulated annealing process.

Simulated annealing algorithms are a broad class of methods inspired by the Metropolis algorithm\textsuperscript{184}. In a simulated annealing process, the state of a complex system is evolved iteratively according to a Metropolis-Hastings transition probability. We define some cost function \(f\) which measures the ‘potential energy’ of any given realisation of the system. We begin with an initial realisation and measure its potential energy \(E_i\). We then propose a modified realisation, closely related to the initial state, whose potential energy we measure as \(E_j\). We compare the potential energies of the initial and modified states, and form a transition probability \(p\) given by

\[
p = \min \left[ 1, e^{(E_i - E_j)/\gamma} \right],
\]

(7.1)
where $T$ is a user-controllable variable. We see that if the energy of the proposed state is lower than the initial state, the transition probability is equal to unity. In this case, the proposed state is accepted and the system is evolved. If the energy of the proposed state is higher than the initial state, then the acceptance probability is distributed on $0 < p < 1$. To decide if the proposed network is accepted, we generate a uniformly distributed random number $a$ on this interval. If $a < p$, we accept the new state and evolve the system. If $a > p$, we retain the existing state of the system.

The process is repeated iteratively, at each stage proposing a modified state, derived from the current state of the system, and accepting or rejecting this modification probabilistically according to Eqn. 7.1. The variable $T$ is thus analogous to the temperature at which the annealing process is performed. Consider the case where $E_j > E_i$. If $T$ is large, the probability of accepting the modified state is significant; a high temperature can increase the energy of the system. If $T$ is low, transitions to higher energy states become unfavourable; this can drive the system into a low energy state.

The states of the model evolved according to this simulated annealing process form a discrete-time Markov chain. All states are mutually accessible, although almost always not directly, and so the system is ergodic. Consider now sampling the Markov chain after it has taken a large number of steps. It can be shown that the probability $p_n$, with which we will detect a given state $n$ of the system, is given by a Boltzmann distribution\textsuperscript{185}. We write this probability as

$$p_n = \frac{1}{Z} e^{-E_n/T}, \quad (7.2)$$

where $Z$ is the partition function, given by

$$Z = \sum_i e^{E_i/T}. \quad (7.3)$$

It is possible to drive the system to a deep local minimum of the potential function by gradually lowering the temperature from some $T_{\text{max}}$ to zero according to a user-defined annealing schedule. It can be proven that an annealing schedule where $T(k) = c/\log(1 + k)$, for $k$ the number of steps that the Markov chain has taken, will converge to the global energy minimum so long as the constant $c$ is greater than the depth of the deepest non-global energy minimum\textsuperscript{186}.

Logarithmic annealing schedules are, however, often impractical due to the slow rate at which the temperature is reduced; in most practical cases a faster annealing schedule is required. Rapid annealing may prevent convergence to the global minimum and instead force the system into a deep local minimum of the potential energy function $f$. Fortunately, the glassy states which we seek are themselves only local minima of the energy function; employing a rapid annealing schedule therefore works to our advantage.
7.1.2 Specifics of the WWW Algorithm

7.1.2.1 Core Process

I now outline the core steps of the WWW algorithm. Consider a CRN of degree $\gamma$. The network comprises a set of $N$ vertices with known positions $\{r_i\}$. The topology of the network is described by a bonding table of size $\gamma \times N$, where the $i$th column records the $\gamma$ vertices to which vertex $i$ is connected. We prepare the CRN in an arbitrary initial state; the choice of initial state is important but this is discussed later. To evolve the network into a glassy configuration, we apply the following steps:

1. Introduce a random topological defect.
2. Relax the network by altering the atomic positions, thus achieving the energy minimum for the given topology.
3. Accept or reject the new configuration according to equation 7.1.
4. Iterate steps 1 to 3 until a satisfactory amorphous state is found.

In step 1, the topology of the network is modified; this is achieved by introducing a random Stone-Wales defect. The Stone-Wales defect provides a recipe for reconnecting the vertices in the region of a particular bond. Fig. 7.1 illustrates this recipe for the $\gamma = 3$ case, although it is equally applicable to any network of degree $\gamma \geq 3$. Four vertices, $[A, B, C, D]$, are chosen; $B$ and $C$ are directly connected via a bond, and $A$ and $D$ are connected to $B$ and $C$ respectively (Fig. 7.1A). In the Stone-Wales defect, vertices $B$ and $C$ exchange a neighbour while the connection between them, and the position of each vertex, remains fixed (Fig. 7.1B).

In step 2, the positions of all vertices are optimised to drive the network into a potential energy minimum. We define a potential energy function $f$ which measures the extent to which the vertices are arranged according to some ideal geometry. In the case of amorphous silicon, the function $f$ is called the ‘Keating energy’; it takes the form

\[
A \quad B \quad C \quad D
\]

\[
A \quad B \quad C \quad D
\]

\[
A \quad B \quad C \quad D
\]

**Figure 7.1:** A Stone-Wales defect for a 3-fold connected network. The defect is defined by 4 vertices $[A, B, C, D]$ (A). Vertices $B$ and $C$ exchange a neighbour while the bond between them, and the position of each vertex, remains fixed (B). The network is then relaxed to relieve strain and the vertex positions will adjust to accommodate the new topology (C).
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\[ f(\{ r_i \}) = \alpha \sum_i \sum_j (r_{ij} \cdot r_{ij} - d_0^2)^2 + \beta \sum_i \sum_{j \neq k} \left( \frac{r_{ij} \cdot r_{ik}}{|r_{ij}| |r_{ik}|} + \frac{1}{3} \right)^2, \]  

(7.4)

where \( r_{ij} = r_i - r_j \) is the edge vector between bonded vertices \( i \) and \( j \).

The first term is a `bond stretching` term; we choose a target bond length \( d_0 \) and all edges not equal to this length contribute a non-zero value to the potential energy. The second term is a `bond bending` term; it is greater than zero for bond angles not equal to the ideal tetrahedral bond angle of \( \cos^{-1}(-1/3) \) (approximately 109.5°). For a vertex \( i \), the bond angle contribution is summed over all pairs of neighbour vertices \( j \) and \( k \) where \( j \) is not equal to \( k \). The scalar coefficients \( \alpha \) and \( \beta \) provide a means of weighting the relative contributions of the bond length and bond angle terms to the overall potential; increasing \( \alpha \), for instance, results in structures with tighter bond length distributions at the expense of the bond angle distribution width.

The generalisation of the Keating energy for use in amorphous gyroid modelling is straightforward. In this case, the potential energy function \( f \) is written as

\[ f(\{ r_i \}) = \alpha \sum_i \sum_j (r_{ij} \cdot r_{ij} - d_0^2)^2 + \beta \sum_i \sum_{j \neq k} \left( \frac{r_{ij} \cdot r_{ik}}{|r_{ij}| |r_{ik}|} + \frac{1}{3} \right)^2. \]  

(7.5)

\( f \) is thus almost identical to the regular Keating energy. As before, the first term penalises deviation from a fixed target bond length. The bending term now favours inter-edge angles of \( \cos^{-1}(-1/2) = 120° \); this reflects the geometry of the planar trihedral units that describe the vertex configuration about a given point in a single network gyroid.

Having defined an appropriate potential energy function, the point positions are varied until an energy minimum is found; this is referred to as relaxation. Efficient implementations of the WWW algorithm have employed custom-built optimisers to perform this relaxation\(^{83,118,183}\). Here, I employ a regular conjugate gradient optimisation method to relax the vertex positions.

The effect of relaxation on a Stone-Wales defect is illustrated schematically in Fig. 7.1C; the vertices move to lower the potential energy of the configuration by regularising the defect.

Once relaxed, the modified network state is accepted probabilistically according to Eqn. 7.1. If accepted, the modified network becomes the new current state and the WWW process begins again at step 1. If rejected, the state of the network prior to the introduction of the Stone-Wales defect is retained. The WWW process then begins again at step 1 by proposing a different modified state.

Note that the CRN is modelled inside a finite domain to which a periodic boundary condition is applied. The CRN is defined inside a cubic domain of side length \( L = \sqrt{N} \); the resulting network thus has unit vertex density. To apply the periodic condition, a translation vector is associated with every edge.

Consider a vertex \( i \), located near the surface of the domain, which is bonded to a vertex \( j \). If \( j \) lies towards the centre of the domain, the edge between the two vertices is recorded as untranslated. \( j \) can, however, lie on the far side of the system. In this case, the edge is recorded together with
an appropriate translation vector. A translation vector of $[1, 0, 0]$, for instance, records that $i$ is connected to a copy of vertex $j$ that has been translated by a vector of $L[1, 0, 0]$. In this way, the edge between the two vertices is allowed to pass through the surface of the finite domain. The edge then re-enters on the opposite side of the domain. In this example, we associate a translation vector of $[-1, 0, 0]$ with the connection from vertex $j$ to $i$; vertex $j$ is thus bonded to a copy of vertex $i$, translated in the opposite sense.

7.1.2.2 Efficiency Enhancements

Numerous enhancements of the core WWW algorithm have been developed\textsuperscript{83,118,183}. These enhancements increase the scalability and convergence time of the process such that large CRN models can be efficiently generated. Here I discuss only those enhancements which were implemented in my WWW procedure.

**Quenching** Due to its stochastic search trajectory, the rate at which the WWW procedure converges on a deep local potential energy minimum is slow. Further, as the temperature is decreased, the number of Stone-Wales defects that must be tried before any single defect is accepted increases significantly. Quenching provides an efficient means of terminating a simulation run and guarantees that the network produced lies in a deep local energy minimum.

A quench is a strictly downhill search in which the only accepted alterations are those which lower the structure’s potential energy. This is equivalent to applying the WWW process at zero temperature. To implement a quench, we must construct a list of all possible Stone-Wales defects. For each Stone-Wales defect, we consider the contribution made by the vertices $B$ and $C$ (Fig. 7.1A) to the total potential energy; the defect list is then sorted according to this energy contribution. We then apply the WWW procedure at zero temperature, attempting in turn all the Stone-Wales defects on the defect list.

If a defect results in an energy decrease, the network is evolved. A new Stone-Wales defect list is then created and we try all defects in turn again. The quench is completed once all defects have been attempted and none have been found to lower the potential energy. At this point, there is no topological modification which can be made to instantaneously reduce the potential energy of the network. The CRN has thus been driven into a deep local energy minimum.

**The Initial Configuration** Wooten et al. used a crystalline diamond network as the initial state of the CRN\textsuperscript{117}. The crystal was randomised by the addition of a multitude of Stone-Wales defects at high temperature and subsequently annealed by reducing the temperature. The method could produce glassy networks but was not guaranteed to do so. In some cases, annealing was observed to return the CRN to the crystalline state.

Here, I follow the method of Barkema and Mousseau\textsuperscript{118} and initialise the WWW process with a randomly-generated state. Initialising with a random state eliminates the possibility that the random network encodes some ‘memory’ of an initial crystalline configuration; it thus increases the likelihood of generating a truly amorphous configuration. To generate a random initial
Figure 7.2: Illustration, for $\gamma = 3$, of a forced topological alteration during a quench. During a quench, two points, here $A$ and $B$, can become non-physically close without sharing a connection (A). If this happens (B), $A$ is forcibly connected to $B$. To maintain strict $\gamma$-valency, vertices $A$ and $B$ each lose a neighbour vertex. These neighbours, $C$ and $D$, are then forcibly connected.

state, $N$ vertices are distributed randomly inside the simulation domain. These vertices are then connected, subject to the periodic boundary condition, to produce a CRN in which every vertex is connected to $\gamma$ distinct other vertices.$^{118}$

This initial configuration is highly strained and so it is immediately quenched. During this initial quench, it is possible for two atoms to come into close proximity without being bonded. If this occurs, they are forcibly bonded together according to the topological modification illustrated in Fig. 7.2. Typically, many forced reconnections are implemented during the quench; for this reason, the exact method used to connect the initial random configuration is unimportant. Once quenched, the resulting network is a high-energy glassy CRN which can be used as an initial configuration for simulated annealing.

Parallelisation

Parallelisation is key to rapid execution of the WWW algorithm, particularly at low temperatures where it can be necessary to test $O(1000)$ Stone-Wales defects before a modified state is accepted.

Efficient parallelisation schemes for the WWW process have been suggested.$^{183}$ Here, I employ a simple bulk-synchronous parallelisation of algorithm steps 1 and 2. $T$ distinct Stone Wales defects are proposed. These defects are then simultaneously implemented and relaxed by $T$ separate threads. Once all threads have completed, $T$ distinct acceptance probabilities are calculated (Eqn. 7.1), and a single random number is generated. If none of the proposed states are accepted, a further $T$ distinct defects are proposed and trialled. If several of the proposed states are accepted, one of these is chosen at random and the network is evolved.

Local relaxation of defects

Optimisation of all $3N$ vertex degrees of freedom during a relaxation is computationally expensive. More efficient relaxation is achieved by relaxing only those vertices in the vicinity of a recently-introduced defect.$^{83}$ Further, relaxation of a local region greatly increases the scalability of the algorithm; large CRNs can be simulated without significantly increasing the time taken to relax the network.
Here I implement local relaxation in step 2 of the WWW process. Specifically, only the 120 closest vertices to the position of the defect are relaxed. This renders the number of optimised variables independent of the total size of the structure and makes the algorithm more scalable. Every 100 times a defect is accepted, a global relaxation of the network is performed in order to relieve any additional strain caused by the local relaxation.\textsuperscript{83}

### 7.1.3 Annealing Methodology

To generate models of amorphous gyroid I apply the enhanced WWW procedure to a three-dimensional 3-fold connected CRN. Randomly generated glassy CRNs are used as initial states. For the potential energy function, $f$, I employ the adapted Keating energy of Eqn.7.5 with $\alpha = \beta = 1$ and $d_0 = 1/\sqrt{2}$ (the edge length in a unit-density single network gyroid). Annealing schedules were of the form

$$T(k) = \begin{cases} \varepsilon + \frac{c}{k} & : k \leq k_c \\ \varepsilon + \frac{c}{k} - m(k - k_c) & : k > k_c \end{cases}, \quad (7.6)$$

where $\varepsilon$, $c$ and $m$ are constants, $k$ is the iteration number and $k_c > 1$ is the critical iteration value. After a large number of iterations $k_c$, the network was globally relaxed and quenched. The annealing schedule was then switched from a slow $1/k$ type decay to a more rapidly decaying linear function, and the network was subjected to a second round of annealing.

A number of different size networks were generated. In all cases, total annealing times were such that, on average, each vertex of the network was directly involved in $O(10^2)$ bond transposition events, not including the initial quench reconnections.

### 7.2 Results

#### 7.2.1 Type-1 and Type-2 Amorphous Gyroids

Once generated, CRNs are characterised by plotting histograms of their geometrical properties. These properties are edge length, inter-edge angle, dihedral angle and skew angle, and will, for a general CRN, display a variety of possible values.

Edge length measures the distance between connected vertices and the inter-edge angle $\theta$ describes the angle between edges that share a common vertex.

The skew angle measures the extent to which a network’s component trihedra are coplanar. Fig. 7.3A shows a single trihedron comprising a central vertex and three edges described by vectors $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3\}$. We choose two edges, for instance $\mathbf{e}_1$ and $\mathbf{e}_2$, and calculate the unit normal $\tilde{\mathbf{n}}$ to the plane which they describe. A skew angle $\chi$ of the trihedron is then the angle between the unit normal and the remaining edge vector. A single trihedron thus displays three possible skew
Fig. 7.3: Illustration of skew and dihedral angles. The skew angle $\chi$ measures the coplanarity of a trihedron (A); two edges form a plane, the skew angle is the angle between the plane normal and the remaining edge vector. The dihedral angle is the ‘twist’ angle between two trihedra, $a$ and $b$, which share a common edge.

angles, all of which take a value of $90^\circ$ when all edges are coplanar. A skew angle histogram describes the distribution of values that the trihedron skew angles take in a CRN.

By extension, the dihedral angle is the angle between intersecting trihedral planes. Alternatively, it is the angle through which two trihedra, which share a common edge, are twisted. Fig. 7.3B shows two trihedra, $a$ and $b$, which share a common vertex. We label the edge vectors of the trihedra $[e^a_1, e^a_2, e^a_3]$ and $[e^b_1, e^b_2, e^b_3]$ and define $e^a_1$ and $e^b_1$ as the common edge. We then form the vectors $\mathbf{n}_a = e^a_2 \times e^a_3$ and $\mathbf{n}_b = e^b_2 \times e^b_3$ which describe the normals of the two trihedral planes; the dihedral angle $\phi$ is the angle between these two normals. In a single network gyroid crystal, all dihedral angles take a value of $\cos^{-1}(-1/3) \approx 109.5^\circ$.

I calculate also the ring lengths as a means of characterising topological uniformity. A ring is a non-trivial path within the network that starts and ends at the same vertex. Here, I define and measure rings using the shortest path (SP) rings approach. An SP ring satisfies an irreducibility criterion requiring that the path length between any pair of vertices within the ring is the shortest path length possible given the network topology. The shortest path criterion has been shown to find the rings that are intuitively perceived when visually inspecting a network.

Figs. 7.4A, B & C present the characteristic geometries and SP ring distribution for a 1000-vertex single network gyroid structure. Panel A shows that the edge lengths are all identical. Panel B shows that all inter-edge angles ($\theta$) are equal to $120^\circ$ and all trihedra are perfectly coplanar due to their $90^\circ$ skew angles ($\chi$). The dihedral angle ($\phi$) is observed to take two possible values; this is an artefact resulting from the calculation of plane normals through an edge vector cross product. Without a consistent edge labelling scheme, the cross product order of operation can be flipped and the plane normal thus negated. We therefore measure dihedral angles of $\cos^{-1}(\pm 1/3) \approx 109.5^\circ$ & $70.5^\circ$. The SP ring distribution (Panel C) reflects the characteristic decagonal rings of single network gyroid.

Equivalent histograms for a 1000-vertex amorphous gyroid network, the result of annealing with the modified Keating potential, are shown in Figs. 7.4D, E & F. As a glassy network, the geometrical properties and SP ring lengths describe extended distributions. The edge length
A B C
D E F

Figure 7.4: Comparison between the characteristic geometries and topologies of single network gyroid (top row) and type-1 amorphous gyroid (bottom row). Panels A & D show edge length histograms. Panels B & E show histograms for the inter-edge angles $\theta$, the dihedral angles $\phi$ and the skew angles $\chi$. Panels C & F present the distributions of SP rings within the networks.

distribution is tightly focussed on the target edge length $d_0$ and the inter-edge angle distribution is concentrated around $120^\circ$. These characteristics are inherited from single network gyroid and show that the CRN possesses significant short-range structural order.

It is clear, however, that the network is significantly disordered at intermediate lengthscales. The skew angle distribution ($\chi$) shows that the majority of trihedra are not coplanar. The dihedral angle distribution ($\phi$) bears no resemblance to that of single network gyroid; it extends across the full range of possible angles and indicates an absence of structural order on the length-scale of three edges. Similarly, the SP ring distribution implies significant structural and topological inhomogeneity. Short rings of length 6 correspond to almost-planar honeycomb-like rings, embedded within the three-dimensional network. SP rings significantly longer than 10 edges signify the existence of substantial voids within the sample. Overall, the SP ring distribution suggests that the density of the network varies throughout.

The geometrical and topological characteristics of Figs. 7.4D, E & F are typical of amorphous gyroids annealed using the modified Keating potential; I call these networks ‘type-1’ amorphous gyroids. However, compared to the best amorphous silicon CRN models\textsuperscript{187}, type-1 amorphous gyroids are a poor realisation of a hypothetical amorphous gyroid.

Amorphous silicon CRNs display substantial dihedral angle order\textsuperscript{187}. In a typical amorphous silicon CRN the dihedral angle is widely distributed but clusters significantly around the crystalline values of $0^\circ$, $120^\circ$ and $240^\circ$. Type-1 amorphous gyroid networks show no such dihedral angle order. Further, their component trihedra are non-coplanar. They are poor models of amorphous gyroid in the sense that no dihedral or skew angle order has been inherited from the crystal.
It is interesting to note that amorphous silicon CRNs appear to acquire their dihedral angle order spontaneously, despite being annealed with a simple Keating potential. This may be a result of the comparatively simple topology in diamond; the diamond SP rings have length 6 compared to length 10 in single network gyroid. Alternatively, dihedral order may arise only slowly such that its production requires a long annealing time. Here, I annealed a 1000-vertex type-1 amorphous gyroid for 100,000 WWW iterations and observed no dihedral order in the resulting network.

To remedy the lack of dihedral angle order in type-1 amorphous gyroids, I introduce a new ‘potential energy’ function \( f \) that can drive the CRNs towards more faithful amorphous gyroid geometries. This function takes the form

\[
f = \alpha f_1(\{d\}) + \beta f_2(\{\theta\}) + \gamma f_3(\{\phi\}) + \delta f_4(\{\chi\}),
\]

(7.7)

where \( \alpha, \beta, \gamma \) and \( \delta \) are coefficients, and the functions \( f_1, f_2, f_3 \) and \( f_4 \) operate on the edge lengths, inter-edge angles, dihedral angles and skew angles of the CRN respectively. These functions are written as

\[
f_1 = \sum_i \sum_j (r_{ij} \cdot r_{ij} - d_0^2)^2,
\]

(7.8)

\[
f_2 = \sum_i \sum_{j \neq k} (\hat{r}_{ij} \cdot \hat{r}_{ik} + \frac{1}{2})^2,
\]

(7.9)

\[
f_3 = \sum_i \sum_j (|\hat{n}_{i,i_2} \cdot \hat{n}_{j,j_2}| - 1/3)^2,
\]

(7.10)

\[
f_4 = \sum_i \sum_j (\hat{r}_{ij} \cdot \hat{n}_{i,i_2})^2 + (\hat{r}_{ij} \cdot \hat{n}_{j,j_2})^2.
\]

(7.11)

Together, the functions \( f_1 \) and \( f_2 \) describe the adapted Keating energy, in which edge length deviation from a target value \( d_0 \) and inter-edge angle deviation from \( \cos^{-1}(-1/2) \) both contribute non-zero values to the potential energy. To these, I add the term \( f_3 \), which favours dihedral angles \( \phi \) of \( \cos^{-1}(\pm 1/3) \), and \( f_4 \), which favours skew angles of 90°.

To understand the functions \( f_3 \) and \( f_4 \), consider two vertices \( i \) and \( j \) which share a common edge. Each vertex has three connections to vertices \([j,i_1,i_2]\) and \([i,j_1,j_2]\) respectively. Let \( \hat{r}_{ij} \) represents the unit vector from \( i \) to \( j \) and \( \hat{n}_{i,i_2} \) the unit normal to the plane containing the vectors \( r_{i,i_1} \) and \( r_{i,i_2} \).

We see that \( f_3 \) is minimised when the cosine of twist angle between two edge-sharing trihedra is equal to \( \pm 1/3 \); this describes geometries in which the dihedral angles \( \phi \) are equal to \( \cos^{-1}(\pm 1/3) \approx 70.5° \) & 109.5°. These two possible dihedral angle values are allowed due to the unpredictability of the sign on the plane normals \( \hat{n}_{i,i_2} \) and \( \hat{n}_{j,j_2} \). In doing so, we accept that, unlike in single network gyroid, trihedra with mixed dihedral angles may be created.

The function \( f_4 \) favours configurations in which the shared edge vector \( \hat{r}_{ij} \) is orthogonal to the two dihedral plane normals \( \hat{n}_{i,i_2} \) and \( \hat{n}_{j,j_2} \). For a given vertex \( i \), \( f_4 \) contains a sum over the
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3 possible choices of vertex \( j \). The function is thus minimised by coplanar trihedra with skew angles of 90°.

Overall, I call the potential energy function of Eqn. 7.7 the ‘triamond potential’. Using the triamond potential, I repeated the annealing simulations according to Section 7.1. A careful balance was needed between the four terms of the triamond potential. Specifically, large values of \( \gamma \) were found to distort the CRNs, causing them to fold in on themselves and never recover. After some trial and error, a suitable set of weightings was found to be \( \alpha = \beta = 0.7, \gamma = 0.3 \) and \( \delta = 0.4 \). As before, annealing times were such that each vertex of the network was directly involved in \( O(10^2) \) bond transposition events.

I refer to CRNs annealed through the triamond potential as ‘type-2’ amorphous gyroids. The geometrical and topological characteristics of a 1000-vertex type-2 amorphous gyroid are shown in Fig. 7.5D, E & F. The same characteristics of a type-1 network are shown in Fig. 7.5A, B & C for comparison.

We observe that a type-2 amorphous gyroid is a much higher quality amorphous gyroid than a type-1 network. Specifically, the dihedral (\( \phi \)) and skew (\( \chi \)) angle distributions are now focussed around their corresponding values in single network gyroid (Fig. 7.5E). The dihedral angle distribution is broad, but is concentrated around \( \phi \approx 70.5° \) & 109.5°. The skew angle distribution is tightly centred on 90° and shows that the network’s trihedra are generally almost perfectly coplanar. We note that the edge length (Fig. 7.5D) and inter-edge angle (\( \theta \), Fig. 7.5E) distributions are broader than in a type-1 network. This is a trade-off; optimisation of the dihedral and skew angle distributions introduces extra edge length and inter-edge angle strain.
The SP ring distribution of the type-2 network is shown in Fig. 7.5F. Compared to the SP rings in a type-1 network (Fig. 7.5C), we see that short (length $\leq 7$) and long (length $\geq 13$) rings are suppressed. The ring length is distributed around the crystalline value of 10. The reduced spread in the ring length distribution implies a significantly improved density homogeneity.

To illustrate the two types of amorphous gyroid, Fig. 7.6 shows two ball-and-stick renderings of a 1000-vertex type-1 network (A) and a 1000-vertex type-2 network (B). The two networks are clearly difficult to distinguish from visual inspection alone.

### 7.2.2 Total Scattering Structure Functions

I now investigate the total scattering structure functions (TSSFs) of type-1 and type-2 amorphous gyroids. TSSFs were calculated by fast Fourier transform (FFT) according to Eqn. 2.5. I decorate the amorphous gyroid networks with cylinders of uniform radius $r$. Here, the cylinder radius is chosen such that the networks have a volume fill fraction of 27.5%. The aperture function was then calculated by voxelisation, performed in the MIT photonic bands package, of the rod-decorated networks. Aperture functions were averaged to zero by subtraction of their mean value; this removes the straight through diffraction peak and allows us to access a more faithful scattering intensity for near-zero momentum transfers.

As three-dimensional structures, the network TSSFs are defined over three orthogonal directions in momentum transfer space. To visualise the diffraction patterns, the TSSFs are sliced in the $k_z = 0$ plane. For both network types, I calculate the TSSFs of 5 distinct CRNs and sum the results incoherently. This process averages out finite size effects that result from the small size of the 1000-vertex structures.
Figs. 7.7A & C show the average slice in the $k_z = 0$ plane for type-1 and type-2 networks respectively. In both cases, the diffracted intensity is normalised to the maximum value in the type-2 network diffraction pattern. The axes are normalised by the $a$ value with which the basis vectors of single network gyroid are defined (Eqn. 3.34); here, the networks have a unit vertex density and $a$ is thus also unity.

We observe that the diffraction pattern of type-1 networks (A) is significantly more diffuse than that of type-2 networks (C). Type-1 networks are weakly amorphous, exhibiting a perceptible but poorly-defined annulus of scattering intensity. The TSSFs show significant diffracted intensity in the vicinity of $k = 0$; the networks are thus far from hyperuniform, possessing density inhomogeneities which scatter long wavelength radiation.

Type-2 networks (C), on the other hand, scatter light only weakly in the vicinity of $k = 0$ and thus appear significantly more hyperuniform. They display a prominent and intense primary diffraction ring that is a characteristic of amorphous materials and indicates the presence of medium-range structural correlations.

Figs. 7.7B & D show azimuthal averages of the type-1 and type-2 network TSSFs respectively. As before, both structure factors are normalised to the maximum value of the type-2 azimuthal average. Here, the increased hyperuniformity of type-2 networks is clear (although it is not apparent that the structure is strictly hyperuniform, with an exact structure factor zero at

![Figure 7.7](image-url)
Locally Self-Uniform Amorphous Gyroid

$k = 0$). The primary diffraction ring of type-1 networks is significantly broader and, at its maximum, weaker by a factor of approximately 0.65.

### 7.2.3 LSU Distributions

I now investigate the local self-uniformity (LSU) distributions of type-1 and type-2 amorphous gyroid networks. Note that I do not display for comparison the LSU distributions of single network gyroid, which, as a strongly isotropic network, will each comprise a single peak at unity.

Fig. 7.8 shows a selection of LSU distributions comparing type-1 (top row) to type-2 (bottom row) amorphous gyroids. From panels A and C, we observe that both network types possess significant short range structural order which decays with distance. In type-1 networks (panel A), this decay is rapid; the means of the 1-tree and 2-tree LSU distributions are 0.94 and 0.76 respectively, corresponding to a spatial similarity reduction of 0.18.

Compared to type-1 networks, type-2 networks (panel C) display higher levels of LSU. For each tree depth, the mean spatial similarity is substantially greater. Further, the 1-tree and 2-tree LSU distributions have means of 0.99 and 0.89 respectively corresponding to a significantly smaller spatial similarity decrease of 0.1. Type-2 amorphous gyroids thus possess near-identical 1-trees

**Figure 7.8:** Comparison of LSUs for type-1 (top row) and type-2 (bottom row) amorphous gyroid networks. LSU distributions of type-1 networks for a selection of tree depths (A) and localities (B) show the CRNs are structurally homogeneous but weakly ordered at length scales greater than 1 edge. LSU distributions of type-2 networks for a selection of tree depths (C) and localities (D); these indicate that type-2 networks are a more faithful amorphous gyroid and possess significant locally automorphic character.
and retain this structural order to a significant degree as the tree size is increased. Overall, the LSU distributions of type-2 networks demonstrate considerable locally automorphic character.

Panels B & D compare the $\Phi_{2d}$ distributions for a number of localities $l$. For both type-1 (B) and type-2 (D) networks, the LSU distributions are unaffected by their locality. The similarity of a pair of trees is thus independent of their internal separation within the network; both networks are homogeneous in the sense that all their component trees are spatially similar to a comparable degree. In this particular sense, both types of amorphous gyroid are comparable to amorphous silicon CRNs; all these networks are structurally homogeneous and contain no crystallites.

Comparison of Figs. 7.8A & C suggests that the rate with which mean spatial similarity decays with depth is a further classifier of the extent of a network’s local structural order. I now show that this decay can be modelled using a power law. Specifically, I calculate the mean spatial similarity $\Phi_{nl}$ of each LSU distribution and observe how this evolves with tree depth $n$. I then model the decay of $\Phi_{nl}$ with a power law of the form $\alpha n^\beta$.

Fig. 7.9 shows the evolution of $\ln(\Phi_{nl})$ with depth $n$ for both type-1 (blue) and type-2 (orange) amorphous gyroids. We observe that, in both cases, the decay of the mean spatial similarity describes a straight line; for the 3 depths considered here, the decay thus appears to be well-modelled by a power law. The exponent $\beta$ was measured by linear regression; I observe $\beta_1 = (-0.195 \pm 0.009)$ and $\beta_2 = (-0.113 \pm 0.007)$ for type-1 and type-2 networks respectively. In particular, $\beta_2$ is observed to be significantly smaller than $\beta_1$; this reflects the improved locally automorphic character of type-2 compared to type-1 amorphous gyroids. Note that any strongly isotropic network would be described by a $\beta$ that is precisely zero; its LSU distributions would comprise spatial similarities of unity for all tree depths.

\[ \text{Figure 7.9: Power law fits to the decay of mean spatial similarity with tree depth. The natural logarithm of the mean spatial similarity } \Phi_{nl} \text{ is plotted as a function as depth } n \text{ for both type-1 (blue) and type-2 (orange) amorphous gyroids. Linear fits were calculated through regression. The comparatively slow decay of the mean spatial similarity for type-2 amorphous gyroids (orange) reflects their increased local self-uniformity.} \]
7.2.4 Photonic Band Gaps

The photonic band structures of rod-decorated type-1 and type-2 amorphous gyroids were calculated by plane wave expansion, implemented in the MIT photonic bands package\textsuperscript{79}. CRNs are simulated as supercells, with the result that band structures are folded into an artificially small supercell Brillouin zone. In spite of this, the frequencies of calculated eigenmodes remain accurate and the spectral ranges of any photonic band gaps can be readily measured.

Supercells were formed by decorating the edges of the CRNs with cylinders of fixed radius $r$ comprising dielectric material of relative permittivity $\varepsilon_r = 13$. Using a type-2 amorphous gyroid, the cylinder radius was optimised to maximise the size of the fundamental PBG; this was found to occur for a dielectric fill fraction of 27.5%. Due to the time required to complete a full optimisation, this fill fraction was taken to be the optimum for all amorphous gyroid CRNs.

Photonic band structures for a pair of 216-vertex type-1 and type-2 amorphous gyroid CRNs are presented in Fig. 7.10. Band structure is calculated for a $k$ space path that traverses the high symmetry points of a regular cubic Brillouin zone.

Panel A shows the folded band structure of a type-1 network. At low frequencies, the dispersion relation of the structure may be approximated by the lightline of an index-averaged homogeneous medium\textsuperscript{152}. This one-to-one dispersion is folded into the supercell Brillouin zone where it manifests as anisotropic primitive cell-like band structure. As the frequency increases, the utility of the Bloch wavevector $k$ diminishes. The one-to-one dispersion of the effective medium breaks down and the sum of all eigenmodes at a given frequency describes comprise a continuum of momentum states $k$. The band structure thus appears as a dense collection of flat bands. Within this, we observe a perceptible density reduction in the band density between $0.19 < af/c < 0.215$ which we may associate with a reduction in the density of states. Numerous small PBGs exists.

![Figure 7.10](image-url)
within this frequency region, the largest of which has width 0.9% and is shaded purple. The presented band structure is typical of type-1 amorphous gyroid networks.

Panel B shows the folded band structure of a type-2 amorphous gyroid. As before, we observe anisotropic band structure at low frequency which transitions into a dense collection of flat bands as the frequency increases. The most striking feature of the band structure is the large, complete photonic band gap that falls between 0.188 < \( \alpha f/c < 0.221 \) and has width 16.1%. A sizeable PBG is a typical property of type-2 amorphous gyroids. In high quality (the most locally self-uniform) type-2 networks, the gap consistently falls between bands \( N/2 \) and \( N/2 + 1 \) of the supercell band structure, where \( N \) is the total number of vertices in the CRN. As the network quality decreases, defect bands which bisect the PBG may be created; in such cases, the largest discrete gap is not guaranteed to fall between bands \( N/2 \) and \( N/2 + 1 \).

I investigated also the extent to which the PBGs in type-2 amorphous gyroids are influenced by network size. I began by generating a spectrum of type-2 amorphous gyroids for network sizes of 108, 216, 324, 512 and 1000 vertices. For each network size, I selected a subset of 4 or 5 distinct CRNs. To ensure a fair comparison of PBG size between the subsets, subsets were chosen such that their component networks had 22 values in the vicinity of a target spatial similarity of 0.89. Fig. 7.11B presents a summary of the LSU characteristics of the 5 subsets considered. For each network size, it plots the mean of the means < 22 > with vertical error bars corresponding to the standard deviation of the 22 values in the subset. Note the y-axis scale; the standard deviation of each set is very small and all sets have a mean LSU < 22 > approximately equal to the target value of 0.89.

Using rod-decorated CRNs, a permittivity contrast of 13 : 1 and a dielectric fill fraction of 27.5%, PBG sizes were calculated for the spectrum of networks. Fig. 7.11A plots the mean PBG width for each subset, together with the standard error of the mean plotted as vertical error bars. Two possible fits to this data are also shown; the blue line represents a simple linear fit, while the dashed green line shows a possible stationary fit.

**Figure 7.11:** The effect of network size on PBG width for type-2 amorphous gyroids. The mean PBG width is plotted as a function of network size for 5 distinct subsets of amorphous gyroid networks (A); error bars reflect the standard error of the mean. The mean of the 22 values for each subset is also shown (B); error bars reflect the standard deviation of the 22 values in each set.
First, we observe that large 1000-vertex type-2 amorphous gyroids retain a sizeable PBG. The average PBG width of the 1000-vertex subset was 15.1%, while the single largest gap in the set had width 17.0%. We note, however, that the mean gap width of 1000-vertex networks appears systematically narrow than that of smaller type-2 amorphous gyroid networks.

Ideally, we would observe that the PBG width is unaffected by network size; the green dashed line (Fig. 7.11A) conveys how this relationship would fit the data. Although the stationary fit is plausible given the error bars, a simple linear fit appears more appropriate. I therefore suggest that PBG size decreases slowly with increasing network size.

### 7.3 3D-Printing of Amorphous Gyroid Models

The fabrication of three-dimensional disordered network architectures is not a straightforward process. It is clearly important to choose a manufacturing technique which can, with a minimum of expensive adaptations, produce prototypes of structurally complex components. Additive manufacturing techniques, usually referred to as ‘3D-printing’, offer great flexibility in the shapes and structural complexity of the components than can be produced. When coupled with a method for fabricating components in high refractive index material, additive manufacturing is an ideal solution for prototyping photonic band gap structures.

Several recent studies have employed additive manufacturing techniques to fabricate advanced disordered photonic structures. Stereolithography has been used successfully to fabricate both two-dimensional hyperuniform and three-dimensional quasicrystalline networks. The stereolithographic process, however, involves the curing of a photo-sensitive liquid polymer by a laser. The refractive index of any components produced is thus limited to that of common polymers and is usually of the order of 1.6.

Photonic amorphous diamond structures have been successfully fabricated in high index material using a selective laser sintering method\(^9\). Here, a mixture of nylon and TiO\(_2\) powder was sintered layer-by-layer using a laser. The resulting sintered material was approximately 40% porous, and PAD models were thus infiltrated with water and frozen to increase the refractive index as much as possible. The refractive index of the ice-infiltrated material was estimated to be 3.0 at microwave frequencies around 22 GHz\(^9\).

Most recently, amorphous diamond-like networks, derived from maximally jammed sphere packings, have been engineered on micron scales using a multi-step direct laser writing technique\(^8\). High index networks, \(n = 3.3\) around 120 THz, were successfully produced by coating polymer templates first with TiO\(_2\) and then, following a sintering step, with silicon. The technique can fabricate complex connected networks in both high index material and at high resolution. Weighed against these benefits is the complexity of the manufacturing process.

Here, I fabricate the first prototypes of amorphous gyroid at a centimetre lengthscale in high index Al\(_2\)O\(_3\) ceramic. To achieve this, I employ a novel lithography-based ceramic manufacturing (LCM) process which can print in either Al\(_2\)O\(_3\) or ZrO\(_2\), and achieve sub-millimetre feature resolution with a minimum of post-processing steps\(^1\).
7.3.1 Design and Fabrication Process

The design and manufacturing process was undertaken in partnership with the Fraunhofer institute for Ceramic Technologies and Systems (Fraunhofer IKTS), Dresden. The machine utilised to print the components was a CeraFab 7500, supplied by Lithoz GmbH.

To print a ceramic component, a paste comprising a mixture of photo-sensitive polymer resin and ceramic micro-particles is selectively cured in a layer-by-layer fashion using an LED array. The resulting component, of which Fig.7.12A shows an example, contains a mixture of ceramic particles and cured polymer resin and is called the ‘green’ component. Post-processing consists of two similar steps. First, a de-binding step occurs in which the green component is baked at around 900°C. Baking degrades and de-binds the cured polymer from the ceramic material, leaving behind a pure ceramic structure. Following this, components are sintered at high temperature (around 1600°C) in order to fuse the ceramic microparticles and produce a dense, strong component. Fig. 7.12B shows a sintered component in the kiln; note the colour difference between the green and sintered component.

The CeraFab 7500 has a maximum build envelope (∆x, ∆y, ∆z) = (75, 45, 150)mm. The nominal achievable resolution is 40µm laterally, and between 25 and 100µm in the vertical direction. Tests at Fraunhofer IKTS indicate that the minimum achievable feature size is ∼100µm. Together, the de-binding and sintering post-processing steps shrink the green component. The shrinkage coefficients for alumina material are typically (s_x, s_y, s_z) = (0.803, 0.803, 0.784), such that a component shrinks to approximately 80% of its original linear dimension along any horizontal axis, and 78% along the vertical axis.

The networks which were printed required careful design. Specifically, two main challenges had to be overcome. First, all exterior surfaces of the component had to be printed with a temporary supporting structure. Consider printing a finite random network layer-by-layer. Many layers will contain network fragments which, although connected into the network, are unsupported by material which is strictly beneath them. When printed, these unsupported fragments will form inaccurately or simply drop off, causing manufacturing defects. To overcome this, all components were surrounded with a continuous vertical supporting wall of thickness 0.5mm. This supporting wall was then removed after sintering by grinding it away; this step is shown in Fig.7.12C. Components were also designed with a thin baseplate of thickness 0.05mm to assist in

![Figure 7.12: Snapshots of the lithography-based ceramic manufacturing process. Green components (A) are printed by selective exposure of a photo-sensitive polymer/ceramic paste. Baking and sintering (B) de-binds the polymer and fuses the ceramic particles respectively. Once sintered, the hard components can be finished to remove excess material (C).](image-url)
removal of the printed component from the build tray; the baseplate was removed after sintering in a similar fashion.

Second, any unexposed paste must be cleaned off the freshly-printed green component; compressed air and cleaning fluid is used to achieve this. However, the introduction of supporting walls and a baseplate seals in this unexposed paste. It was thus necessary to incorporate a large number of holes into the supporting walls and baseplate such that the paste could be effectively removed. This was a fiddly task. An algorithm was written which generated holes in areas where the network was not directly in contact with the supporting wall. Nonetheless, final designs required human quality control to ensure that these extra holes did not create unsupported regions of either the CRN or the supporting wall itself.

All connected networks were designed by decorating a chosen edge and vertex pattern with cylinders of fixed radius. Subject to this, two distinct types of component, distinguished by their overall shape, were designed. The first type was a simple cuboid of connected network; Figs. 7.13A & B show top-down and perspective views of a cuboidal amorphous gyroid design. Note the vertical supporting walls which surround the network on four sides; these walls include the holes which facilitate the removal of the unexposed paste.

For the second type of component, I produced a cylindrical portion of amorphous gyroid network. The cylinder was too large to fit inside the printer build envelope; it was thus manufactured as two

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Figure 7.13: Final designs of amorphous gyroid networks for 3D ceramic printing. Top down (A) and perspective (B) views of an amorphous gyroid cuboid; thin supporting walls support the network during printing while the holes facilitate the removal of unexposed paste. Top down (C) and perspective (D) views of one of the amorphous gyroid semi-cylinders.
separate pieces. Figs. 7.13C & D show top-down and perspective views of one of these pieces. The semi-cylinder was surrounded on its cylindrical surface by a hole-y cylindrical supporting wall. A solid supporting wall was used for the flat vertical surface. The cylinder was manufactured as two semi-cylinders and then, once sintered and finished, assembled into a single component. Note that each half was manufactured with an extra 0.1mm of material along the common surface. This extra material provided a safety margin such that component-crucial material was not removed accidentally during the finishing process.

7.3.2 Results

In total, three components were successfully fabricated. These were two cuboidal samples, one of single network gyroid and one of amorphous gyroid, and a cylinder of amorphous gyroid. Plan views of the printed and finished components are shown in Fig. 7.14. The top panel shows a top-down view, while the bottom panel shows a view along the optic axis of the sample (this is the axis along which microwave radiation will be incident in the experiments of Section 7.4).

The single network gyroid cuboid is shown in Fig. 7.14A. For ease of comparison with band structure, a gyroid high symmetry axis was oriented along the optic axis of the experiment. For this, I chose the [111] axis; this axis presents air-channels which pass through the structure and appear hexagonally packed (Fig. 7.14A, lower panel).

Fig. 7.14B shows plan views of the cuboidal amorphous gyroid sample. These panels demonstrate the quality of the connected network that can be achieved using the LCM technique. The connected network is without defects, and all the cylinders appear well-resolved. Similarly, Fig. 7.14C shows plan views of a single amorphous gyroid semi-cylinder.

\[\text{Figure 7.14: Alumina 3D-printed networks. A cuboid of single network gyroid, designed to present a [111] plane on its major face (A). A cuboid of amorphous gyroid (B). A single semi-cylinder of amorphous gyroid (C), one half of a larger cylindrical sample. Scale bars in all cases are 10mm. Note that the bottom row shows views looking down the } z \text{ axis, which forms the optic axis for the transmission experiments of Section 7.4.}\]
Fig. 7.15 presents perspective views of the printed components. Panel A shows the single network gyroid and amorphous gyroid cuboids together. Panel B shows the completed amorphous gyroid cylinder, assembled from the two semi-cylinders. The two semi-cylinders were observed to fit together perfectly. The shared faces of the semi-cylinders were totally flat such that the components were everywhere in contact with one another. No matching defects were visible at the seam between the two components.

Networks were designed to have a network scaling parameter $a$ (Eqn 3.34) of 3.08mm in order to centre the expected PBG around 22GHz. Note that components were designed to be artificially large to account for the expected shrinkage during sintering. The precise shrinkage factor, however, was not known. The sintered sample dimensions were thus measured in the laboratory, and alumina fill fractions were measured by a water displacement method. Table 7.1 summarises the results of these measurements. The true network scaling parameter $a$ was measured by comparison of the single network gyroid block size to its expected post-sintering size. This was measured to be $a = (3.13 \pm 0.05)$ which is in good agreement with the target value. I assumed uniform shrinkage factors across the three components, adopting an $a$ value of 3.13mm as the scaling parameter in each case.

<table>
<thead>
<tr>
<th>Component</th>
<th>$L_x$ [mm]</th>
<th>$L_y$ [mm]</th>
<th>$L_z$ [mm]</th>
<th>Fill [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNG Block</td>
<td>$60.655 \pm 0.065$</td>
<td>$60.18 \pm 0.06$</td>
<td>$29.56 \pm 0.05$</td>
<td>$27.1 \pm 0.3$</td>
</tr>
<tr>
<td>a-Gyroid Block</td>
<td>$59.725 \pm 0.025$</td>
<td>$60.655 \pm 0.165$</td>
<td>$29.67 \pm 0.37$</td>
<td>$27.9 \pm 0.6$</td>
</tr>
<tr>
<td>a-Gyroid Cylinder</td>
<td>$64.545 \pm 0.025$</td>
<td>–</td>
<td>$56.455 \pm 0.025$</td>
<td>$28.9 \pm 0.3$</td>
</tr>
</tbody>
</table>

Table 7.1: Summary dimensions and alumina fill fractions for the 3D-printed models. Note that $L_z$ is the sample thickness along the optic axis.
7.4 Microwave Experiments with Amorphous Gyroid

My collaborators and I employed an established microwave transmission method\textsuperscript{89,120} to probe the photonic band gaps of our alumina models. Fig. 7.16A shows a schematic diagram of our set-up in which a number of components are labelled. Two microwave horn antennae, each connected to an HP-8510C vector network analyser (VNA), were positioned facing each other at opposite ends of an optical rail. A linearly polarised microwave mode was coupled through the horns and the VNA was run in transmission mode such that one horn acted as a transmitter and the other as a receiver. As designed, the HP-8510C VNA is sensitive to $-65\text{dB}$ of attenuation in the transmitted signal. This limit is imposed by ‘dark noise’, which is the signal measured by the receiver horn in the absence of a signal from the transmitter.

Two custom-made teflon microwave lenses (components 1) were placed in front of the horns to focus radiation onto the sample. The sample (component 4) was placed directly between the horns. A large sheet of microwave absorbing material (component 2), into which a window was cut, was placed between the transmitter horn and the sample; this window restricted the microwaves such that they were incident on the centre of the sample. Finally, the sample was clad in a second sheet of microwave absorbing material (component 3); this cladding ensured that transmitted signal measured by the receiver horn necessarily passed through the sample, rather than being spuriously reflected off the sample surface.

Cuboidal samples were oriented to present their large flat surface towards the incident microwave radiation. Accordingly, their thin axis was parallel to the optic rail. The cylindrical sample was positioned on a rotating mount with its cylindrical axis normal to the optic axis. The cylindrical sample was free to rotate around its cylindrical axis, as indicated by the arrow in Fig. 7.16A.

Transmission spectra were recorded by sweeping the microwave frequency from 15 to 35 GHz. Background spectra were recorded as the transmitted intensity through the set-up without any sample in place. Our use of microwave absorbing material (components 2 & 3, Fig. 7.16A) attenuated the maximum transmitted power by $-30\text{dB}$. As a result, our set-up reduced the transmission contrast that could be measured by the VNA to 35 dB (the designed contrast of

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure7.16.png}
\caption{Schematic diagram of the experimental set-up for microwave transmission measurements. The sample (item 4) is placed between two horns, a transmitter and a receiver. Teflon microwave lenses (items 1) were used for focusing. Microwave absorbing material with a window (item 2) restricted the microwave beam, and microwave absorbing cladding (item 3) eliminated spurious reflections off the sample surface. Panel B shows a photo of the set-up; note that item 3 is absent in this photo, and that the sample is incorrectly oriented.}
\end{figure}
65dB minus the background). Transmission spectra were recorded as either normalised, with the background spectrum subtracted, or raw data.

7.4.1 Results

In Fig. 7.17 normalised transmission spectra for the single network gyroid (panel A) and amorphous gyroid (panel B) blocks are compared. We see that both samples exhibit pronounced transmission gaps with peak to trough contrasts of around 35dB. We observed that transmission spectra suffered from noise, particularly in the transmission gaps where the detected signal is weak and dark noise becomes significant. Accordingly, spectra were low-pass filtered to reduce the magnitude of high-frequency noise; it is these filtered spectra that are shown in Fig. 7.17.

In the case of the SNG sample, both edges of the transmission gap are clearly defined; the lower edge is marked by the sharp drop around 20.6GHz, while the upper edge corresponds to the sharp increase around 22.8GHz. The transmission gap of the amorphous gyroid sample appears less clearly defined. The signal reduces smoothly as the frequency is increased, before bottoming out at $\sim -35$dB of contrast between 20 and 26 GHz.

We estimated the refractive index of the alumina material by comparing the frequencies of the SNG sample’s gap edges with band structures. We calculated the band structure of a single network gyroid, defined by $a = 3.13$mm and a dielectric fill fraction of 27.1% (Table 7.1), for a spectrum of permittivity contrasts. For each relative permittivity, we recorded the frequencies of the lower and upper gap edges for the stop gap along the [111] direction. Note that an accurate calculation of the stop gap width along this axis requires consideration of $k$-space points beyond the first Brillouin zone. Specifically, band structure must be calculated along a path from $\Gamma \rightarrow P \rightarrow H'$, where $\Gamma$ and $P$ refer to the usual high symmetry points of the BCC first Brillouin

![Figure 7.17: Transmission spectra for single network gyroid and amorphous gyroid blocks. Transmission along the SNG [111] axis (A) shows a clear transmission gap with well-defined edges. The amorphous gyroid block (B) displays a pronounced transmission gap, although it is less clearly defined. Band gap edges, as predicted by band structure, are overlaid as vertical dashed lines.](image)
zone. H’ lies outside the first BZ along the Γ→P direction, and is exactly halfway to the next Γ point along this axis\(^{140}\).

We find that the theoretical and experimentally-observed PBGs overlap effectively for an alumina permittivity of \(\varepsilon_r = 9.45\); the lower and upper edges of the matched band structure gap are shown as dashed vertical lines in Fig. 7.17A. Consideration of the uncertainties associated with the scaling parameter and fill fraction of the SNG sample suggests a final permittivity estimate of \(\varepsilon_r = 9.5 \pm 0.3\). This estimate is in good agreement with the results of a thorough characterisation of aluminium oxide\(^{189}\), which measured the permittivity of 99.6% pure alumina as \(\varepsilon_r = 9.424\) at 17GHz.

Using this permittivity estimate and the appropriate fill fraction (Table 7.1), we calculated and overlaid the band-structure predicted gap edges on the transmission spectrum of the amorphous gyroid block; these are shown as vertical dashed lines in Fig. 7.17B. Here, we observe that measured transmission gap appears significantly wider than the predicted gap.

Using the cylindrical sample, we investigated the extent to which the amorphous gyroid PBG is isotropic. The cylinder was rotated about its cylindrical axis, and a transmission spectrum was recorded every 2\(^°\). This set of measurements was performed across the range 17 to 27 GHz so as not to probe frequencies which couple inefficiently in and out of the horns. The transmission spectra are presented as a polar heat-map in Fig. 7.18A, in which the radial coordinate describes the frequency axis and the angular coordinate records the cylinder rotation angle. The data presented shows raw attenuation without subtraction of the background. Background subtraction was observed to increase the effects of noise in strongly attenuated frequency regions; the raw transmission data was found to be of higher quality and suffices to probe the isotropy of the gap.

The amorphous gyroid transmission gap is visible in Fig. 7.18A as the blue/green ring. The expected gap edges, as predicted by photonic band structure, are overlaid as a pair of solid black
rings. We observe that, in spite of the noise, amorphous gyroid exhibits a significantly isotropic transmission gap, similar to that of two-dimensional hyperuniform structures.\(^{89,120,143}\)

For comparison, I measured the gap isotropy using an FDTD simulation method.\(^{190}\) I modelled the cylindrical design in Lumerical.\(^{130}\) Specifically, I employed the relevant scaling parameter, fill fraction (Table 7.1) and dielectric permittivity, and positioned the cylinder at the origin, orienting its cylindrical axis along the z direction. 720 point-like detectors were arranged in a ring of radius 20a; this ring was centred on the cylinder and lay in the z = 0 plane. E and H fields were recorded by these monitors and the detected intensity calculated as the magnitude of the Poynting vector at that point. All simulations were performed using a uniform 0.1mm mesh.

First, the effective permittivity of the amorphous gyroid cylinder was calculated by volume averaging to be \(\varepsilon_r = 3.44\). The cylindrical sample was deactivated, and the FDTD region was filled with a homogeneous material of this effective permittivity. A single dipole source was placed at the origin and a background spectrum was recorded for this set-up. Second, the homogeneous material and single dipole were discarded and the amorphous gyroid cylinder reactivated. 50 dipole sources, each with a random phase and orientation, were located randomly about the origin within a sphere of radius a. The raw transmission spectrum for this set-up was recorded and then normalised through division by 50 times the background intensity. Note that some transmission enhancement, up to a factor of \(\sim 2\), was observed. A final normalisation was thus performed by dividing the normalised transmission spectra by the single largest value recorded by all the detectors.

The results of my FDTD simulations are shown in Fig. 7.18B. The expected gap edges, as predicted by photonic band structure, are also overlaid here for reference; these are marked by the pair of solid white rings. Fig. 7.18B corroborates our experimental results; FDTD predicts a similarly isotropic transmission gap and the experimental and theoretical results are in good qualitative agreement. A close comparison of the two results, however, reveals the significant impact of noise on the experimental data. Further, the FDTD results appear noticeably more isotropic. I address both of these points below.

### 7.4.2 Discussion

A similar microwave transmission method was employed to study the PBGs of photonic amorphous diamond models.\(^{90}\) These models were made from a mixture of nylon, TiO\(_2\) and ice; the permittivity of this material was estimated to be \(\varepsilon_r = 9\) at 22 GHz. The results of this study are thus very relevant. Particularly, the PAD transmission spectra were well-resolved, displaying a typical peak to trough contrast of 45dB.

Further, scattering was observed to significantly effect the quality of the amorphous diamond transmission spectra. The scattering mean free path was measured and was found to be minimal at both the lower PBG edge and for a significant range of frequencies above the gap.\(^{90}\) For these frequencies, transmitted radiation was strongly scattered both away from the receiver horn and into undetectable polarisation states. As a result, the transmitted intensity never recovered its peak value at frequencies above the PBG.
Transmission spectra for an equivalent crystalline diamond sample were less affected by scattering processes\textsuperscript{90}. Here, the transmission was thought to be predominantly ballistic; most radiation passed through the sample without scattering. Accordingly, the edges of the transmission gap were well defined and the transmission was observed to effectively recover its peak value at frequencies above the gap.

These observations help to illuminate some of the problematic features of our results. First, due to our use of microwave absorbing material, the accessible transmission contrast was limited to 35dB; this is 10dB less than the 45dB we might expect is needed to fully resolve the bottom of any transmission gaps. Transmission spectra thus ‘bottom-out’ at a normalised transmission of −35dB and, at these low intensities, are significantly affected by noise.

In spite of this, the edges of single network gyroid [111] axis stop gap (Fig. 7.17A) are well-resolved. Although the transmission is likely thresholded at −35dB, the predominantly ballistic transmission leads to well-defined gap edges.

Together, the effects of scattering and thresholding can account for the apparent width of the amorphous gyroid transmission gap compared to the theoretically expected gap (Fig. 7.17B). In particular, strong scattering of radiation at frequencies above the gap significantly reduces the transmission measured by the receiver horn. The transmission gap thus appears to extend to higher frequencies than the theory suggests. For identical reasons, the transmission gap for the amorphous gyroid cylinder (Fig. 7.18A) is only diffusely defined.

Similarly, noise and thresholding are principally responsible for the minor discrepancies between the experimental and theoretical polar heat-maps of Fig. 7.18. Specifically, the FDTD data does not suffer from thresholding; it resolves transmission spectra fully and measures a peak to mid-gap contrast of \(\sim 60\)dB. When displayed on the same colour scale as the experimental data, the bottom of the gap is thus resolved only as a sharp and uniformly blue ring. The experimentally measured PBG, on the other hand, appears noisy.

Close inspection of the gap edges in Fig. 7.18A reveal, however, a number of features which are not immediately attributable to noise and scattering. Consider, for instance, the yellow/green region near the upper gap edge for \(15^\circ \lesssim \theta \lesssim 30^\circ\); this feature lies above the noise threshold and appears to be a reliable element of the data. We associate this feature, and others like it, with transmission through surface modes of the sample.
7.5 Local Self-Uniformity and PBG-Forming Ability

In Section 6.7, I suggested that the extent of a network’s automorphic character - as measured by its LSU distributions - is connected to its ability to form a complete PBG. The demonstration of a sizeable and complete PBG in locally self-uniform amorphous gyroid networks goes some way to confirming the connection between LSU and PBG-forming ability. In this section, I explore this connection further.

I begin by presenting results for amorphous gyroid networks and two-dimensional hyperuniform disordered honeycombs that demonstrate a striking correlation between LSU and PBG size. Following this, I discuss at length the fundamental physics underpinning LSU’s efficacy as a measure of PBG-forming ability. I highlight similarities between PBG formation and the formation of spectral gaps in electronic systems. In particular, I argue that the electromagnetic properties of a high index connected network arise through coupling the modes of its isolated scattering units in a photonic tight-binding-like regime. Using an FDTD method, I explore how LSU distributions act as a quality measure for the component scattering units of a network. Empowered by the implications of a photonic tight-binding argument, I close by positing a solution to the champion structure problem.

7.5.1 Results

I employed my implementation of the WWW algorithm to generate an ensemble of 57 distinct 216-vertex amorphous gyroid CRNs. Specifically, I manipulated the coefficients of the triamond potential (Eqn. 7.7) to generate networks that spanned a wide spectrum of disorder. For instance, type-1 networks were annealed using \([\alpha, \beta, \gamma, \delta] = [1, 1, 0, 0]\), type-2 networks using \([\alpha, \beta, \gamma, \delta] = [0.7, 0.7, 0.3, 0.4]\) and states of intermediate network order using ad-hoc sets of coefficients, for example \([\alpha, \beta, \gamma, \delta] = [1, 1, 0.05, 0.1]\).

A photonic band structure was calculated for each network using the plane wave expansion method implemented in MIT photonic bands\(^79\). Amorphous gyroids were simulated as cubic supercells and bands were calculated along the k-space path \(\Gamma \rightarrow X \rightarrow M \rightarrow R \rightarrow \Gamma\), where these points refer to the usual high symmetry points of a cubic Brillouin zone. Supercells were formed by decorating amorphous gyroid vertices and edges with dielectric spheres and cylinders respectively, both of fixed radius \(r\). Note that the spherical vertex decorations prevent the formation of air voids within highly deformed vertices which could generate spurious defect states. The dielectric fill fraction of the resulting structures was, on account of the disorder, variable; on average the fill was 27.5%. In all cases, a dielectric contrast of 13 : 1 was used.

I also calculated the \(\Phi_{22}\) set of spatial similarity statistics for each network. LSU distributions were plotted, and the mean spatial similarity \(\bar{\Phi}_{22}\) of each network was calculated.

In Fig. 7.19 I plot the folded band structures for 5 of the 216-vertex networks. The mean spatial similarity \(\bar{\Phi}_{22}\) of the networks is shown in the top line; this increases from left to right. The bands immediately above and below the largest observable band gap have been highlighted in black, and the band gap between them expressed as a percentage.
We observe that increased local self-uniformity is associated with larger PBGs. This can be quantified in two ways. Firstly, it is clear that the raw PBG size increases from left to right. Secondly, my results show that the PBG of the associated single network gyroid structure of identical permittivity contrast and fill fraction exists between $0.184 < \alpha/\lambda < 0.233$. We define this interval as a critical frequency region (the associated SNG PBG for short), and observe that the density of bands within this region is progressively reduced with increasing LSU. This behaviour reflects a decreasing density of states ($\rho(\omega)$, DOS, Eqn. 3.32) in the frequency region of the associated SNG PBG.

Note that a 216-vertex cubic supercell of single network gyroid exhibits its PBG between bands 108 and 109. Indeed a general $N$-vertex supercell has a PBG from bands $N/2$ to $N/2 + 1$. It is thus reasonable to suggest that the PBG of amorphous gyroid networks should also be measured from bands 108 to 109.

We observe, however, that the largest single PBG in the band structure falls between bands 108 and 109 only for the more ordered networks shown in panels D & E. In the more disordered structures of panels A, B & C, numerous bands fill the region of the associated SNG PBG relatively sparsely. These bands may be associated with defect modes that are formed around structural imperfections of the CRN. These defect modes crowd the SNG PBG region in an unpredictable way, with the result that the gap from bands 108 to 109 is not necessarily the largest gap. Measurement of the PBG between bands 108 to 109 is thus not guaranteed to
faithfully reflect a network’s true gap width. Instead, PBGs were measured as the largest visible gap in the band structure.

Accordingly, I measured the PBG width for each of the 57 networks. In Fig. 7.20A, I plot these PBG widths against each network’s mean spatial similarity $\Phi_{22}$. The approximate regions of spatial similarity associated with type-1 and type-2 networks are annotated in orange. A fit line (cubic polynomial, blue) is also superimposed to demonstrate the trend, but this fit is illustrative only.

We observe from Fig. 7.20A that a network’s PBG width is strongly correlated with the mean of its $\Phi_{22}$ LSU distribution. However, for a given $\Phi_{22}$ there is significant spread in the set of observed PBG widths. As discussed above, measurement of the gap size as a single dimensionless width is affected by the unpredictable crowding of the associated SNG PBG region by defect modes. We observed numerous instances in which sizeable gaps were cut almost in half by a single, or several, defect bands. In cases like this, measuring the width of the single largest observable gap is likely to be a noisy process. The network’s ‘true’ effective gap size will be reduced by the presence of mid-gap defect states; the unpredictable frequencies of these states contributes to the significant spread of PBG sizes observed at a fixed $\Phi_{22}$.

For a similar reason, PBG size is observed to increase super-linearly with increasing LSU. Consider artificially eliminating the defect mode at the upper gap edge in Fig. 7.19C; as a result, the PBG size would increase significantly. Indeed, the band structures of the 57 amorphous gyroids studied here (of which 5 are shown in Fig. 7.19) suggest that, in general, removal of a well-chosen gap-edge defect state would cause the PBG size to increase in proportion to its existing size. For a given amorphous gyroid, I associate the gap-edge states with electromagnetic defect resonances supported by the network’s worst structural inhomogeneities. With increasing LSU, these inhomogeneities are suppressed, together with the defect resonances they support. Accordingly, the PBG size exhibits exponential growth with increasing $\Phi_{22}$, as shown in Fig. 7.20A.
In order to reduce the observed spread of PBG sizes around the trend line, I now make use of the density of states. Specifically, I count the number of photonic bands that exist within, either fully or partially, the frequency region of the associated SNG PBG (measured to be $0.184 < a/\lambda < 0.233$). With reference to Eqn. 3.32, this count can be interpreted as an integrated measure of the DOS over the specified frequency region.

Fig. 7.20B presents the integrated DOS $N(\omega)$ for each network plotted against its $\Phi_{22}$ value. As before, a trend line (blue) is superimposed for illustrative purposes. Here, we observe an even more striking correlation between a network’s LSU and its PBG-forming ability. The integrated DOS decreases smoothly with increasing $\Phi_{22}$. The spread of data values at a given $\Phi_{22}$ has been significantly reduced and data cluster tightly around the trend line.

Since no amorphous gyroids with $\Phi_{22} > 0.9$ were successfully generated, the PBG sizes of networks with significant but imperfect $\Phi_{22}$ remain unobserved. It is clear that for a $\Phi_{22}$ value of unity, the network will condense to a single network gyroid with a $23.5\%$ PBG. Accordingly, the exponential growth of the PBG size (Fig. 7.20A) for $0.7 < \Phi_{22} < 0.9$ will not persist as the LSU tends to one.

Exploration of amorphous gyroids with $\Phi_{22} > 0.9$ may yield interesting results. Specifically, the stop gaps of a single network gyroid photonic crystal (see Fig. 3.8) are each significantly wider than the overall complete PBG. The PBG size is suppressed by the anisotropy of the crystal system; this leads to imperfect spectral alignment of the stop gaps along different propagation directions. The observed exponential growth of PBG size in Fig. 7.20A thus suggests an interesting possibility. If an amorphous gyroid characterised by a $\Phi_{22} > 0.9$ could be annealed, it might possess, on account of its statistical isotropy, a complete PBG larger than that of a fill-fraction matched single network gyroid structure. Alternatively though, further annealing of amorphous gyroids may cause condensation into a paracrystalline gyroid glass; this would break the statistical isotropy of the network and the PBG would be limited to the single network gyroid value.

I now briefly investigate the correlation between LSU and PBG-forming ability in two-dimensional systems. Specifically, I consider gaps for TE polarised light in hyperuniform connected dielectric network architectures. A set of 30 hyperuniform patterns was generated using an established optimisation process. Patterns were generated for $\chi$ values of 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6. For each $\chi$ value, 5 distinct 2000-point hyperuniform patterns were produced. Each pattern was then Delaunay tessellated, according to the procedure of section 2.4.2.3, thus forming a hyperuniform disordered honeycomb-type connected network.

Photonic band structures were calculated for each hyperuniform network using the supercell method. Network vertices were decorated with dielectric cylinders of diameter $d$ and edges were connected with rectangular dielectric walls of total thickness $d$. The average dielectric fill fraction was 36.1\%, although this varied a small amount due network disorder. In all cases, a dielectric contrast of 13 : 1 was used. Fig. 7.21A shows four examples of these decorated networks for $\chi$ values of 0.2, 0.3, 0.4 and 0.5 and illustrates the evolution of network structural order with increasing hyperuniformity.
As before, for each network I calculated the $\Phi_{22}$ set of spatial similarities and its mean $\overline{\Phi}_{22}$. The PBG width for each network was measured as the size of the largest observable gap in the band structure. As in the three-dimensional case, this gap fell between bands $N/2$ and $N/2 + 1$ for the most structurally ordered networks, but was only in the vicinity of band $N/2$ for networks with significant structural disorder. Fig. 7.21B presents each network’s PBG width plotted against its $\overline{\Phi}_{22}$ value; the blue trend line (a cubic polynomial) is illustrative.

Again, we observe that a network’s PBG-forming ability is strongly correlated with its LSU. The data is bunched into 6 discrete regions, these correspond to the 6 distinct $\chi$ values sampled, increasing from left to right. Highly disordered $\chi = 0.1$ networks have the lowest LSU, as measured by $\overline{\Phi}_{22}$, and do not form a PBG. The precise $\overline{\Phi}_{22}$ value at which significant PBGs begin to form is not well-defined, although this occurs for spatial similarities in the region of 0.85. The trajectory of the trend beyond spatial similarities of 0.97 is unclear, although we can say with certainty that the PBG for a spatial similarity of 1 is 55.1%, corresponding to the gap of the associated fill-fraction matched honeycomb network.

Taken together, Figs. 7.19, 7.20 & 7.21 categorically demonstrate the correlation between LSU and the ability of a trivalent network, either two or three-dimensional, to form a PBG.

Further, with reference to section 6.1, we note that LSU reflects the natural hierarchy of PBG-forming structures in two ways. Firstly, for a given vertex coordination number $\gamma$, the largest PBGs are associated with translationally periodic networks comprising highly symmetric trees.* As the tree symmetry decreases, PBGs narrow; amorphous diamonds, amorphous gyroids and disordered honeycombs all possess smaller gaps than their maximally symmetric, translationally periodic realisations. For a given $\gamma$, networks comprising maximally automorphic trees are the most locally self-uniform. As a result, translationally periodic networks formed from highly symmetric trees score highly, while amorphous networks incorporating low symmetry trees receive
a lower score. LSU thus reflects the trend from large to small PBGs with increasing structural disorder.

Secondly, several distinct networks comprising uniformly coordinated vertices exhibit sizeable PBGs (Table 6.1). To make a fair comparison, we consider rod-decorated networks only for a permittivity contrast of 13 : 1. With this in mind, we observe that the PBG of a rod-decorated photonic crystal generally narrows with increasing vertex coordination number. LSU broadly reflects this trend by awarding low scores to highly co-ordinated vertices. As the co-ordination $\gamma$ increases, a larger proportion of root-edge permutations become inaccessible and the LSU will decrease.

### 7.5.2 Discussion

Overall, I have shown that LSU is an effective measure of a network’s PBG-forming ability. However, although LSU is an effective measure, the way in which a network’s LSU affects the scattering of light needs further exploration. This is a key issue, the understanding of which will inform both the future study and engineering of complex photonic structures.

In this section, I address at length the physical connection between LSU and photonic band gap formation. I begin by outlining the similarities between band gap formation in electronic and photonic systems. In particular, I observe that both electronic gaps in the nearly-free electron picture and PBGs in low index contrast photonic crystals form through a Bragg scattering mechanism. Further, electronic gaps in amorphous group IV semiconductors can be analysed using a tight-binding formalism but generalisation of this treatment to photonic systems poses several challenges. Nevertheless, I argue that high index PBG materials exhibit electromagnetic modes that are characteristic of a photonic tight-binding regime.

Accordingly, I advance a tight-binding-like perspective of PBG formation in connected networks in which gaps form due to generalised resonant scattering by the network’s trees. Then, using an FDTD method, I illustrate how LSU measures the extent to which a network’s trees are structured to favour PBG formation. Finally, I suggest that symmetry under permutation - as measured by LSU - is the characteristic of an optimal PBG-forming scattering unit; this insight explains why the strongly isotropic networks exhibit the largest PBGs, thus solving the champion structure problem.

The similarities between the mathematical formalism of quantum mechanics and the Maxwell curl equations in linear lossless media have been variously noted. First, consider a single electron interacting with a position dependent electrostatic potential $V(r)$; it’s eigenstates are described by the Schrodinger equation $\hat{H}\psi = E\psi$, where the Hamiltonian $\hat{H} = \hat{p}^2/2m + V(r)$, with momentum operator $\hat{p}$, describes the electron’s kinetic energy and its interaction with the potential $V$.

The Maxwell equations may be expressed in a similar fashion when written in Hamiltonian form (as shown in Appendix C). In this case, the Maxwell curl equations take the form $\hat{H}(\hat{E}, \hat{H}) = \ldots$ 

*Note that diamond, simple cubic and FCC8 trees are all maximally symmetric given their coordination number $\gamma$. Single network gyroid trees are chiral, and non-superimposable with their mirror image; their symmetry could be increased by choosing a dihedral angle of 90°. However, no such translationally periodic structure is known.
\( \omega | \vec{E}, \vec{H} \rangle \), where \( | \vec{E}, \vec{H} \rangle \) is a six component vector, time-harmonic with frequency \( \omega \), which describes the states of the six field components \([E_x, E_y, E_z]\) and \([H_x, H_y, H_z]\). The Maxwell equations thus describe a vectorial eigenvalue equation that is Schrodinger-like. We may expect the solution process for this equation to be formally similar to that of the scalar Schrodinger equation for an electron in a potential.

Solutions to the single electron Schrodinger equation are the starting point for understanding the electronic properties of solids\(^\text{78}\). As a result, a great variety of methods have been developed to analyse the properties of the electron eigenmodes. Here, I highlight two common approaches to the electronic problem whose characteristics parallel the observed behaviour of electromagnetic systems.

Consider a single electron moving in an atomic lattice. Let the lattice present a periodic potential \( V(\mathbf{r}) \) which varies only weakly with position. Such a potential corresponds to a small perturbation in a homogeneous potential; an effective solution may thus be found through a first order perturbation theory in which we expand the wavefunction in the eigenstates of a free space electron. Specifically, on supplying a Bloch wave expansion for \( |\psi\rangle \) of the form

\[
\sum_i \phi(G) \exp(i[\mathbf{k} - G \cdot \mathbf{r}])
\]

and solving for the Fourier coefficients \( \phi(G) \), we find that leading order corrections to the electron energy levels are significant only when the Bloch wavevector \( \mathbf{k} \) is near a Bragg plane\(^\text{78}\). The electron dispersion is free-space like throughout the \( \mathbf{k} \) space, except that, where \( \mathbf{k} \) lies on a Bragg plane, a spectral gap between adjacent bands opens.

More intuitively, the dispersion of the electron can be interpreted in the language of Bragg scattering. When an electron wave’s principal momentum component lies at the Brillouin zone edge it is Bragg scattered into states which are precisely counter-propagating. The coupling of propagating and counter-propagating electron waves causes standing waves to form. The degeneracy of these standing waves is lifted by the alignment of wavefunction nodes and antinodes with the underlying periodic potential. Low energy and high energy states thus form and the spectral gap between these states defines an electronic band gap.

The described solution to the single electron problem is known as the nearly free electron model. Although simple, it can effectively describe the electron bands of metals in groups I-IV of the periodic table for which the potential \( V(\mathbf{r}) \) presents a weakly varying background\(^\text{78}\). Here, I observe that the mechanism through which electronic band gaps form in the nearly free electron model is completely analogous to the Bragg mechanism of photonic band gap formation in photonic crystals. Further, it was shown in Section 4.4.3 and Appendix C that ‘nearly free photon’ treatments of structured dielectric media can be effective models of photon dispersion in the low refractive index limit. Solutions to the single electron Schrodinger and photonic crystal Maxwell equations thus possess comparable properties in the weak perturbation regime.

Photonic crystals, however, typically employ large refractive index contrasts. As a result, their dielectric distributions cannot be modelled as weak perturbations to a homogeneous medium. Similarly, the majority of solids present electrostatic potentials \( V(\mathbf{r}) \) which vary significantly with position. In such cases, it is not accurate to treat \( V(\mathbf{r}) \) as a small perturbation to an empty potential well and nearly free electron solutions are thus not applicable.
Instead, it is possible to adopt an alternative perspective of electron delocalisation in a solid. Specifically, consider assembling an array of \( N \) identical atoms with positions \( \{ \mathbf{R}_i \} \) and characterised by an average nearest-neighbour separation \( a \). Let \( a \) be large such that the interatomic distances are much greater than the radius of the valence electron orbitals. In this limit, electrons are bound only to their parent atoms and the energy levels of the system are well described by the Hamiltonian \( \hat{H}_{\text{at}} \) of the isolated atomic species\(^{78}\).

Consider now compressing the array such that the parameter \( a \) decreases uniformly. As the interatomic separations decrease, valence electron orbitals begin to overlap and electrons may delocalise throughout the atomic array. In the intermediate regime, where valence orbitals of nearby atoms overlap only weakly, we can employ a tight-binding solution to the single electron Schrödinger equation. Specifically, we propose a candidate wavefunction of the form \( |\psi_i\rangle = \sum_{j,k} C_{ij,k} |\phi_j(\mathbf{r} - \mathbf{R}_k)\rangle \), where the \( |\phi_j(\mathbf{r} - \mathbf{R}_k)\rangle \) are the eigenstates of an isolated atom at position \( \mathbf{R}_k \).\(^{196}\) Once an appropriate Hamiltonian has been chosen\(^{196,197}\), we can solve for the coefficients \( C_{ij,k} \) and determine the electron energy levels of the array.

In the tight-binding regime, the overlap between valence orbitals is relatively weak. In regions local to any given atom of the array, the overall electron density retains the character of the isolated atomic eigenfunctions. Further, the tight-binding approach makes no assumptions about the periodicity of the array; the formalism has thus been applied to model a diverse range of aperiodic systems\(^{198,199}\). In particular, a tight-binding approach shows that a complete electronic band gap can exist in tetrahedrally bonded amorphous materials under certain conditions\(^{200,201}\). Specifically, the network should comprise four-coordinated \( sp^3 \) hybridised atoms and the variation of its atom number density, within a sampling window of fixed volume, should be bounded from both above and below. Interestingly, these conditions are similar to the association of hyperuniformity with photonic band gap formation in two-dimensional amorphous trivalent networks\(^{62}\).

The successes of electronic tight-binding have stimulated efforts to engineer a comparable formalism to solve the Maxwell equations in the strong perturbation regime. However, adaptation of the tight-binding method to electromagnetic problems is non-trivial.

Electron orbitals are bound states of negative energy. They are thus localised in space, and overlap integrals between the orbitals of nearby atoms are mathematically well defined. For the same reason, the electron energy levels are also discrete and quantised. Localisation of photons, however, occurs only in exceptional circumstances; in general, the electromagnetic modes which they populate are fully delocalised. Tight-binding-like overlap integrals between the eigenmodes of nearby scattering centres can thus become divergent\(^{126,192}\). Further, the electromagnetic modes of a given system describe a continuum of possible photon energies. A tight-binding-like expansion, in terms of the modes of a fundamental resonator, can no longer be written as a discrete superposition.

It is well known, however, that localised electromagnetic modes can form at structural defects in PBG materials. A defect mode, whose frequency lies within the gap, is localised by an absence of propagating modes to which it can couple. Further, the well defined cavity resonances at such a defect suggest an obvious basis of tight-binding-like eigenstates in which to expand the field. In
this way, the dispersion relations of coupled-defect waveguides can be calculated using a tight-binding approach. Further, the frequencies of defect modes within the PBG of dielectric cylinder arrays can be predicted using a linear combination of Mie resonances method. In the continuum, outside a complete PBG, electromagnetic modes are not localised. Nonetheless, efforts have been made to engineer tight-binding-like schemes based on the superposition of electromagnetic basis states that are localised by mathematical design. These Wannier function methods perform ab-initio calculations of the eigenmodes of a system, typically via a plane wave expansion calculation, and derive an appropriate set of localised basis states (the Wannier functions) from these results. The Wannier function basis facilitates efficient computations concerning defect modes in the system of interest, but is otherwise unsuitable for performing ab-initio calculations of the photonic properties of an arbitrary system.

Clear mathematical difficulties face the development of a rigorous electromagnetic tight-binding protocol. These difficulties, however, do not invalidate observations that the eigenmodes of high index electromagnetic systems display clear tight-binding character. Foremost, the success of coupled defect treatments demonstrates that electromagnetic modes can be viewed as a superposition of localised resonant states. Further, just as the electron density is atomic orbital-like around the ion cores of a tight-binding solid, the electromagnetic modes of structured dielectric media exhibit, at a local level, field profiles which are characteristic of the local scattering unit. This point is most clearly illustrated by the field profiles of two-dimensional PBG materials, as discussed in Sections 3.7 & 3.8. Briefly, the extended modes of dielectric cylinder arrays exhibit field profiles derived from the interaction of a plane wave with an isolated cylindrical scattering unit. Below the PBG, propagation is mediated by a zeroth-order Mie resonance, while above the gap, propagation is mediated by a first-order Mie resonance. Similarly, gap-edge states of disordered honeycombs exhibit ‘cell-type’ and ‘stripe-type’ distributions of field nodes. These characteristic distributions are derived from the interaction of a plane wave with an isolated honeycomb 2-tree.

Consequently, I suggest that the modes of a high index dielectric structure can be viewed as a superposition of the modes of its local scattering units. In other words, the fragments which comprise a complex structure can be analysed in isolation. Once the modes associated with these fragments are known, they can be used in a tight-binding-like basis in which to expand the overall structure’s modes.

In the case of planar dielectric cylinder arrays, the structure’s fragments are well defined and the appropriate basis set is the continuum of Mie solutions. Using this basis set, the modes of an arbitrarily structured cylinder array may be constructed through linear superposition. Then, so long as the cylinders are well isolated, the nature of any given mode in the vicinity of a single cylinder is similar to the Mie solution. Properties of the Mie solution are thus preserved at a local level. In particular, for TM radiation the cylinders scatter light in anti-phase to the incident field for frequencies just above the zeroth and first Mie resonances (see Section 3.7). This anti-phase scattering creates localised standing waves which inhibit the propagation of radiation and, in the limit of a large structure, lead to PBG formation. The stipulation that the cylinders should be well isolated ensures that the overlap between the modes of nearby cylinders is weak;
this preserves the properties of the Mie solution in the vicinity of each cylinder, ensuring PBG formation through Mie resonant scattering.

I now advance a similar perspective on the formation of TE PBGs in planar architectures and complete gaps in three dimensional structures. However, this perspective is conceptually more challenging in a number of respects. Firstly, the fundamental structural units of a network are less clearly defined. Here, network fragments are defined according to the \( n \)-tree formalism introduced in Section 6.5. Secondly, once a particular fragment has been chosen, the continuum of modes which it supports is not analytically defined. In the absence of an analytical solution, the electromagnetic characteristics of the isolated fragment may be probed by an FDTD solver. Thirdly, the structural fragments of a network are directly connected; it is not clear that the modes of adjacent fragments overlap only weakly (i.e. the overlap is in the tight-binding regime). However, in Section 3.8 I observed that the PBG-edge eigenmodes of hyperuniform disordered honeycomb networks exhibit the characteristic field profiles of an isolated trivalent 2-tree. Evidence therefore suggests that, when coupled into a network, the electromagnetic modes of an isolated network unit are preserved at a local level; this behaviour is characteristic of a tight-binding regime.

To make the connection between LSU and PBG-forming ability clear, I now perform an FDTD experiment on a number of honeycomb 2-trees. I employ an identical methodology to that of Section 3.8. I position trees at the origin of the FDTD domain and illuminate them with a TE polarised plane wave whose wavevector is parallel to the \( y \)-axis. All trees, both ordered and disordered, are drawn from unit vertex density networks and scaled to optical sizes using a scaling parameter \( a \). The scattering cross-section was measured by a monitor box and the Mie efficiency determined through division by \( 2a \) (the approximate size of each 2-tree in profile). Power transmitted through each tree was measured by a line-monitor of cross-section \( 2a \) centred at the origin and oriented normal to the incident plane wave. Mie efficiency and transmission results are presented as a function of normalised frequency \( af/c \).

Fig. 7.22 presents results for three trees. Tree A, which is shown in outline in panels 1A-3A, is a perfectly self-uniform tree drawn from a honeycomb network. Tree B, shown in outline in panels 1B-3B, is a slightly deformed honeycomb 2-tree drawn from a \( \chi = 0.5 \) Delaunay-tessellated hyperuniform network. Tree C (outlines, panels 1C-3C) is a low symmetry 2-tree drawn from a \( \chi = 0.4 \) hyperuniform network. Trees A, B and C possess spatial similarity statistics (when overlapped with themselves) of 1, 0.96 and 0.91 respectively.

The Mie efficiencies for trees A, B and C are shown in red, green and blue in Fig. 7.22A respectively. The scattering efficiencies of all three trees display similar peaks. Let us focus specifically on the first two of these peaks which I refer to as the first and second scattering resonances respectively. We observe that as the tree symmetry decreases (red \( \rightarrow \) green \( \rightarrow \) blue), the scattering power of the first scattering resonance decreases while its peak frequency remains relatively constant. The scattering power of the second resonance is observed to increase slightly, while its peak frequency shifts significantly towards lower frequencies.

The transmitted power through the line monitor is shown in Fig. 7.22B. All three trees exhibit pronounced transmission gaps in the frequency region between the peak of their respective first
scattering resonance and the rising shoulder of their second scattering resonance. We observe that as the tree symmetry decreases (red → green → blue), the extent of the transmission gap decreases in both frequency width and absolute depth.

The panels to the right of Fig. 7.22 present representative snapshots of the interaction of the plane wave with the trees as visualised using the $H_z$ field component. The label of each panel describes the particular tree shown (A, B or C) and the frequency at which the snapshot was taken (corresponding to the annotated frequencies in Fig. 7.22A). The colour map represents the sign and magnitude of the $H_z$ component; blue reflects a negative $H_z$ component, red a positive component and white a magnetic field node.

Frequency 1 corresponds approximately to the peak of the first scattering resonance and lower transmission gap edge. The corresponding field profiles (panels 1A-1C) are qualitatively similar. In all cases, the magnetic fields are characteristically ‘cell-type’, as introduced in section 3.8. Frequency 3, on the other hand, corresponds approximately to the rising shoulder of the second scattering resonance and upper edge of the transmission gap. For all three trees (panels 3A-3C), we observe that the magnetic field is characteristically ‘stripe-type’, as introduced in section 3.8.

Frequency 2 lies at the approximate centre of the transmission gap for all three trees; corresponding characteristic $H_z$ profiles are shown in panels 2A-2C. Further, characteristic Poynting vector snapshots for frequency 2 are shown in Fig. 7.23. Each panel plots the component of the
Poynting vector - $S_y$ - that is parallel to the incident plane wave's wavevector; gold corresponds to forward propagation while green represents backward propagation (back-scattering). We observe that the intensity of the back-scattered radiation decreases with decreasing tree symmetry.

Overall, I conclude that LSU can be used as a proxy for a tree's scattering characteristics. The perfectly self-uniform tree - Tree A - exhibits pronounced first and second scattering resonances. By analogy with the scattering resonances of a dielectric cylinder (Section 3.7), the scattering resonances of a 2-tree may be associated with a phase change between incident and scattered radiation. Specifically, incident and scattered fields are out of phase at frequencies just above the first scattering resonance; this leads to the formation of a localised standing wavefront. As the tree LSU decreases, the positions of the first and second scattering resonances shift; this accordingly affects the position of the transmission gap. Further, the extent to which a scatterer suppresses transmission decreases with increasing LSU; lower symmetry scattering centres cannot form complete standing wavefronts.

From the perspective of generalised resonant scattering, LSU distributions are thus descriptive of the quality of a network's component scattering units. In particular, a potential champion PBG structure will possess maximal LSU distributions; this renders all scattering centres structurally identical and ensures that they possess degenerate electromagnetic resonances. As a result, the spectral ranges for which each scatterer inhibits transmission are maximally aligned and propagating radiation can be maximally suppressed. Networks described by LSU distributions that are not maximal comprise structurally non-identical scattering centres. Structural deformation of the scattering centres breaks the degeneracy of their scattering resonances; any existing PBG is thus narrowed by imperfect overlap of the spectral ranges for which each scattering centre suppresses transmission.

Further, LSU reflects the observed hierarchy of PBG size in rod-decorated crystalline networks (as discussed in Section 6.1). Briefly, networks comprising simple network vertices - that is vertices with a low coordination number - tend to possess the largest PBGs and PBG size is observed to decrease with increasing coordination number. The champion structures - the diamond and honeycomb networks - and the near-champion single network gyroid architecture all possess unit LSU distributions; two trees drawn from any one of these structures can be perfectly overlapped for all root-edge alignment permutations. This shared property of the champion
and near-champion PBG architectures suggests that perfect symmetry under permutation is an important property of an optimal PBG-forming scattering unit. In particular, I suggest that symmetry under permutation minimises the number of distinct scattering resonances that a scattering unit supports. As a result, the frequency gaps between scattering resonances are maximised; this simultaneously maximises the spectral width of the region above resonance for which transmission through the scatterer is suppressed. Networks built from scatterers which are perfectly self-uniform are thus expected to exhibit the largest known complete PBGs; this explains the origin of champion and near-champion PBGs in the strongly isotropic photonic crystals.

7.6 Conclusions

I concluded chapter 6 with the suggestion that a hypothetical amorphous gyroid network should possess significant local self-uniformity (LSU) and was likely to display a sizeable photonic band gap. In this chapter, I have designed, fabricated and characterised the first known examples of such amorphous gyroid networks. Specifically, I have confirmed the intuition, most notably demonstrating, both experimentally and theoretically, that carefully designed amorphous gyroids possess PBGs with widths comparable to photonic amorphous diamond - the only other known 3D disordered PBG structure.

Amorphous gyroid is a completely novel glassy continuous random network (CRN) that is the trivalent relative of the famous amorphous silicon CRN. It is defined by characteristically gyroidal geometrical properties, as evidenced by its edge length, inter-edge angle, dihedral angle and skew angle distributions.

Amorphous gyroids were designed using a modified implementation of the Wooten-Winer-Weaire (WWW) algorithm. The WWW algorithm is the core process that has been adapted to successfully engineer large amorphous silicon CRNs. I find that the WWW process is applicable to amorphous gyroid design with one major modification. Specifically, I find that annealing using the regular Keating energy can only generate CRNs with gyroidal structural order on the lengthscale of two edges; I call CRNs with this property ‘type-1’ amorphous gyroids. I solve this problem with the ‘triamond potential’, which enforces fixed edge lengths, inter-edge angles of 120°, dihedral angles of \(\cos^{-1}(\pm 1/3)\) and perfectly coplanar edge arrangements about a shared vertex (skew angles of 90°). CRNs annealed with the triamond potential possess geometrical characteristics which are more faithfully gyroidal; I call CRNs with this property ‘type-2’ amorphous gyroids.

I characterised type-1 and type-2 amorphous gyroids with total scattering structure functions (TSSFs) and local self-uniformity (LSU) distributions. Both type-1 and type-2 networks exhibit structure factors that are characteristic of amorphous materials. Compared to type-1 networks, type-2 networks display a sharper and more intense principal diffraction ring and are significantly closer to being hyperuniform. The diffraction peaks of both network types are broad and not Bragg-like. LSU distributions show that type-2 networks possess significantly greater strongly
isotropic character than type-1 networks; this is particularly evident in the comparison of the higher order LSU sets $\Phi_{22}$ and $\Phi_{32}$.

I fabricated centimetre scale amorphous gyroid samples using an advanced lithography-based ceramic manufacturing (LCM) method. The LCM method produced high quality, structurally complex components in high refractive index alumina ($\varepsilon_r = 9.5 \pm 0.3$ at 22 GHz). I note also that the LCM technique was not pushed to its limits. Attainable feature sizes remain an order of magnitude smaller than that realised in the prototypes; this makes LCM an attractive choice for realising complex photonic architectures for a broad spectrum of gigahertz applications.

Once printed, ceramic amorphous gyroid samples were characterised through microwave transmission experiments. Although results were adversely affected by noise, amorphous gyroid transmission spectra were significantly attenuated (up to $-35$ dB) in the expected region of their PBG. Further, by using a cylindrical sample, I demonstrated that the amorphous gyroid PBG is statistically isotropic with respect to propagation direction through the network; this result was corroborated by FDTD simulation.

I have demonstrated the striking correlation between LSU and PBG-forming ability in both two and three-dimensional trivalent networks; PBG size was observed to increase with increasing LSU in both amorphous gyroids and hyperuniform disordered honeycombs. I rationalise the physical connection between LSU and PBG formation by advancing a picture of photonic tight-binding in high index PBG-forming architectures. I argue that the electromagnetic properties of a network, like those of TM-gap cylinder arrays, are strongly influenced by the electromagnetic modes of its component scattering units. Using an FDTD method, I demonstrated that isolated honeycomb 2-trees suppress the propagation of radiation for frequencies between their first and second scattering resonances; they achieve this through a generalised resonant scattering process that is analogous to the Mie scattering mechanism of PBG formation. Further, the LSU of a tree is a proxy for the extent to which its electromagnetic resonances are optimised for PBG formation; a reduction in tree LSU is associated with perturbation of its scattering cross section and a reduced ability to suppress transmission.

LSU distributions thus measure the quality of a network’s scattering units from a perspective of PBG formation. Networks with maximal LSU distributions possess structurally identical scattering units; all units thus support degenerate electromagnetic resonances and any PBG is maximised by perfect spectral overlap of the frequencies for which each scatterer suppresses transmission. With decreasing LSU, the degeneracy of the scattering units’ resonances is broken and any PBG is narrowed. Naturally, champion PBG networks comprise scattering units whose scattering resonances are optimally distributed for PBG formation. I argue that perfect symmetry under permutation minimises the number of scattering resonances that a tree can support; this maximises the gaps between resonances and, accordingly, the spectral width of the PBG. The strongly isotropic networks are thus all champion or near-champion PBG architectures.
Chapter 8

Naturally-Occurring Amorphous Gyroid

The exploitation of complex photonic band gap-enabled technologies requires a versatile and industrially scalable manufacturing process. This process should be able to fabricate the most desirable PBG architectures, specifically the champion structures and ideally disordered architectures, at lengthscales applicable to near-infrared and optical signal processing. Naturally, the technological and societal implications of such a manufacturing process are such that research into advanced fabrication techniques is a hot topic in photonics and optics.

The most suitable matrices for photonic engineering are the three-dimensional complete PBG structures. Traditional nanofabrication techniques, like those used for semiconductor-based electronics, are therefore not directly applicable. Further, conventional ‘engineering-type’ approaches, in which every feature of a nanophotonic structure is explicitly fabricated, are useful in the laboratory\(^{81,82}\) but otherwise expensive and not industrially-scalable. Fabrication through holographic lithography\(^{203}\) suffers from similar scalability issues and, although effective at patterning periodic structures, it is not applicable to the manufacture of technologically desirable aperiodic PBG materials.

Manufacture through self-assembly is thus an attractive long term goal. In a self-assembly process, a system of interacting components spontaneously separates, under appropriate conditions, to form desirable architectures. Once perfected, self-assembly processes are expected to be cheap and inherently scalable\(^{204}\).

Two major self-assembly routes have so far been explored. First, colloidal self-assembly, in which polymer spheres are deposited from a suspension, has been extensively studied\(^{205,206}\). Successes of the technique include the fabrication of inverse opal photonic crystals\(^{29}\) and glassy sphere packings\(^{205}\). However, precipitated spheres tend to form dense packings\(^{206}\); this renders the fabrication of low fill fraction structure, such as diamond and gyroid, a difficult prospect. More fundamentally, the assembly of hard spherical particles cannot form the rod-decorated connected networks of the true champion PBG structures.
Self-assembly by block copolymer (BCP) phase separation, on the other hand, is more naturally suited to forming the champion structures. BCPs consist of two or more chemically distinct polymer chains connected through a covalent bond. An unfavourable energetic interaction between the two blocks can lead to phase separation and, under appropriate conditions, the formation of ordered network structures at optical and UV lengthscales. BCP self-assembly has successfully generated gyroidal architectures, but the diamond phase appears to be absent from the BCP phase diagram.

It is remarkable, therefore, to note that living creatures have been self-assembling the champion PBG structures at optical length scales for 500 million years. A huge variety of these natural photonic architectures are known to exist in avian feather barbs, butterfly wing scales, fruit and other natural systems. The function of these structures is typically, but not exclusively, to scatter light for camouflage and signalling and their study is thus known as ‘structural colour’.

By studying the ways in which structural colouration architectures develop, we stand to learn much about the self-assembly of complex systems. Beyond this, millions of years of evolution by natural selection can produce highly optimised photonic architectures which can inspire novel means of controlling light.

In this chapter, I seek to demonstrate that naturally occurring amorphous gyroid-like architectures exist at optical lengthscales. The observation of a natural amorphous gyroid will, in the long term, facilitate its fabrication by a bio-inspired self-assembly technique. This should enable the integration of amorphous gyroid-based components into next-generation photonic devices.

The chapter is structured as follows. I begin by introducing the interdisciplinary approach of structural colour research with a case study of the butterfly Papilio nireus. Following this, I briefly review both the existence of natural champion photonic crystal architectures and the use of disorder to generate structural colouration. Having laid this important groundwork, I discuss in detail the gyroidal photonic crystal in the wing scales of green hairstreak butterflies. Specifically, I demonstrate that topological and structural defects can form within gyroidal architectures. Following this, I introduce and characterise the disordered network that lends the scales of the butterfly Pseudolycaena marsyas their striking turquoise-blue colouration. I demonstrate the similarity of this network to amorphous gyroids, and show that amorphous gyroid models are compatible with the butterfly’s reflectance spectrum. I end the chapter by highlighting several other amorphous gyroid-like architectures which are worthy of further investigation.
8.1 Elements of Structural Colour

8.1.1 Case Study: *Papilio nireus*

There is no one single way to achieve a structural colour. For instance, butterflies of the genus Morpho are rendered a vivid iridescent blue by the Christmas tree-like multilayer reflectors on their wing scales\textsuperscript{215}. This is, however, only the most famous example of a variety of structures which are known to produce structural blue. These structures include the helicoidal cellulose stacks of Pollia berries\textsuperscript{9} and, in butterfly wing scales, reflecting laminae\textsuperscript{216,217}, perforated multilayer stacks\textsuperscript{218,219} and three-dimensional photonic crystals\textsuperscript{220,221}. On top of this, colouration can be the result of a complex interplay between structure and material properties\textsuperscript{222}. Specifically, broadband structural reflectances are often refined and optimised by absorbing pigments to achieve a more precise function\textsuperscript{217,223–225}.

As a result, studies of structural colouration employ a diverse set of methods which may include optical and electron microscopy\textsuperscript{19,226,227} transmission and reflectance characterisation\textsuperscript{215–217}, imaging scatterometry\textsuperscript{17,216,218}, X-ray scattering\textsuperscript{213,228} and structural modelling and simulation\textsuperscript{221,229,230}. These diverse approaches and their applications are best illustrated by way of an example. In the following, I thus explore as a case study the colouration mechanism in the butterfly *Papilio nireus*.

*Papilio nireus*, shown in Fig. 8.1A, is a large African swallowtail butterfly of the family Papilionidae. Its wings exhibit narrow bands of blue-green colouration and are otherwise black. As a butterfly, its wings are covered in microscopic scales. Scales are cell-like structures, made predominantly from the biopolymer chitin, whose sizes are of the order of 100 µm. Like many butterflies, the wings of *P. nireus* are covered in both coloured cover scales and dark ground scales; Fig. 8.1D shows a single coloured cover scale. Trzeciak et al. studied in detail the mechanism through which the *P. nireus* scales generate colour\textsuperscript{217}; here I present their findings.

Single *P. nireus* scales were sliced with a razor blade and imaged in cross-section using a scanning electron microscope (SEM). The micrograph in Fig. 8.1B presents a scale cross-section which reveals its major anatomical features. The upper surface of the scale comprises a thick upper lamina, marked by a red arrow in the figure, which is perforated by a dense disordered honeycomb-like array of air pillars. This upper lamina is supported by widely spaced ribs which run the length of the scale. The lower surface of the scale, marked by white arrows, consists of a thin, flat lamina. These two laminae enclose a hollow air cavity; they are connected together by pillars (trabeculae), presumably for structural strength.

Scales were also imaged as thin sections using a transmission electron microscope (TEM). The TEM section, shown in Fig. 8.1C, reveals several interesting features. First, the lower lamina, highlighted by the black arrow, appears to comprise three distinct thin layers. Second, the outer two layers of the lower lamina show a much higher contrast compared to the inner layer. Third, the thick upper lamina and ribs of the upper scale surface also show distinct contrasts, appearing dark and light respectively. Overall, these dark features in the TEM suggest the presence of a pigment in the both the upper lamina and outer two layers of the lower lamina.
Figure 8.1: The colouration mechanism in the blue scales of *Papilio nireus*. Specimen of *P. nireus* (A). SEM image of a razor blade scale cross section (B) exposes a hollow core between a honeycomb-like diffuser (top, red arrow) and a thin lamina (bottom, white arrows). TEM scale cross section showing dark staining associated with pigmentation (C). Bottom surface of a single scale (D) characterised by imaging scatterometry (E). Light is incident at 0°, 15°, 30°, and 45° and reflections, labelled 0 – 3 respectively, are sharp, specular, and blue shift with increasing scattering angle. The reflectance of a single scale (F, blue line, left axis) and the extinction coefficient of the pigment (F, red line, right axis), calculated from absorbance data. Scale bars: 2µm (B), 1µm (C) & 50µm (D). All figures and data reproduced from Trzeciak et al.²¹⁷.

Single scales were also investigated via imaging scatterometry.¹⁷,²¹⁷,²¹⁸ The technique employs an ellipsoidal mirror which collects light in a full hemisphere around its first focal point. Samples are placed at the first focal point and illuminated through a small aperture in the mirror. The directional scattering of the sample is recorded by the mirror and focussed at its second focal point. Masking of the straight through beam then allows the scattering pattern of the sample to be visualised.

A small region of the underside of a single *P. nireus* scale was illuminated using the imaging scatterometer; the scale and illumination region are shown in 8.1D. Scattering patterns were recorded for illumination at incident angles of 0°, 15°, 30°, and 45°. The four separate scattering patterns were combined into a single result which is displayed in Fig. 8.1E. The circular plot is a projection of the hemispherical scattering pattern into a plane; the red rings mark polar angles of 30°, 60° and 90° from the centre outwards. Each pattern scattering showed a clear maximum around twice the angle of incidence; these maxima are annotated with the numbers 0 – 3. It was also noted that, as the scattering angle increases, the wavelength of peak reflectance blue shifts. These two phenomena are characteristic of scattering from a multilayer stack.⁸ An equivalent experiment, performed by illuminating the top surface of the scale, yielded scattering patterns which, although more diffuse, exhibited similar multilayer character. These experiments suggest
that the principal colour-generating structure in \textit{P. nireus} scales is the thin lower lamina, and that the thick upper lamina acts as a diffuser.

Trzeciak et al. went on to optically characterise single scales using an integrating sphere method\textsuperscript{217}. Specifically, the absorbance of a single scale was measured in order to quantify the effect of the pigmentation (Fig. 8.1C). To achieve this, the scale was immersed in a refractive index-matching fluid ($n = 1.56$) in order to eliminate light scattering. The transmittance was then measured and, in the absence of reflectance, the absorbance trivially determined. Using this absorbance data, the complex refractive index of the pigmented chitin was estimated to be $n + i\kappa = 1.56 - 0.11i$ at 390nm. Here, I use the same absorbance data to calculate the extinction coefficient $\kappa$ across the range [360, 700]nm; the result of this calculation is the red line shown in Fig. 8.1F.

Comparison of the extinction coefficient with reflectance of a single \textit{P. nireus} scale (Fig. 8.1F, blue line) shows the significance of the pigmentation. The peak of the pigment absorption coincides with a minimum of the scale’s reflectance; the pigment thus dampens reflections from the lower lamina for near-UV wavelengths. Simple multilayer models which account for both the pigment absorbance and natural variation in the thickness of the upper and lower laminae are in good agreement with the observed reflectance of a single scale\textsuperscript{217}.

The colouration mechanism in \textit{Papilio nireus} scales is an extremely instructive example of the factors that must be considered in structural colour studies. In particular, it demonstrates the importance of considering the interplay between structure and material properties. Beyond \textit{P. nireus}, there is a growing number of organisms whose overall colouration, although fundamentally structural, is a result of modulation by a pigment\textsuperscript{216,221,230–232}.

### 8.1.2 Strongly Isotropic Architectures

All the strongly isotropic architectures have been observed at optical lengthscales in the microstructures of living creatures. Naturally occurring examples of these architectures are made from biopolymers whose refractive indices are around 1.55 at optical wavelengths\textsuperscript{233}; they thus do not possess complete photonic band gaps. Nonetheless, these architectures retain significant photonic stop gaps whose central frequencies vary with propagation direction\textsuperscript{221,229}. These stop gaps selectively reflect light and generate orientation-dependent iridescent colour. Although examples of honeycomb are known\textsuperscript{234,235}, here I present a brief review focussing on examples of the three-dimensional gyroid and diamond networks.

Several butterfly species are now known to exhibit structural colour derived from gyroidal photonic crystals within their wing scales. The most famous examples of these butterflies are \textit{Parides sesostris} (the emerald-patched cattleheart) and numerous species of the genus Callophrys, collectively known as the green hairstreaks. The remarkable structures in their wing scales have been known for some time\textsuperscript{236}, but it is only recently that their gyroidal nature has been categorically demonstrated\textsuperscript{19}. Specifically, small angle X-ray scattering (SAXS) has definitively assigned the gyroid space group ($I\bar{4}d2$) to the microstructures in the coloured scales of \textit{Parides sesostris}, \textit{Callophrys gryneus}, \textit{Callophrys dumetorum}, \textit{Cyanophrys herodotus} and \textit{Teinopalpus imperialis}\textsuperscript{14}. 

Figure 8.2: Natural single gyroid and diamond network photonic crystals. Green scales of the butterfly *Parides sesostris* (A) are coloured by a gyroidal microstructure. A single scale (B) contains distinct crystalline grains which may be observed when viewed without (top panel) and through (bottom panel) crossed linear polarisers. SEM cross-sections (C) reveal the gyroid photonic crystals (white letters ‘PC’) lying beneath a thick diffusing layer (white letter ‘h’). A diamond photonic crystal in the scales of the weevil *Lamprocyphus augustus* (D), viewed along several crystal high symmetry directions. Scale bars 20\(\mu\)m (B) & 2\(\mu\)m (C). Panel C reproduced from Wilts et al.\textsuperscript{225}, panel D from Galusha et al.\textsuperscript{16}.

Perhaps the most striking illustration of these naturally-occurring gyroids is the overlap between a single network gyroid crystal structure and a full three-dimensional reconstruction of the *C. rubi* photonic crystal by electron tomography\textsuperscript{20}. Here I exemplify these structures with the natural gyroid photonic crystals in the wing scales of *P. Sesostris*.

*Parides sesostris*, of which a specimen is shown in Fig. 8.2A, is a large neotropical butterfly of the family Papilionidae. Its characteristic wing markings comprise a pair of emerald patches on an otherwise black background. These patches contain numerous scales which, when viewed from above, appear a vivid but diffuse green. These scales are known to contain large domains of a highly ordered gyroidal microstructure from which they derive their colouration.

The two images in Fig. 8.2B present views of an upside-down single *P. sesostris* scale illuminated with white light. They contrast the appearance of the scale under regular viewing conditions (top) and when viewed through crossed linear polarisers (bottom). When viewed through crossed polarisers, only light whose polarisation state is altered by interaction with the scale is observed. In the lower panel, we observe that the scale is separated by colour into several distinct domains. These domains are associated with discrete grains of the gyroidal microstructure that is contained within the scale. Adjacent grains can be differently oriented; their interaction with polarised light is sensitive to the grain’s orientation such that grains can be separated under crossed polarisers\textsuperscript{225,227}. 
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*P. sesostris* scales are known to comprise two layers. The SEM of Fig. 8.2C shows a cross-section of a green scale that has been fractured to expose its internal structure. The surface layer, labelled by the white letter ‘H’, consists of a thick honeycomb-like diffuser. This layer is similar in form and function to the upper lamina of *P. nireus* scales. The *P. sesostris* diffuser has been shown to contain UV-absorbing pigmentation which filters the reflectance of the gyroidal microstructure\(^{225}\). Without the top diffusing layer, *P. sesostris* scales appear electric blue\(^{221}\). The lower layer of the scale, labelled by the letters ‘PC’ in Fig. 8.2C, is the gyroidal photonic crystal. Of the known lepidopteran gyroids, the *P. sesostris* structure appears to be the most ordered; the sizes of the crystallites were estimated by SAXS to be approximately 4.5\(\mu\)m.

Naturally occurring diamond networks are less well-studied. Examples are, however, known to exist in the coloured scales of several species of weevil\(^{16,18,237}\). A diamond-structured photonic crystal was first observed in the scales of *Lamprocyphus augustus*\(^{16}\); several views of this architecture, looking down various high symmetry directions, are presented in Fig. 8.2D. A similar photonic crystal has been observed in scales of *Entimus imperialis*\(^{18}\). Like the gyroid photonic crystal in *P. sesostris* wing scales, several diamond-structured grains exist together within a single *E. imperialis* scale. Interestingly, these grains are quite large, appearing around 40\(\mu\)m across. A single grain was characterised via imaging scatterometry and the first Brillouin zone of the FCC lattice was clearly resolved\(^{17}\).

### 8.1.3 Structural Colour Through Disorder

Structural colour need not arise from a highly ordered microstructure. Several examples of aperiodic colour generating microstructures are now known. Here I briefly review a number of architectures of interest.

SAXS studies have revealed an abundance of disordered ‘channel-type ’ architectures in the feather barbs of a great variety of bird species\(^{213,232,238}\). Many of these architectures appear to be three-dimensionally connected networks and their SAXS spectra reveal the presence of characteristically amorphous short range structural order\(^{213,238}\). Their colour is thus thought to predominantly results from coherent scattering of light by Bragg processes. It has even been suggested that the structure in feather barbs of the scarlet macaw is that of photonic amorphous diamond\(^{239}\).

Within butterflies, numerous small blue lycaenids of the sub-family Polyommatinae possess wing scales filled with an apparently disordered connected network of chitin\(^{218–220}\). A comparison between distinct blue and discoloured specimens of the species *Polyommatus daphnis* shows that the blue colouration is directly associated with the disordered connected network\(^{240}\). My own observations of *Polyommatus daphnis* confirm this; I note that brown regions within scales are associated with incomplete formation of the disordered network. Close study of scale cross-sections by TEM, however, reveals that the connected network is formed into parallel planes which are interconnected only to a limited degree\(^{219,220}\). Further, imaging scatterometry of single scales shows that the blue colouration is multilayer in origin\(^{218}\). The microstructures in Polyommatinae butterfly scales have thus been dubbed perforated multilayers.
Turning to Coleoptera, the mechanism through which Cyphochilus spp. and Lepidiota spp. beetles derive their brilliant white colouration has generated some considerable excitement\textsuperscript{11–13,241–243}. Cyphochilus scales, in particular, exhibit the lowest transport mean free path so far observed in a low refractive index system\textsuperscript{12}. The scales scatter light very efficiently for all wavelengths of the visible spectrum, thus appearing a bright white.

Fig. 8.3A shows a specimen of Cyphochilus candidus; the numerous white scales which covers the beetle’s shell can be resolved. A scale cross-section, Fig. 8.3B, reveals the structural origin of the colour. Each white scale contains a densely packed (estimated 50 – 60% chitin fill fraction\textsuperscript{13}) and highly disordered network of chitin. Scales of Lepidiota stigma, of which a specimen is shown in Fig. 8.3C, are similarly white and derive their colour from an equivalent disordered network structure (Fig. 8.3D).

The Cyphochilus disordered network exemplifies the development of highly optimised photonic architectures through natural selection. The thickness of Cyphochilus scales, which is usually between 5 – 9µm\textsuperscript{13}, is much less than the typical optical path lengths required to generate white colouration through multiple scattering\textsuperscript{12}. Strong scattering is achieved, at least in part, by an engineered anisotropy of the disordered network. Specifically, the network is compressed along the out-of-plane direction; this maximises the density of scattering centres along the axis of observation and increases the scale’s scattering power\textsuperscript{13}. It has been suggested that the dual requirements of white camouflage and weight minimisation have driven the evolution of the Cyphochilus colouration mechanism.
8.1.4 Taking Stock

I have presented a review of the study of structural colour and the architectures which have captured the interest of the optics community. In Section 8.1.1, I introduced methods and approaches to structural colour research with a case study of colouration in *P. nireus*\textsuperscript{217}. The *P. nireus* investigation sets a solid benchmark for structural colour studies, characterising in detail the two key factors - physical structure and material properties - that influence optical function. In Section 8.1.2, I highlighted the existence of three-dimensional champion and near-champion photonic band gap architectures in the scales of butterflies and beetles. Following this, I drew attention to a number of architectures whose function is enabled by aperiodic structuring. In particular, I presented the strongly scattering microstructure in *Cyphochilus* spp. beetles as an example of the power of evolutionary optimisation.

A great variety of colour generating microstructures are known to exist in the natural world. The study of these architectures has a broad scope; it influences our understanding of evolution, taxonomy and the physics of light scattering. Most importantly, the existence of naturally occurring, technologically relevant structures demonstrates that their self-assembly at optical lengthscales is a real possibility.

Going further, it is clear that structurally disordered architectures are, from a developmental point of view, equally viable means of generating structural colour. It is possible, therefore, that amorphous gyroid structures have developed in the context of structural colouration. If true, natural amorphous gyroids will provide valuable bio-inspiration in the development of advanced self-assembly methods for disordered photonic structures at optical lengthscales. With this goal in mind, I now explore evidence for the existence of naturally occurring amorphous gyroids.

8.2 Topological Disorder in Green Hairstreak Scales

Butterflies of the genus *Callophrys*, collectively known as the green hairstreaks, are widely understood to derive their green colouration from a gyroidal photonic crystal in their wing scales. This gyroidal structuring appears to occur consistently across similar but distinct species\textsuperscript{19}. Specifically, gyroid was first identified by microscopy in *Callophrys rubi* scales and this species has since been studied extensively\textsuperscript{19,20,226,230}. Scales of two different green hairstreaks, *Callophrys dumetorum* and *Callophrys gryneus*, have been characterised by microscopy and SAXS\textsuperscript{14}. The microstructures contained therein appear similarly gyroidal, and diffraction spectra conclusively demonstrate their gyroidal symmetry. Despite the volume of literature published concerning *C. rubi*, no SAXS data has so far been made available for this species.

In this section, I study the structure of the green hairstreak gyroidal photonic crystal from a novel perspective. Specifically, I look for topological and structural disorder within the chitin network with a view towards demonstrating that topologically imperfect gyroids can self assemble. I explore the microstructure of *C. rubi* and demonstrate that existing data points to the existence of topological and structural defects in the thin grain boundaries between the network’s
crystalline domains. Following this, I build models of the green hairstreak microstructure by incorporating a limited amount of topological and positional disorder into single network gyroid crystals. I then explore the compatibility of these models with existing X-ray scattering data for *C. gryneus*.

### 8.2.1 Microstructure

*Callophrys rubi*, shown in Fig. 8.4A, is a small Eurasian butterfly whose wings are, on their ventral side, coloured a bright grass green. Fig. 8.4B presents a light micrograph of a single wing scale’s coloured tip. Even when viewed without crossed polarisers, the granular nature of the gyroidal microstructure is clear. The scale appears divided into different coloured domains; each domain reflects the presence of a gyroidal grain with a unique orientation.

Fig. 8.4C shows an SEM micrograph of a central region of a *C. rubi* scale. The scale surface comprises a mesh of bulky longitudinal ribs and smaller cross-ribs which support the underlying photonic crystal. The gyroid itself is visible through the large open holes between the ribs. Region a, orange letter ‘a’ in Fig. 8.4C, exhibits a clear view down the gyroid [111] axis; this appears as a hexagonally packed array of air holes. Note that these air holes are not enclosed by planar 6-membered rings but by 9-segment helices that run parallel to the [111] axis. These helices propagate down into the scale and do not form closed loops. In spite of this, the limited depth resolution of micrographs can make these helices appear as planar hexagonal rings.

Region a (Fig. 8.4C) thus forms part of a highly ordered gyroid grain. The overall *C. rubi* microstructure is formed from numerous gyroid grains. The boundaries between these grains can be clearly resolved using TEM micrographs\(^\text{20}\). Here, I annotate two regions, orange letters ‘b’ and ‘c’ in Fig. 8.4C, which appear to interrupt the local periodicity of the microstructure. I tentatively suggest that these regions correspond to grain boundaries. It has also been noted...
that, although not evident in Fig. 8.4C, the gyroidal microstructure can exhibit variable chitin fill fractions within the same scale\textsuperscript{\ref{schroder-turk2011}}.

Using a process called electron tomography, the *Callophrys rubi* microstructure has been three-dimensionally reconstructed by Schroder-Turk et al.\textsuperscript{\ref{schroder-turk2011}}. To accomplish this, a thin slice of the microstructure was imaged at a range of viewing angles in a TEM. These images were then computationally combined into a voxelised three-dimensional map of the chitin distribution. The medial axis of the distribution, corresponding to its skeletal net, and a best fit parallel gyroid surface were determined algorithmically\textsuperscript{\ref{schroder-turk2011}}.

Fig. 8.5 presents the voxelised medial axis of the *Callophrys rubi* chitin distribution (blue voxels) together with the single network gyroid structure (yellow) of the corresponding best fit parallel gyroid; panels A & B present identical data, viewed from just off a [111] axis and just off a [100] axis respectively. Overall, we observe that the voxelised medial axis and parallel gyroid net are very well aligned. The tomographic reconstruction is a striking demonstration of the gyroidal character of the *Callophrys rubi* microstructure.

I note, however, that the tomographic data presented was specifically selected to show the agreement between the *Callophrys rubi* and gyroid nets. Grain boundary regions of the microstructure were avoided\textsuperscript{\ref{schroder-turk2011}}. Regarding grain boundaries in the *Callophrys rubi* microstructure, Schroder-Turk et al.\textsuperscript{\ref{schroder-turk2011}} remark that “it is clear that these crystalline domains are rather small, extending only over a few unit cells in any direction. Often, the angles between neighbouring domains are small, and distinct structures within the grain boundaries are not seen; the chitin network appears to traverse distinct ‘grains’ uninterrupted.”

I have highlighted one region of the tomographic data, red arrows Fig. 8.5A & B, in which the *Callophrys rubi* chitin net appears to deviate significantly from the parallel gyroid net. This deviation is pronounced, with several edges in the highlighted region deviating systematically from a
perfect gyroidal configuration. Although not explicitly stated by Schroder-Turk et al., I associate this deformed region with a thin boundary between adjacent gyroid grains. It thus appears that, in order to maintain a continuous chitin network that traverses grain boundaries without interruption, the C. rubi network deforms both structurally and topologically in the region of the grain interface.

8.2.2 Green Hairstreak Diffraction Modelling

Tomographic reconstruction of the gyroidal network in C. rubi suggests that topological and structural defects exist at the boundaries between gyroid grains. Here, I appeal to existing SAXS data for green hairstreak butterflies to substantiate this suggestion. Specifically, I propose two candidate models for the gyroidal microstructure and investigate whether these models can fit the SAXS data. Given the absence of published data for C. rubi, I employ SAXS data for Callophrys gryneus gathered by Saranathan et al.14. The gyroidal microstructures in the two species are similar and I assume that remarks concerning the C. rubi structure are equally applicable to that of C. gryneus.

The C. gryneus SAXS data was acquired using a focussed X-ray beam with a 15µm cross section. From Fig. 8.4B, we observe that a beam of this size will illuminate more than a single gyroidal grain. The resulting SAXS spectrum is thus a result of diffraction by multiple distinct grains. I model this process as a powder diffraction experiment. Specifically, I assume that the positional correlations between adjacent grains are destroyed by misalignment at the grain boundaries. Light diffracted by distinct grains will thus not interfere, and the total diffraction pattern can be considered an incoherent superposition of the diffraction patterns from each of the illuminated gyroid grains.

For my first model, I propose a simple translationally periodic structure derived from the level-set approximation to the gyroid surface. The function

\[ f(x, y, z) = \sin(x) \cos(y) + \sin(y) \cos(z) + \sin(z) \cos(x) = t, \]

for \( t \), a scalar parameter, defines a surface in three-dimensional space. In the case where \( t = 0 \), the surface is a first order approximation to the gyroid minimal surface. When \( t \neq 0 \), the surface divides space into two interpenetrating labyrinths, both of single network gyroid symmetry but having unequal fill fractions14. To generate a voxelised single network gyroid aperture function \( \rho(x, y, z) \), the level-set surface \( f(x, y, z) = t \) is interrogated with a set of positions. Where we find \( f > t \), we set \( \rho(x, y, z) = 1 \), otherwise we set \( \rho(x, y, z) = 0 \). By varying the parameter \( t \), I generated a set of 10 distinct cubic level-set models, each comprising 1000 single network gyroid vertices, for chitin fill fractions between 16% and 42%. I refer to these 10 models as the level-set basis set.

For my second model, I attempt to reproduce the tomographic data of Fig. 8.5 by generating partially disordered gyroids (PDGs). To achieve this, I begin with a 1000-vertex single network gyroid edge and vertex pattern and introduce small amounts of both topological and positional
disorder. Specifically, I employ my implementation of the Wooten-Winer-Weaire algorithm (Section 7.1) to introduce 10 Stone-Wales topological defects. These defects were distributed randomly throughout the samples.

Positional disorder was incorporated by applying 50 randomly generated offsets to the network’s vertex positions. The magnitude of these offsets was normally distributed with mean zero and standard deviation $\sigma$ expressed as a percentage of the single network gyroid edge length. To render these perturbations physical, they were propagated through the network with their magnitude decaying with depth. Specifically, consider two vertices $a$ and $b$ separated by a shortest path of length $d$ network edges. If I perturb the position of vertex $a$ by a vector of magnitude $v$, then I perturb also the position of vertex $b$ by the same vector but with reduced magnitude $v/\beta^d$. The value of the parameter $\beta$ was chosen, subject to $0 < \beta < 1$, to control the rate at which the perturbation decays with increasing vertex separation. By applying perturbations in this manner, vertex positions retain significant local correlations while long distance correlations are suppressed.

Overall, I generated 4 distinct PDG designs, each characterised by a unique pair of $\sigma$ and $\beta$ values. Then, for each design, I generated 10 voxelised aperture functions for chitin filling fractions between 16% and 42%. I refer to these 40 aperture functions as the PDG basis set. One of these 40 PDG aperture functions is shown in Fig. 8.6, panels A & B. Panel A shows a view of the PDG model looking down a [100] axis of the seed single network gyroid. Similarly, panel B shows a view down the SNG [111] axis. It is clear that PDG, although it includes a small amount of topological and positional disorder, still appears very much gyroidal. Comparison of Fig. 8.4C, region ‘A’ and Fig. 8.6B show that PDG is, at least superficially, a plausible model of the green hairstreak chitin network.

Following this, I calculated the total scattering structure function (Eqn. 2.5) for each aperture in the level-set and PDG basis sets. TSSFs were then azimuthally averaged (Eqn. 2.7) to produce one-dimensional SAXS profiles comparable to $C. gryneus$ data\textsuperscript{14}. Then, I generate best fit models to the SAXS data by forming a weighted summation of the TSSFs within each basis set. These weights were found by optimising the fit to minimise $R_{wp}$, the Reitveld weighted-profile $R$ value\textsuperscript{244}; note that the fitting was unweighted and all data points contributed equally to the goodness of fit.

Fig. 8.6C presents the observed SAXS spectrum of $C. gryneus$ (green line) together with the calculated best fits using the level-set basis set (orange line) and the PDG basis set (blue line). The upper $x$ axis records the quadrature sum of the miller indices $(hkl)$ associated with the expected Bragg reflections of the single network gyroid ($I4_132$) space group\textsuperscript{14,245}. $R_{wp}$ values for the level-set and PDG fits are 980 and 645 respectively, suggesting that PDG is a superior model of the $C. gryneus$ scale structure. Indeed, Fig. 8.6C shows that the PDG model is a good overall fit to the SAXS data. The pure level-set model produces overly prominent peaks, particularly between the (110) and (211), and (400) and (420) Bragg reflections. The inclusion of topological and positional disorder dampens the network correlations and reduces this contrast across the whole PDG diffraction spectrum. The quality of the disordered PDG fit
is most evident for high \((hkl)\) values, where the overall profile of the pattern is well-captured, particularly the signature double peak from the (321) and (400) planes.

I note that, although the PDG basis set contains a significantly larger number of basis TSSFs than the level-set basis set, the PDG fit is dominated by a single PDG aperture function. This aperture function, which is shown in Fig. 8.6A & B, contributes 80% to the total weight of the PDG fit. It is characterised by perturbation magnitudes with a standard deviation of \(\sigma = 20\%\), a perturbation decay rate of \(\beta = 0.8\) and a chitin fill fraction of 30%.

In summary, I have highlighted the existence of topological and geometrical disorder in the gyroidal photonic crystals of green hairstreak butterflies. Micrographs (Fig. 8.4C) and tomographic reconstruction (Fig. 8.5) of the \(C.\ rubi\) photonic crystal suggest that its chitin network propagates continuously, without interruption, through the grain boundaries of adjacent gyroidal crystallites. For this to occur, the chitin network must incorporate a limited amount of topological and geometrical disorder to accommodate the structural mismatch at grain boundaries.

Partially disordered gyroids, derived from perfect single network gyroids by introducing small amounts of topological and positional disorder, were generated as candidate models for the \(C.\ gryneus\) microstructure. I have shown that PDGs are a better fit to \(C.\ gryneus\) SAXS data than idealised level-set models. Further, the agreement between PDG and observed diffraction spectra is consistent with the existence of topological and vertex positional disorder in the grain boundary regions of the \(C.\ gryneus\) photonic crystal.
8.3 Structural Blue in *Psuedolycaena marsyas*

Given the likely existence of topological disorder in the green hairstreak photonic crystal, it is plausible to suggest that complete amorphous gyroids may have developed in taxonomically related species. The Theclinae group of butterflies, a sub-family of the Lycaenidae, contains numerous butterflies, including the green hairstreaks, whose scales contain apparently gyroidal and perforated multilayer-type architectures. Exploration of colour-generating architectures in the Theclinae may therefore yield the discovery of amorphous gyroid-like structures.

In this section, I present the colour-generating microstructure in the wing scales of *Pseudolycaena marsyas* (the Cambridge blue, Theclinae). I observe that this structure comprises a disordered and apparently trivalent chitin network which, unlike the perforated multilayers of the Polyommatinae, is interconnected in three dimensions. I explore similarities between this structure and amorphous gyroid networks. In particular, I construct models of the network derived from amorphous gyroid designs and show that these models are compatible with the reflectance spectrum of a *Pseudolycaena marsyas* wing.

### 8.3.1 Microstructure

*Pseudolycaena marsyas* (Theclinae, Lycaenidae), common name the Cambridge blue, is a neotropical hairstreak. Fig. 8.7A shows a male specimen, collected in Los Tuxtlas, Mexico. Its wings appear turquoise-blue when observed along the axis of illumination, but display vivid electric blue when observed off axis. The species is sexually dimorphic; the wings of the female (not shown) display uniform blue colouration without a perceptible green hue.

Fig. 8.7B shows a single *P. marsyas* scale, actually a composite of two images, observed under an optical microscope. The scale appears uniformly and diffusely coloured. Observation through crossed linear polarisers does not reveal any inhomogeneities in the internal scale structure.

Single scales were isolated, sputter coated with a 4nm gold layer, and imaged in an SEM. Fig. 8.7C presents a micrograph of the scale microstructure; similar to the green hairstreaks, it comprises a lattice of sturdy longitudinal ribs and smaller cross-ribs which together support a connected network of chitin. This network is clearly visible through the holes in the ribbing. The chitinous network does not appear crystalline; no gyroidal high symmetry directions can be observed and it appears to be everywhere disordered like the perforated multilayers of the Polyommatinae. The disordered network is clearly associated with the scale’s blue appearance; brown regions at the scale root (Fig. 8.7B) correlate with regions where the chitin network is underdeveloped.

Using a focussed ion beam (FIB), I milled through the scale to expose an internal cross section; Fig. 8.7D presents an image of this cross-section imaged with 52° of tilt. We observe that the scale is quite thin; accounting for the tilt, I estimate its thickness to be (1300 ± 200)nm. In cross section, the chitin network appears interconnected in all three dimensions. It is difficult to categorically determine the degree of the network’s connectivity. Its similarity, however, to known trivalent butterfly microstructures strongly suggests that its connectivity is three-fold.
Pseudolycaena marsyas has been investigated previously by Vértesy et al.\textsuperscript{220} Although no thorough exploration of the internal scale microstructure was undertaken, both a TEM cross section and a reflectance spectrum were published. The TEM cross section, as shown in Fig. 8.7E, reveals that the \textit{P. marsyas} scale structure is distinct from the perforated multilayers of the Polyommatinae. It does, however, demonstrate some anisotropy; in some regions, the chitin network appears to align in the plane of the scale, while in others the network appears three-dimensionally disordered. Importantly, we observe that the lower half of the scale appears much darker than the top half. Discussions with Z. Vértesy confirm that this dark banding, having been observed in several different cross sections, is representative of \textit{P. marsyas} scales. Similar to the case of \textit{Papilio nireus}\textsuperscript{217}, this dark banding may be associated with pigmentation.

I compare the \textit{P. marsyas} structure to depth-shaded type-2 amorphous gyroid 3D models in Fig. 8.8. Panel A shows detail from Fig. 8.7D compared, in panel B, to a similarly tilted planar surface of an amorphous gyroid block. Panel C shows detail from Fig. 8.7D, which I compare, in panel D, to a planar amorphous gyroid surface viewed from above. In both cases, the amorphous gyroid models have network fill fractions of 25%. We observe that amorphous gyroid is a qualitatively good match to the \textit{P. marsyas} network. In particular, gyroidal nine-segment helices are visible in both Figs. 8.8C & D. These helices appear comparable to those
visible along the single network gyroid [111] axis and, in SEM micrographs, appear deceptively as planar hexagonal rings (Section 8.2).

8.3.2 Reflectance Modelling

I now model scales of *Pseudolycaena marsyas* as amorphous gyroid networks. Specifically, I calculate a theoretical reflectance via finite difference time domain (FDTD) simulations and assess its compatibility with existing experimental reflectance data\(^\text{220}\).

In order to estimate an appropriate scaling parameter for the models, I first assume that the *P. marsyas* network is an amorphous gyroid. Computationally, I calculate that the apparent radius \( r \) of a gyroid nine-segment helix, as observed along the [111] axis, satisfies the approximate relation \( 2\pi r = 7.732l \) where \( l \) is the single network gyroid edge length. By measuring the diameter of any clearly hexagonal rings in Fig. 8.7C, I estimate the network’s edge length to be \((117 \pm 6)\text{nm}\); this corresponds to an effective single network gyroid primitive cell parameter of \( a = l\sqrt{2} = (166 \pm 8)\text{nm} \) (Eqn. 3.34).

Vértesy et al. illuminated a large wing area of *P. marsyas* from above and measured its reflectance spectrum using an integrating sphere\(^\text{220}\). The *P. marsyas* reflectance peaks at around 480nm. By scaling the normalised wavevector of amorphous gyroid’s primary structure factor resonance (Fig. 7.7) to this wavelength, a second estimate of the single network gyroid primitive cell parameter may be produced. Specifically, this method suggests a value of \( a = 169\text{nm} \) which corroborates the microstructure-based estimate of \( a = (166 \pm 8)\text{nm} \).
Naturally-Occurring Amorphous Gyroid 225

P. marsyas structure models are derived from 1000-vertex type-2 amorphous gyroid network designs, scaled to optical lengthscales by multiplication by $a = 166\text{nm}$. I note that the P. marsyas chitin network exhibits some natural variation in edge thickness (Fig. 8.7C & D). To model this, I decorate the amorphous gyroid designs with cylinders whose radii are randomly drawn from a normal distribution with mean $0.31a$ and a standard deviation of $15\%$. Networks generated using these parameters have an approximate material fill fraction of $25\%$. I make the models as wide, in the plane of the scale, as the amorphous gyroid networks allow and set their transverse thickness to $1300\text{nm}$ in accordance with the observed scale thickness.

Non-pigmented regions of the scale structure, corresponding to the top half in the TEM cross section of Fig. 8.7E, are modelled as non-absorbant chitin. For this, I employ the frequency dependent refractive index of chitin as measured by polarising interference microscopy for the butterfly Graphium sarpedon. In the absence of specific experimental data for the absorbance of a single P. marsyas scale, I propose a plausible complex refractive index $n + i\kappa$ for the pigmented chitin observed in the lower half of the TEM cross-section. For the real component, $n(\lambda)$, I take the Graphium sarpedon chitin data. Then, to model the extinction coefficient $\kappa(\lambda)$, I make some assumptions. Specifically, I assume that the pigment is UV-absorbing and suggest that its extinction coefficient can be modelled by that of P. nireus (Fig. 8.1F). To justify this, several butterflies are known to employ blue and UV-absorbing pigments to sculpt their reflectance profiles. For instance, the gyroidal photonic crystal in P. sesostris scales appears blue when separated from the upper pigmented layer. The overall colouration of P. sesostris, however, is green, while that of P. marsyas is a blue-turquoise more comparable to the wing bands of P. nireus. I therefore suggest that the extinction coefficient of the P. nireus pigment is a plausible model for the P. marsyas pigment.

Scale models were loaded into Lumerical FDTD solutions and centred at the origin of the simulation region. Lumerical’s in-built refractive index modelling capability was used to fit the combination of $n(\lambda)$ and $\kappa(\lambda)$ values discussed above. In performing this fit, the contribution of the extinction was given extra weight in order to reliably model the absorption. I refer to the resulting optical properties, which are shown in Fig. 8.9A, as the theoretical model of pigmented chitin. Cylinders in the bottom half of the FDTD region, defined as $z < 0$, were modelled using the pigmented chitin data. Cylinders in the top half of the region were modelled as non-absorbing chitin.

Models were illuminated from above using a total field scattered field (TFSF) source. A three-dimensional monitor box, comprising 6 planar monitors, was arranged to completely enclose both the model and the TFSF source. A broadband light pulse was injected and the scattered nearfields recorded by the monitor box. Using Lumerical’s farfield projection algorithm, I then project the scattered nearfields onto a hemisphere in the upper halfspace. This process models the integrating sphere measurements of Vértesy et al.

In total, I simulated the reflectance of six distinct models of the P. marsyas structure, each derived from a different amorphous gyroid vertex and edge pattern. These six spectra were
Figure 8.9: Modelling the reflectance of a *Pseudolycena marsyas* wing. I suggest a plausible refractive index model $n + i\kappa$ for the pigmented chitin in the lower half of the *P. marsyas* scales (A). Scales were modelled as amorphous gyroids and a reflectance spectrum, an average of six models, was calculated via FDTD. The model reflectance (B, blue line) is in good qualitative agreement with the experimental reflectance (black line). Divergence is associated with the approximate refractive index model.

then averaged to generate a final theoretical reflectance. Fig. 8.9B presents the results of this modelling (blue line) compared to the experimental *P. marsyas* reflectance data (black line).

The agreement between the experimental and theoretical reflectances is qualitatively good. My calculations show that an amorphous gyroid with a UV-absorbing pigment can generate the signature blue-turquoise of *P. marsyas* wing scales. Clearly there is some divergence between the two spectra at both red and near-UV wavelengths. The divergence at red wavelengths is likely attributable to the experimental data, which, having been measured on a large wing area, includes reflectances from ground scales and other architectures which have not been modelled. The divergence at near-UV wavelengths is likely a result of two factors. Foremost, I have made significant assumptions in building the theoretical model of pigmented chitin (Fig. 8.9A). Ideally, a future study will measure directly the absorbance of single *P. marsyas* scales and determine an accurate complex refractive index. Beyond this, the TEM cross section (Fig. 8.7E) shows that the *P. marsyas* network displays some multilayer character. Amorphous gyroids, on the other hand, are glassy throughout; multi-layer type effects are thus absent from the theoretical reflectance spectrum.

I have presented the microstructure contained within the wing scales of *Pseudolycena marsyas* (Theclinae). The scales contain a disordered connected network of chitin which is responsible for the blue colouration. This network exhibits complete three-dimensional interconnectivity and is structurally distinct from previously reported perforated multilayers. Although it is difficult to be sure from micrographs alone, the network is, by comparison with gyroidal and perforated multilayer architectures, trivalently connected. TEM cross sections suggest that the network is actually a mixture of fully amorphous network regions and partially-formed multilayers. Further, the dark banding of the lower half of the scales, observed via TEM, suggests that pigmentation influences the overall scale colour.

I built models of the *P. marsyas* network, derived from type-2 amorphous gyroid designs, and calculated their reflectance using an FDTD method. The lower half of each scale was modelled using a plausible combination of refractive index data for chitin and extinction coefficient data for the UV-absorbing pigment in *Papilio nireus* scales. The upper half of each scale was modelled as non-absorbant chitin. Having scaled the structure under the assumption that it is an amorphous
gyroid, I find that the calculated reflectance spectrum is in good agreement with experimental data. Divergence between the model and experiment at blue wavelengths is likely a result of the approximate refractive index model for the *P. marsyas* pigment.

Overall, I have demonstrated that amorphous gyroid is a good model of the *P. marsyas* connected network. Although the network is unlikely to be a true glassy amorphous gyroid, it displays significant amorphous gyroid character.

### 8.4 Discussion

In section 8.2, I presented evidence that topological defects form in the gyroidal photonic crystals of green hairstreak butterflies. I went on to show, in section 8.3, that a fully three-dimensional topologically disordered network self-assembles in the wing scales of *Pseudolycaena marsyas*. Through analysis of micrographs and electromagnetic modelling I demonstrated that the *P. marsyas* network is morphologically similar to amorphous gyroid.

I note that the *P. marsyas* microstructure is unlikely to be unique. Several taxonomically related neotropical hairstreaks display a similar blue-turquoise on their dorsal wing surfaces; an example of this, a specimen of *Arcas tuneta*, is shown Fig. 8.10A. Investigation of single *A. tuneta* scales via SEM (Fig. 8.10B) reveals that they contain a disordered connected network of chitin similar to the *P. marsyas* microstructure. Beyond this brief survey, I have not performed a detailed characterisation of the *A. tuneta* scale structure. Interestingly, scales of *Arcas imperialis* (Fig. 8.10C), a butterfly from the same genus as *A. tuneta*, are known to contain a gyroidal microstructure \(^{247,248}\), shown in Fig. 8.10D. A recent SAXS study of the *A. tuneta* scale structure has shown that it comprises distinct gyroid crystallites whose interfaces can be mediated by topological defects in the chitin network \(^ {248}\). The observation of such defects parallels my argument, made in section 8.2, for the existence of topological defects in the gyroidal microstructures of green hairstreak butterflies.

The observation of gyroidal architectures in the taxonomic relatives of *P. marsyas* echoes the conclusions of a recent phylogenetic classification, informed by wing scale microstructure, of the genus *Parides* \(^ {249}\). Specifically, numerous *Parides* butterflies which produce colouration through perforated multilayer architectures were found to be closely related to the gyroidal species *P. sesostris* and *P. childrenae*. The close evolutionary relationship between these two architectures suggests that they may each be self-assembled with only a small alteration to the conditions of their development. Indeed, gyroidal, lamellar and metastable perforated lamellar phases are closely related in block copolymer systems, and direct transitions between these phases have been observed \(^ {210,250}\). The existence of a gyroidal photonic crystal in *A. imperialis* \(^ {248}\) thus strengthens the suggestion that disordered relatives of the gyroid architecture have developed in *A. tuneta*, *P. marsyas* and other related species.

Looking beyond butterfly scales, Saranathan et al. studied via SAXS the feather barbs of 230 distinct bird species \(^ {213}\). A great variety of disordered keratin networks, located within the barbs, were observed. Fig. 8.10E presents one of these networks, found in the feather barbs of *Passerina cyanea*, which possesses significant and potentially gyroidal short range order in the absence of...
Figure 8.10: Possible amorphous gyroids in lepidopteran scales and avian feather barbs. Specimen of *Arcas tuneta* (A), which appears similarly coloured to *P. marsyas*. Its scales contain a disordered and apparently trivalent connected network (B). Specimen of *Arcas imperialis* (C). The structure in its scales appears characteristically gyroidal (D). Avian feather barbs can also contain disordered connected networks; both the microstructures in *Passerina cyanea* (E) and *Alcedo atthis* (F) possess amorphous gyroid character. Scale bars 1µm (B), 2µm (D), 1µm (E) & 2µm (F). Panel D reproduced from Ingram & Parker, E from Saranathan et al., & F from Stavenga et al.

long range periodicity. Fig. 8.10F presents a similar microstructure, here found in feather barbs of *Alcedo atthis*, which also exhibits striking similarity to amorphous gyroid.

Determining a self-assembly pathway for amorphous gyroid is likely to be both complex and rewarding. A natural place to start is with investigation of the rich phase diagram of block copolymer systems. In particular, non-equilibrium configurations in the vicinity of the gyroidal and hexagonally perforated lamellar phases may prove interesting. Realistically, however, major progress towards industrially applicable self-assembly methods will be made by detailed studies of scale cell development and characterisation of the complex organic molecules which control the process.

8.5 Conclusions

The observation of a natural amorphous gyroid at optical lengthscales has dual technological relevance. First, studying the growth of a structurally ordered but aperiodic architecture can inform and inspire the development of advanced self-assembly techniques. Second, amorphous gyroids with photonic band gaps at near-infrared and optical wavelengths may see applications in next-generation signal processing components.

Here, I have explored the possible existence of amorphous gyroid as a structural colouration architecture in butterfly wing scales. I have presented evidence that topological and structural defects form even in the highly-ordered gyroidal microstructures of the green hairstreaks. Specifically, I demonstrated that SAXS spectra can be effectively reproduced by single network gyroid models incorporating small amounts of topological and vertex positional disorder.
Following this, I presented the topologically disordered connected network found within the wing scales of *Pseudolycaena marsyas*. This appeared trivalent and fully interconnected in three dimensions. It bore a strong visual similarly to amorphous gyroid, although TEM cross-sections revealed that it possessed a partial multilayer character. I modelled the *P. marsyas* scale structure and showed, given the assumptions made, that amorphous gyroid can account for the butterfly’s reflectance spectrum.

I conclude that the *P. marsyas* disordered network exhibits significant amorphous gyroid character. Further, the architecture is not likely to be unique; several amorphous gyroid-like structures appear to exist in the scales of related butterflies and in avian feather barbs.
Chapter 9

Conclusions

A material’s interaction with light is intimately connected to its sub-wavelength structure. This thesis has explored this connection in detail, focussing in particular on understanding the mechanisms that govern the formation of complete photonic band gaps. In doing so, I presented two novel perspectives on the electromagnetic analysis of arbitrarily-structured media. In the first instance, I have made significant progress towards a complete formulation of a generalised photonic band structure; by calculating the spectral function, complete dispersion relations for both periodic and aperiodic structures can be resolved. In the second instance, I formulated local self-uniformity (LSU) as a measure of locally-automorphic character in connected networks of fixed valency. I showed that LSU is a successful measure of PBG-forming ability. Further, I demonstrated that an understanding of localised resonant scattering processes can both explain the existence of sizeable PBGs in aperiodic media, and suggest a solution to the champion structure problem. In this section, I summarise the major findings of this thesis, breaking the work into two major sections as per the two novel perspectives that have been advanced. I also highlight a number of questions, the investigations of which form possible future research directions.

9.1 The Spectral Function Method

Photonic band structure is an effective means of presenting the dispersion relation of light in a translationally periodic structure. In this specific case, the Bloch wavevector is a ‘constant of the motion’; it is a good solution label for electromagnetic eigenstates of the system. In the absence of periodicity, however, it is not possible to define a Bloch wavevector and, by extension, a regular photonic band structure. I have shown that generalised band structures may be calculated using the spectral function method. To begin, the system’s eigenmodes are calculated using a finite difference time domain solver. The spectral function $M(k, \omega)$ is then constructed by projection of the electric or magnetic field distributions into a plane wave basis. As a result, a complete frequency-momentum decomposition of the structure’s modes is obtained.
I showed that, when applied to a planar honeycomb photonic crystal, the spectral function method reproduces the conventional band structure. I then calculated spectral functions for a pair of hyperuniform disordered networks; the resulting generalised band diagrams revealed the complete dispersion relation of the structures. In general, these dispersion relations were statistically isotropic, and comprised an intense effective medium-like band that, with increasing frequency, was progressively folded back into the light cone. For low refractive index contrast, I formulated a first-order Born approximation to the Maxwell equations. This solution revealed that the coupling rate between two momentum states of the light field is proportional to the material’s structure factor at the corresponding momentum transfer. As a result, in the low index limit, the dispersion relation may be approximated by a convolution of the structure factor with the momentum states of a homogeneous effective medium. This convolution was found to be the principal determinant of the dispersion relation in a low index ($n = 1.5$) disordered network. In the high index case ($n = 3.6$), the overall form of the generalised band structure was controlled by Bragg processes, but was significantly perturbed by energetic interactions between the electric field and the underlying dielectric distribution.

Empowered by the spectral function method, I investigated the mechanisms of PBG formation in a Penrose photonic quasicrystal. Specifically, I characterised the transverse magnetic (TM) dispersion of a dielectric cylinder array and the transverse electric (TE) dispersion of a Delaunay-tessellated dielectric network. Penrose quasicrystals are known to support a fractal-like spectrum of complete PBGs. I confirmed this with supercell band structure calculations, and for each structure identified a large fundamental PBG, a significant sub-fundamental gap and, in the case of the TE structure, several smaller mini-gaps. I calculated too the total scattering structure functions for the TM and TE structures, indexed their major peaks and identified their associated pseudo-Jones zones.

Generalised band diagrams were calculated for both the TE and TM Penrose structures. These were found to exhibit fractal-like dispersion which was attributed to folding of an effective medium band by the multiple distinct Bragg processes of the Penrose structure factor. High resolution band diagrams were then calculated in the spectral region of the TM and TE sub-fundamental PBGs. Using these, I analysed in detail the momentum states of the light field at a number of key frequencies. In the TE case, I observed that the edge modes of the sub-fundamental PBG are characterised by momentum localisation at the edges of the major pseudo-Jones zone. Similarly, the edge modes of a second mini-gap exhibited momentum localisation at the edge of a secondary pseudo-Jones zone. The formation of these two gaps is thus associated with standing wave formation as a result of scattering by a strong Bragg process. Modes immediately below the large fundamental PBG exhibited diffuse momentum distributions; no clear localisation at a Jones zone was observed.

The picture was found to be similar for the TM modes of the Penrose cylinder array. Here, momenta were distributed widely throughout the $k$-space due to scattering by three strong Bragg processes; interaction of these major Bragg processes produced a complex dispersion relation. I observed that the edge modes of the sub-fundamental gap localised momentum at a Jones zone edge; the existence of the sub-fundamental gap was thus attributed to a Bragg mechanism. As in the TE case, momentum distributions just below the fundamental PBG appeared diffuse.
I conclude that Bragg processes play a minimal role in the formation of the fundamental PBG in both TE and TM Penrose photonic quasicrystals. In the TM case, this gap is known to form through a Mie scattering mechanism. In the TE case, I associated this fundamental gap with a generalised resonant scattering mechanism. In general, those PBGs that were successfully resolved (with the exception of the fundamental PBGs) were associated with the formation of standing wave modes through Bragg-like scattering. This observation suggests that the fractal-like spectrum of PBGs in Penrose photonic quasicrystals is intimately related to the fractal-like distribution of Bragg peaks that comprise the quasicrystal structure factor.

As a distinct project, my collaborators and I designed, fabricated and optically characterised gold hyperuniform metasurfaces; this work further explored the connections between a material’s optical properties and its reciprocal space characteristics. Specifically, we fabricated a selection of hyperuniform gold pillar architectures for scaling parameters (approximately equal to the mean pillar separation) ranging between $a = 790$ nm and 316 nm. Light scattering by the metasurfaces was observed to be principally diffractive. In addition, for an $a$ value of 474 nm, we observed a scattering peak associated with a surface plasmon resonance of the gold pillars. Next, we excited the metasurface modes using fluorescent dye molecules and spectrally decomposed the emitted light. The farfield distribution of light was annular. With increasing normalised frequency, the radius of this annulus was observed to decrease to zero before increasing linearly; hyperuniform metasurfaces thus exhibit controllable directional emission. I calculated the generalised band structure of a low index ($n = 1.5$) hyperuniform network whose structure was precisely the inverse of the gold pillar architecture; this dispersion diagram was found to be in excellent agreement with the observed directional emission.

### 9.2 Local Self-Uniformity

The existence of sizeable PBGs in photonic amorphous diamond (PAD) and disordered honeycombs (TE polarisation only) can be explained neither through Bragg scattering, nor regular Mie-resonant scattering. This issue is intimately related to the question of champion photonic crystal structures. Specifically, the rod-connected diamond network is known to possess the largest complete PBG of all known photonic crystals. The preservation of a diamond-like PBG in photonic amorphous diamond bears out the suggestion that structures with a connected diamond-like network morphology exhibit a sizeable PBG. To date, however, no satisfactory theory has been advanced to explain why diamond-like structures, either ordered or disordered, are so amenable to PBG formation.

In this thesis, I have re-formulated the ideal structural characteristics of a PBG-forming network. When arranged by gap size, the known varieties of PBG-forming structures exhibit a clear hierarchy; specifically, a network’s gap-forming ability is inversely related to the coordination number of its component vertices. For a fixed coordination number, the largest PBGs occur in networks whose local vertex configurations are maximally symmetrical; PBG size is then observed to decrease with increasing network structural disorder.
I encapsulated these observations in a generalised symmetry measure called local self-uniformity (LSU). LSU measures the geometrical and topological similarities of the local environments in a connected network of uniform valency $\gamma$. Its calculation is based on the tree overlap method. I define $n$-trees as simple fragments of a connected network. Having defined two distinct $n$-trees, I maximally align their root edges and measure the quality of their overlap. To calculate the spatial similarity statistic of two trees, I measure the quality of their overlap for all $\gamma!$ root-edge alignment permutations and then take the average. LSU distributions may then be constructed by forming specific sets of tree spatial similarity statistics, typically by comparing each possible tree to other trees in its local vicinity.

LSU is a continuous measure of the extent to which a network is strongly isotropic\textsuperscript{180}. States of maximal LSU are uniquely defined, and correspond to either the diamond or single gyroid networks (in three-dimensions), or the honeycomb network (in two-dimensions). Strongly isotropic networks possess the property that any permutation of a given vertex’s edge labels extends to a rigid-body transformation of the structure that leaves it invariant (i.e. the transformation is also an automorphism). The magnitude of a network’s LSU thus reflects the extent of its ‘locally-automorphic character’. I presented LSU distributions for PAD and a paracrystalline disordered honeycomb and demonstrated that each network possesses significant LSU. The association of LSU with gap forming ability suggested that a locally self-uniform amorphous gyroid - a trivalent analogue of PAD, with a locally gyroidal vertex configuration - should possess a sizeable PBG.

I applied a modified Wooten-Winer-Weaire annealing protocol to generate the first known amorphous gyroid networks. This protocol followed the established process for amorphous silicon annealing\textsuperscript{117,118}, but introduced a modified ‘potential energy’ function to effectively drive the local geometries into a faithfully gyroidal arrangement. I characterised the resulting amorphous gyroid networks, demonstrating in particular their diffuse total scattering structure functions and, when suitably annealed, sizeable LSU. Supercell photonic band structures were used to probe the PBGs in amorphous gyroid. Specifically, the most locally self-uniform 1000-vertex networks were found to possess complete PBGs of up to 16% for a refractive index contrast of 3.6 : 1.

To confirm my band structure calculations, I designed, fabricated and characterised ceramic amorphous gyroid prototypes. Models were printed at the workshops of Fraunhofer IKTS, Dresden using an advanced ceramic 3D-printing technique. Models were made from alumina, whose relative permittivity was measured to be $\varepsilon_r = 9.5 \pm 0.3$ around 22 GHz. The PBGs of the alumina models were probed using a microwave transmission technique. Although transmission results were adversely affected by noise, transmitted signals were attenuated by up to 35 dB within the expected PBG. Using a cylindrical sample, the transmission as a function of sample orientation was also measured; this revealed amorphous gyroid’s statistically isotropic PBG.

I have demonstrated the striking correlation between a network’s LSU and its PBG-forming ability. Specifically, I generated an ensemble of distinct 216-vertex amorphous gyroid models. For each model I calculated both an LSU distribution and its PBG size as predicted by a supercell photonic band structure. PBG size was found to be strongly correlated with LSU. For each network, I also calculated an approximate integrated density of states; this estimated the number of modes, supported by the amorphous gyroids, within the frequency window of the associated
single network gyroid PBG. When using this density of states measure, the correlation between LSU and PBG-forming ability was striking. I performed a similar analysis for an ensemble of planar hyperuniform connected networks; as in the three-dimensional case, PBG size was observed to be correlated with LSU.

To rationalise LSU’s success as a PBG-forming measure, I advanced a picture of photonic tight-binding in high refractive index PBG-forming architectures. Although the development of a complete photonic tight-binding formalism presents considerable mathematical difficulties, evidence suggests that the modes of high index dielectric structures form in a tight-binding regime. Specifically, the PBG edge modes of planar PBG-forming architectures exhibit field distributions that are derived from the modes of their isolated scattering units. In the case of TM gaps in cylinder arrays, these modes appear as linear superpositions of Mie resonances. In the case of TE gaps in connected networks, the modes exhibit the characteristic ‘cell-type’ and ‘stripe-type’ field profiles of an isolated honeycomb 2-tree.

Using an FDTD method, I demonstrated that LSU measures the quality of a network’s scattering units from a perspective of generalised resonant scattering. Planar 2-trees were observed to suppress transmission by local standing wave formation for frequencies between their first and second scattering resonances; this behaviour is analogous to the Mie resonant scattering behaviour of an isolated cylinder. A reduction in a tree’s LSU perturbs the frequencies of the first and second scattering resonances, and is associated with a reduced ability to suppress transmission.

Perfect LSU ensures that each of the network’s trees is structurally identical. As a result, the scattering resonances of all trees are degenerate, and the frequency regions for which each tree suppresses transmission are maximally aligned; this maximises the PBG size. A decrease in LSU is associated with decreased degeneracy of the scattering resonances of a network’s trees. Imperfect overlap of each tree’s transmission gap creates propagation channels that encroach on the PBG, thus narrowing it. Tree symmetry under permutation - in which every root-edge permutation extends to a congruent transformation of the tree - minimises the number of scattering resonances that it supports. Accordingly, this maximises the gaps between resonances and explains the origin of champion and near-champion PBGs in the strongly isotropic photonic crystals.

I also explored the connection between amorphous gyroid and structural colour in butterflies. A number of butterflies - notably Parides sesostris and several species of the genus Callophrys - are known to derive colour from chitinous single network gyroid photonic crystals contained within their wing scales. I modelled the photonic crystal in the wing scales of Callophrys gryneus and compared my models with existing small angle X-ray scattering (SAXS) spectra. I demonstrated that a partially disordered gyroid (PDG), containing small amounts of topological and positional disorder, is a better fit to the diffraction data than a perfect crystalline level-set gyroid. Together with existing tomographic reconstructions, this data suggests that topological defects form, to a limited degree, in the green hairstreak gyroid photonic crystals.
Following this, I presented an apparently trivalent and topologically disordered microstructure contained within the wing scales of *Pseudolycaena marsyas* (the Cambridge Blue). The microstructure resembled computational projections of amorphous gyroid models with a chitin fill fraction of 25%. A transmission electron micrograph revealed that significant regions of the network are three-dimensionally interconnected; the network is thus clearly distinct from the perforated multilayers contained within wing scales the genus *Polyommatus*\(^{220}\). I modelled the *P. marsyas* scale structure using amorphous gyroid networks. In particular, I constructed a plausible refractive index model for the scale’s pigmented lower layer by deriving the extinction coefficient of the pigmented chitin in *Papilio nireus*\(^{217}\). Using an FDTD solver, I demonstrated that amorphous gyroid models can, given the assumptions of my model, effectively reproduce the observed reflectance spectrum of a *P. marsyas* wing. I concluded that the *P. marsyas* network exhibits significant amorphous gyroid character, and that several other microstructures in butterfly scales\(^{247}\) and avian feather barbs\(^{213}\) resemble amorphous gyroid. The existence of these natural microstructures suggests that the self-assembly of amorphous gyroid or structurally similar networks is theoretically possible.

### 9.3 Outlook

In conclusion, this thesis has made significant progress in understanding the physical processes that govern photonic band gap formation. I have shown that sizeable PBGs form in high index continuous random networks through a mechanism of generalised resonant scattering. Local self-uniformity measures the locally automorphic character of a connected array of trees and is an effective proxy for a network’s generalised resonant scattering power. Although generalised resonant scattering is the dominant formation mechanism in locally self-uniform high index networks, I have shown that Bragg scattering alone can nonetheless give rise to PBGs. The association of the sub-fundamental PBGs in Penrose photonic quasicrystals with the major momentum transfers of the Penrose structure factor is perhaps the first categorical demonstration of a PBG formed through Bragg processes alone.

The findings of this thesis, and the novel tools that have been developed, have the power to influence the direction of future photonics research that is not specifically concerned with PBGs. The fresh perspectives provided by both generalised photonic band structures and local self-uniformity can influence the design of efficient devices for harvesting and emitting light, directional emitters and absorbers, the realisation of three-dimensional Anderson localisation and the design of artificial ultra-white materials.

Materials which can effectively trap incident light are of paramount importance in the design of solar cells\(^{152,251}\). Generalised photonic band structures could become a key tool in tailoring the dispersion relation of patterned slabs to facilitate this trapping. Specifically, through fluorescence emission characterisation of hyperuniform gold metasurfaces, it was shown that the generalised band structure predicts the directional coupling of light out of a slab. Further, the directional emission pattern was set by the metasurface’s structure factor. Accordingly, I suggest the following scheme for the design of an efficient light harvester. First, my Hamiltonian treatment of Bragg scattering (Appendix C) should be developed; accuracy could be improved by increasing...
the order of the perturbation theory, or by implementing a Lippmann-Schwinger-style iterative solution. This numerical prediction of the dispersion relation could then be used as an objective function with which to optimise the material’s reciprocal space. Such a process could create materials with designer dispersion relations that achieve an optimal balance between leaky and non-leaky modes. By extension, this process could be used to design emitters and absorbers with arbitrary directional sensitivity.

Advanced reciprocal space design also suggests new possibilities in the study of Anderson localisation. Specifically, artificial disordered structures could be deliberately engineered to possess ultra-low group velocities. The corresponding real space material should possess interesting light scattering properties that may include sub-diffusional light transport. Further, my work on LSU suggests a complementary direct space approach to the design of Anderson-localising materials. Careful control of the LSU distributions could be used to engineer randomly distributed defect states within an otherwise locally self-uniform material. A sufficiently sparse distribution of defects could support sub-diffusional light transport. Such a proposal is in the spirit of John’s original ambition for the realisation of Anderson localisation in the photon mobility edge of a partially disordered photonic crystal\cite{25}.

Beyond this, the design of ‘ultra-white’ materials, in the style of the colouration mechanism of Cyphochilus spp. beetles, suggests an interesting extension of the LSU concept. Specifically, my conclusions on photonic tight-binding in the high index regime suggest that tailored scattering characteristics can be achieved by forming networks from an appropriate ensemble of primitive scattering units. This arrangement of scattering units does not need to be locally self-uniform. Consider instead a network that has a minimal LSU; such a network would comprise scattering units that are maximally different to one another. Naively, I suggest that the scattering units of the network would saturate a broad range of frequencies with localised scattering resonances; the material may thus be ‘ultra-white’. Implementation of this idea would likely require re-definition of the similarity measure (Eqn. 6.3) with which the overlap quality of two trees is calculated; this modified measure must be mathematically well-behaved in the limit of structural dissimilarity. However this is achieved, ‘ultra-whiteness’ through structural dissimilarity represents an interesting frontier in light scattering physics.
Appendix A

Fourier Transform of the Direct Lattice

In this appendix, a proof that the reciprocal lattice is the Fourier transform of the direct lattice is presented. Viewing the reciprocal lattice as the Fourier transform of the direct lattice makes its physical meaning clear. The farfield diffraction pattern of a crystal is just the Fourier transform of its aperture function (Eqn.2.5). In the case of a crystal, the diffraction pattern is exactly the reciprocal lattice. The points of the reciprocal lattice thus correspond to the favoured momentum transfers in an elastic photon scattering process.

A general vector $r$ in direct space is written in terms of the lattice basis as

$$ r = \alpha_1 a_1 + \alpha_2 a_2 + \alpha_3 a_3. \tag{A.1} $$

Similarly, a general vector $k$ in reciprocal space is written in terms of an as-yet unknown basis $b_i, i = 1...3$, as

$$ k = \beta_1 b_1 + \beta_2 b_2 + \beta_3 b_3. \tag{A.2} $$

We define the direct lattice $L(r)$ of a 3D crystal as a comb of delta functions,

$$ L(r) = \sum_{l,m,n} \delta(r - la_1 - ma_2 - na_3), \tag{A.3} $$

where $l,m$ and $n$ are integers. The Fourier transform of the lattice $L(k)$ is defined as

$$ L(k) = \int_{-\infty}^{\infty} L(r) e^{-ik \cdot r} d^3r. \tag{A.4} $$

Using the above definitions of $r$ and $k$, the exponent in the Fourier transform becomes
\[ \mathbf{k} \cdot \mathbf{r} = \alpha_1 \beta_1 \mathbf{a}_1 \cdot \mathbf{b}_1 + \alpha_2 \beta_2 \mathbf{a}_2 \cdot \mathbf{b}_2 + \alpha_3 \beta_3 \mathbf{a}_3 \cdot \mathbf{b}_3 + \\
\alpha_1 \mathbf{a}_1 \cdot (\beta_2 \mathbf{b}_2 + \beta_3 \mathbf{b}_3) + \alpha_2 \mathbf{a}_2 \cdot (\beta_1 \mathbf{b}_1 + \beta_3 \mathbf{b}_3) + \alpha_3 \mathbf{a}_3 \cdot (\beta_1 \mathbf{b}_1 + \beta_2 \mathbf{b}_2). \] (A.5)

This scalar product can be simplified by a judicious choice of reciprocal space basis vectors. In particular, we stipulate, without loss of generality, that \( \mathbf{b}_1 \) is perpendicular to both \( \mathbf{a}_2 \) and \( \mathbf{a}_3 \), \( \mathbf{b}_2 \) perpendicular to \( \mathbf{a}_1 \) and \( \mathbf{a}_3 \) and \( \mathbf{b}_3 \) to \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \). These conditions may be satisfied when the versors of the reciprocal basis are chosen to be

\[ \hat{\mathbf{b}}_1 = \frac{\mathbf{a}_2 \times \mathbf{a}_3}{|\mathbf{a}_2 \times \mathbf{a}_3|}, \quad \hat{\mathbf{b}}_2 = \frac{\mathbf{a}_3 \times \mathbf{a}_1}{|\mathbf{a}_3 \times \mathbf{a}_1|}, \quad \hat{\mathbf{b}}_3 = \frac{\mathbf{a}_1 \times \mathbf{a}_2}{|\mathbf{a}_1 \times \mathbf{a}_2|}. \] (A.6)

The scalar product of \( \mathbf{r} \) and \( \mathbf{k} \) simplifies to

\[ \mathbf{k} \cdot \mathbf{r} = \alpha_1 \beta_1 \mathbf{a}_1 \cdot \mathbf{b}_1 + \alpha_2 \beta_2 \mathbf{a}_2 \cdot \mathbf{b}_2 + \alpha_3 \beta_3 \mathbf{a}_3 \cdot \mathbf{b}_3, \] (A.7)

and the result of the Fourier transform is thus written as

\[ L(k) = \sum_l e^{-il\beta_1 \mathbf{a}_1 \cdot \mathbf{b}_1} \sum_m e^{-im\beta_2 \mathbf{a}_2 \cdot \mathbf{b}_2} \sum_n e^{-in\beta_3 \mathbf{a}_3 \cdot \mathbf{b}_3}. \] (A.8)

Using Eqn.A.17 (proved below), we may re-express \( L(k) \) as a sum of delta functions.

\[ L(k) = \frac{\pi}{\mathbf{a}_1 \cdot \mathbf{b}_1} \sum_h \delta(\beta_1 - \frac{2\pi h}{\mathbf{a}_1 \cdot \mathbf{b}_1}) \times \frac{\pi}{\mathbf{a}_2 \cdot \mathbf{b}_2} \sum_k \delta(\beta_2 - \frac{2\pi k}{\mathbf{a}_2 \cdot \mathbf{b}_2}) \times \frac{\pi}{\mathbf{a}_3 \cdot \mathbf{b}_3} \sum_l \delta(\beta_3 - \frac{2\pi l}{\mathbf{a}_3 \cdot \mathbf{b}_3}). \] (A.9)

\( L(k) \) is thus a function that is zero unless \( k \) takes specific values. These \( k \) vectors are

\[ k = (\beta_1, \beta_2, \beta_3) = \left( \frac{2\pi h}{\mathbf{a}_1 \cdot \mathbf{b}_1}, \frac{2\pi k}{\mathbf{a}_2 \cdot \mathbf{b}_2}, \frac{2\pi l}{\mathbf{a}_3 \cdot \mathbf{b}_3} \right), \] (A.10)

where \( h, k \) and \( l \) are integeric. We observe that \( L(k) \) describes a Bravais lattice in reciprocal space. The unit vectors of this basis are given by Eqn.A.6. We may subsume the magnitudes into the versors to arrive at the textbook definition of the reciprocal lattice basis vectors. Taking \( h = 1 \) and \( k = l = 0 \) we generate the first of the basis vectors \( k_1 \) as

\[ k_1 = \beta_1 \mathbf{b}_1 = \frac{2\pi}{\mathbf{a}_1 \cdot \mathbf{b}_1} \mathbf{b}_1 = \frac{2\pi}{|\mathbf{a}_1| \cos(\theta_{a_1 b_1})} \mathbf{b}_1 = \frac{2\pi \mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \] (A.11)
Performing the same process for the other two basis vectors, we see that the reciprocal lattice basis set is

\[ \mathbf{k}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}, \quad \mathbf{k}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}, \quad \mathbf{k}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}. \]  

(A.12)

To conclude, we see that the Fourier transform of the direct lattice is itself a Bravais lattice; this lattice is called the reciprocal lattice. Each point in the reciprocal lattice may be indexed using the reciprocal lattice basis. The reciprocal lattice corresponds to the observed farfield diffraction pattern of a crystalline structure. Each reciprocal lattice vector is thus associated with a momentum transfer vector \( \mathbf{q} \) which scatters an incident planewave according to Eqn.2.1.

**Sum of Complex Unity**

Here we prove an important relation (used above) regarding the sum of complex unity. Consider a periodic array of delta functions - a so-called ‘Dirac comb’ - with period \( L \).

\[ f(x) = \sum_{m=-\infty}^{\infty} \delta(x - mL) \]  

(A.13)

As a result of its periodicity, we may express \( f(x) \) using a Fourier series as

\[ f(x) = \sum_{h=-\infty}^{\infty} c_h \exp(-2\pi ih \frac{x}{L}). \]  

(A.14)

The coefficients \( c_h \) can be determined by integration. We note that they all have the same magnitude:

\[ c_h = \frac{2}{L} \int_{-L/2}^{L/2} \exp(-2\pi ih \frac{x}{L}) f(x) dx \]

\[ = \frac{2}{L} \int_{-L/2}^{L/2} \exp(-2\pi ih \frac{x}{L}) \sum_{m=-\infty}^{\infty} \delta(x - mL) dx \]

\[ = \frac{2}{L} \int_{-L/2}^{L/2} \exp(-2\pi ih \frac{x}{L}) \delta(x) dx \]

\[ = \frac{2}{L}. \]  

(A.15)

The Fourier series of a delta comb can thus be written as

\[ \sum_{m=-\infty}^{\infty} \delta(x - mL) = \frac{2}{L} \sum_{h=-\infty}^{\infty} \exp(-2\pi ih \frac{x}{L}) \]  

(A.16)
From this we can obtain an important relation describing the infinite sum of the geometric series of complex unity with ratio $\exp(-2\pi ix/L)$. Let us transform variables from $x \to k$ and relabel the constant $2\pi/L \to C$.

$$\sum_{h=-\infty}^{\infty} \exp(-ihCk) = \frac{\pi}{C} \sum_{m=-\infty}^{\infty} \delta(k - \frac{2\pi m}{C}) \quad (A.17)$$
Appendix B

Bloch’s Theorem

Here I derive Bloch’s theorem as it applies to the magnetic field modes of a photonic crystal. First the theorem is clearly stated. It is then proved by deriving the form of a Bloch wave.

Recall that in a non-magnetic material in the absence of free charge and free current sources, we may write the Maxwell curl equations as the eigenvalue equation \( \hat{\Theta} H(r) = \omega^2/c^2 H(r) \), where the magnetic field operator \( \hat{\Theta} \) takes the form

\[
\hat{\Theta} = \nabla \times \frac{1}{\varepsilon_r(r)} \nabla \times .
\]  

(B.1)

We note that solutions to the Maxwell eigenvalue equation should be considered as distributions\(^{195}\). The equations include boundary conditions that must be satisfied at the interfaces between materials. In this particular case, the components of the \( E \) and \( H \) field which are tangential to a given interface must be continuous across it.

As applied to the photonic crystal, Bloch’s theorem then reads:

**Bloch’s Theorem:** Given the magnetic field operator \( \hat{\Theta}_H \) in a periodic medium such that \( \varepsilon_r(r+R_i) = \varepsilon_r(r) \) for \( R_i \in \mathbb{R} \) then the eigenstates \( H(r) \) of \( \hat{\Theta}_H \) take the form \( H(r) = e^{i k \cdot r} \tilde{H}(r) \) where the vector field \( \tilde{H}_k(r) = \tilde{H}(r + R_i) \) for any \( R_i \in \mathbb{R} \) and \( k \) is an arbitrary vector in reciprocal space.

**Corollary:** The theorem implies that:

\[
H_k(r + R_i) = e^{i k \cdot (r+R_i)} \tilde{H}_k(r + R_i) = e^{i k \cdot R_i} e^{i k \cdot r} \tilde{H}_k(r) = e^{i k \cdot R_i} H_k(r)
\]  

(B.2)

We thus see that an eigenstate of \( \hat{\Theta}_H \) is multiplied by a unit modulus complex number when translated by a lattice vector.
To prove Bloch’s theorem we consider the properties of a translation operator $\hat{T}_R$ whose action on a function is defined as follows:

$$\hat{T}_R f(r) = f(r + R) \quad \text{(B.3)}$$

Using the periodicity of $\varepsilon_r(r)$, it is clear that the translation operator commutes with $\hat{\Theta}_H$:

$$\hat{T}_R [\hat{\Theta}_H H(r)] = \hat{\Theta}_H (r + R) H(r + R)$$

$$= \nabla \times \left[ \frac{1}{\varepsilon_r(r + R)} \nabla \times H(r + R) \right]$$

$$= \hat{\Theta}_H [\hat{T}_R H(r)]$$

$$\Rightarrow [\hat{\Theta}_H, \hat{T}_R] = 0 \quad \text{(B.4)}$$

where we use the square bracket notation to denote the commutator. As a result of their zero commutator, the translation and $\hat{\Theta}_H$ operators share the same set of eigenstates. Thus, if we can determine a useful property of the eigenstates of $\hat{T}_R$ then this can be applied to solve the magnetic field eigenvalue problem.

When two translation operators are applied consecutively, their order of operation does not matter:

$$\hat{T}_R \hat{T}'_R f(r) = f(r + R + R') = \hat{T}_R \hat{T'}_R f(r)$$

$$\Rightarrow \hat{T}_R \hat{T}'_R = \hat{T}_{R + R}' \quad \text{(B.5)}$$

Now consider an eigenstate of the translation and magnetic field operators $H_k(r)$ such that $\hat{T}_R H_k(r) = c_R H_k(r)$. Using the two possible representations for the double translation operator $\hat{T}_{R + R}'$ above, we consider its application on the eigenstate.

$$\hat{T}_{R + R}' H_k(r) = c_R c_{R'} H_k(r) = c_{R + R'} H_k(r)$$

$$\Rightarrow c_R c_{R'} = c_{R + R'} \quad \text{(B.6)}$$

Further, in order for our solutions $H_k(r)$ to be physically sensible for an infinite crystal, repeated application of the translation operator must produce a steady state field which is neither divergent nor zero. Thus, $\hat{T}_R^n H_k(r) = c^n_R H_k(r)$ implies that $|c_R|$ is unity. This, together with equation (B.5), leads us to conclude that the eigenvalues of the translation operator take the form of unit modulus complex numbers - $c_R = e^{ik \cdot R}$ - where we introduce an arbitrary reciprocal space vector $\mathbf{k}$. It follows that

$$\hat{T}_R H_k(r) = H_k(r + R) = e^{ik \cdot R} H_k(r)$$
This constitutes a proof of the corollary of Bloch’s theorem. From here, working backwards, the theorem is clear.
Appendix C

A Hamiltonian Formulation of Bragg Scattering

C.1 Motivation

This appendix is designed as a counterpoint to the calculation of spectral functions via the finite difference time domain method. The projection into the momentum representation of a field mode in a patterned structure yields an often complex and difficult to interpret momentum distribution $M(k, \omega)$. The FDTD method generates an accurate numerical solution to the Maxwell equations. It yields reliable momentum distributions but gives no insight into the physical processes that govern their shape. Here I show that the general form of the momentum distribution in low index contrast structures may be predicted through a perturbative solution to the Maxwell equations.

The key conclusion is that the rate at which a plane wave with wavevector $k_i$ is scattered onto a state with wavevector $k_j$ is proportional to the value of the structure factor at the corresponding momentum transfer $q = k_j - k_i$. The precise coupling between momentum states is complex, but may be approximated by a convolution between the homogeneous medium momentum distribution and the structure factor. Applying the Born approximation, in which the initial state of the light field is taken as the driving field for any scattering processes, the general form of the momentum distribution $M(k, \omega)$ is seen to result from a scattering of the momentum states of the homogeneous medium into $k$ states separated by the resonant momentum transfers of the structure factor.

I designate any scattering process which is chiefly mediated by the momentum transfers of the structure factor a ‘Bragg process’. Bragg processes are the dominant means by which light is scattered in either the low index limit or the low frequency limit. For high index contrasts, or for wavelengths approximately equal to the size of the fundamental scattering centres of the structure, the simple theory below breaks down. In these regimes, multiple Bragg scattering
and alternative scattering mechanisms (such as local resonant scattering processes) play a significant role. The Born approximation is no longer appropriate, and the predicted momentum distributions show more complex behaviour.

In spite of this, an analytical treatment of Bragg processes assists greatly in interpretation of the momentum states of the light field. Here, I derive an approximate solution to the scattering problem using a time-dependent perturbation theory approach. First, I define a Hamiltonian formulation of the Maxwell equations. I then write the Hamiltonian of a structured medium, with a weakly varying position-dependent relative permittivity, as a sum of the homogeneous medium Hamiltonian plus a perturbation. Using this Hamiltonian, I derive a master equation for the scattering rate between two plane wave states. Finally, I construct an approximate solution to the master equation and illustrate its properties by calculating the momentum states of the light field in a low refractive index hyperuniform connected network.

C.2 Maxwell’s Equations in Hamiltonian Form

Consider a large domain containing an arbitrary distribution of non-magnetic dielectric material. We model the distribution using a position-dependent real-valued relative permittivity \( \varepsilon_r(r) \). The domain contains no free charge and no free current. We look for time-harmonic solutions to the Maxwell equations in which \( E(r,t) = E(r) e^{-i\omega t} \) and \( H(r,t) = H(r) e^{-i\omega t} \). The two Maxwell curl equations may thus be written as

\[
\begin{align*}
\nabla \times E &= -\mu_0 \frac{\partial H}{\partial t} = i\omega \mu_0 H \\
\nabla \times H &= \varepsilon_0 \varepsilon_r \frac{\partial E}{\partial t} = -i\omega \varepsilon_0 \varepsilon_r E.
\end{align*}
\]

We may write the Maxwell equations, as they apply to this domain, in Hamiltonian form as follows\(^{253}\). The state of the electromagnetic field at any position and time may be represented by the values of \([E_x, E_y, E_z]\) and \([H_x, H_y, H_z]\). We therefore define the state vector of the electromagnetic field \( |\tilde{E}, \tilde{H}\rangle \) as

\[
|\tilde{E}, \tilde{H}\rangle = \begin{pmatrix} \hat{E} \\ \hat{H} \end{pmatrix} = \begin{pmatrix} \sqrt{\varepsilon_0 \varepsilon_r} E \\ \sqrt{\mu_0} H \end{pmatrix},
\]

which is a column vector with six components. We define the Hamiltonian \( \hat{H} \) of the electromagnetic field in this basis as

\[
\hat{H} = \begin{pmatrix} 0 & \frac{1}{\sqrt{\varepsilon_0 \varepsilon_r}} \nabla \times \frac{1}{\sqrt{\mu_0}} \\ -\frac{1}{\sqrt{\mu_0}} \nabla \times \frac{1}{\sqrt{\varepsilon_0 \varepsilon_r}} & 0 \end{pmatrix}.
\]

Using this Hamiltonian, we may write the Maxwell curl equations as
\[
\left( \begin{array}{cc}
\frac{i}{\sqrt{\mu_0}} \nabla \times \frac{1}{\sqrt{\varepsilon_0 \varepsilon_r}} & 0 \\
\frac{1}{\sqrt{\varepsilon_0 \varepsilon_r}} \nabla \times \frac{i}{\sqrt{\mu_0}} & 0
\end{array} \right) \left| \sqrt{\varepsilon_0 \varepsilon_r} E \right\rangle = i \frac{\partial}{\partial t} \left| \sqrt{\mu_0 \varepsilon_r} H \right\rangle.
\] (C.5)

I call this the time-dependent Maxwell equation. Equivalently, we may use the time-harmonic form of the state vector to evaluate the time derivative. In this case, the Maxwell equations read

\[\hat{H} |\hat{E}, \hat{H}\rangle = \omega |\hat{E}, \hat{H}\rangle,\] (C.6)

where we see clearly that the eigenvalues of the Hamiltonian are the energies \(\omega\) as required. We define also the inner product of two state vectors as

\[\langle \hat{E}, \hat{H} | \hat{E}', \hat{H}' \rangle = \int_{-\infty}^{\infty} \varepsilon_0 \varepsilon_r(r) E^* \cdot E d^3r + \int_{-\infty}^{\infty} \mu_0 H^* \cdot H d^3r.\] (C.7)

It may be shown that the Hamiltonian is Hermitian with respect to this inner product. As a result, the eigenfrequencies are real-valued and eigenfunctions with different eigenfrequencies are necessarily orthogonal. We therefore choose to normalise the eigenfunctions such that they form an orthonormal set; they obey the relation

\[\langle \hat{E}(r, \omega'), \hat{H}(r, \omega) | \hat{E}(r, \omega), \hat{H}(r, \omega) \rangle = \delta_{\omega', \omega}.\] (C.8)

It should be noted that any solution to the time-dependent Maxwell equation (Eqn. C.5) must also obey the Maxwell divergence relations. These stipulate that \(\nabla \cdot [\varepsilon_r(r)E(r, t)] = 0\) and \(\nabla \cdot H(r, t) = 0\), and may be applied to any potential solution at a later stage.

### C.3 Commutator with a Translation Operator

I now briefly show that Hamiltonian \(\hat{H}\) can commute with a translation operator under certain circumstances. Where these circumstances hold, the translation operator and the Hamiltonian will possess a set of shared eigenstates.

We introduce a translation operator \(\hat{T}_R\) which translates a vector field by a lattice vector \(R\) of a Bravais lattice. We define its action on a vector field \(v(r)\) as

\[\hat{T}_R v(r) = v(r + R).\] (C.9)

Consider now the commutator of the Hamiltonian and the translation operator. Clearly we may write

\[\hat{T}_R \hat{H} |\hat{E}, \hat{H}\rangle_r = \omega |\hat{E}, \hat{H}\rangle_{r+R},\] (C.10)
where we have introduced a subscript to indicate the position variable on which a particular quantity depends. To determine the commutator, we consider reversing the order of the operators. We see that

\[ \hat{T}_R \hat{H}_r |\tilde{E}, \tilde{H}\rangle_r = \hat{T}_u \hat{H}_u |\tilde{E}, \tilde{H}\rangle_u , \] (C.11)

where on the final line we have introduced a new variable \( u = r + R \). Subtraction of Eqns. C.10 & C.11 yields an expression for the commutator \([\hat{T}_R, \hat{H}_r]\). Specifically, we may write

\[ [\hat{T}_R, \hat{H}_r] |\tilde{E}, \tilde{H}\rangle_r = (\omega - \hat{H}_{u-R}) |\tilde{E}, \tilde{H}\rangle_u . \] (C.12)

We observe that the commutator is not in general equal to zero. However, if the Hamiltonian is itself periodic in the lattice vectors of the Bravais lattice, then we may write \( \hat{H}_{u-R} = \hat{H}_u \) and the commutator will evaluate to zero. The Hamiltonian can possess such a periodicity when the position dependent relative permittivity is invariant under translation through a Bravais lattice vector \( R \). Such a permittivity distribution describes a photonic crystal.

### C.4 Structured Media as a Perturbation

To begin, consider a homogeneous dielectric medium in which \( \bar{\varepsilon}_r(r) \) is simply a constant. Solutions to the Maxwell equations are plane waves, and the eigenvectors of Eqn. C.6 may be written as

\[ \begin{pmatrix} \tilde{E} \\ \tilde{H} \end{pmatrix} = \frac{\sqrt{\varepsilon_0 \bar{\varepsilon}_r} E^{(0)}_i e^{-i(\omega t - k \cdot r)}}{\sqrt{\mu_0} H^{(0)}_i e^{-i(\omega t - k \cdot r)}} . \] (C.13)

where \( k \) obeys the dispersion relation \(|k| = \sqrt{\bar{\varepsilon}_r} \omega / c\). In the limit of a large domain (or a domain with a periodic boundary condition), the plane wave basis vectors obey the relation

\[ \frac{\sqrt{\varepsilon_0 \bar{\varepsilon}_r} E^{(0)}_i e^{-i(\omega_i t - k_i \cdot r)}}{\sqrt{\mu_0} H^{(0)}_i e^{-i(\omega_i t - k_i \cdot r)}} \frac{\sqrt{\varepsilon_0 \bar{\varepsilon}_r} E^{(0)}_j e^{-i(\omega_j t - k_j \cdot r)}}{\sqrt{\mu_0} H^{(0)}_j e^{-i(\omega_j t - k_j \cdot r)}} = \delta(\omega_i - \omega_j) \delta(k_i - k_j) . \] (C.14)

We now apply a small perturbation to the dielectric distribution. We allow the relative permittivity to be position dependent with the specific form \( \bar{\varepsilon}_r[1 + \Delta(r)] \), where \( \bar{\varepsilon}_r \) is now the average permittivity and \( \Delta(r) \) is a position-dependent fractional perturbation. We require an expression for \( 1/\sqrt{\varepsilon_r}[1 + \Delta(r)] \) which may be approximated using its Taylor expansion. In the limit where \( \Delta(r) \ll 1 \), we write
\[ \frac{1}{\sqrt{\varepsilon_r}}[1 + \Delta(r)]^{-1/2} \approx \frac{1}{\sqrt{\varepsilon_r}} \left[ 1 - \frac{\Delta(r)}{2} \right]. \] (C.15)

Inserting this permittivity into the Hamiltonian (Eqn. C.4), we see that the Hamiltonian \( \hat{H}' \) of the perturbed system may be written as
\[
\hat{H}' = \begin{pmatrix}
\frac{i}{\sqrt{\varepsilon_0}} \nabla \times \frac{1}{\sqrt{\mu_0}} & \frac{1}{\sqrt{\mu_0}} \nabla \times \frac{1}{\sqrt{\varepsilon_0}} \\
\frac{i}{\sqrt{\varepsilon_0}} \nabla \times \frac{1}{\sqrt{\mu_0}} & 0
\end{pmatrix} + \begin{pmatrix}
\frac{i}{\sqrt{\varepsilon_0}} \nabla \times \frac{\Delta(r)}{\sqrt{\mu_0}} & 0 \\
0 & \frac{1}{\sqrt{\mu_0}} \nabla \times \frac{\Delta(r)}{\sqrt{\varepsilon_0}}
\end{pmatrix}.
\] (C.16)

We identify the first element of \( \hat{H}' \) as the Hamiltonian \( \hat{H}_0 \) of the homogeneous medium. We identify the second term as the position-dependent perturbation \( \hat{V}(r) \). The total Hamiltonian is therefore written as \( \hat{H}' = \hat{H}_0 + \hat{V}(r) \).

C.5 General Solution

Consider a homogeneous medium of relative permittivity \( \varepsilon_r \) which contains a bath of radiation of frequency \( \omega \). Such a bath will comprise a linear combination of plane wave states which satisfy the dispersion relation \( |k| = \sqrt{\varepsilon_r \omega/c} \). At time \( t = 0 \) we switch on a small perturbation to the permittivity of the form \( \varepsilon_r \rightarrow \varepsilon_r[1 + \Delta(r)] \). Clearly, the initial state of the radiation field is no longer an eigenstate of the Hamiltonian and the radiation will scatter. We seek to determine the time-evolution of the radiation in response to the perturbation.

The time-dependent Maxwell equation in the presence of the perturbation reads
\[
[\hat{H}_0 + \hat{V}(r)]|\tilde{E}, \tilde{H}\rangle = i \frac{\partial}{\partial t} |\tilde{E}, \tilde{H}\rangle.
\] (C.17)

Let us look for a solution in which the state vector is expanded in terms of eigenstates of the unperturbed Hamiltonian. We write
\[
|\tilde{E}, \tilde{H}\rangle = \sum_i \alpha_i(t) |\tilde{E}_i, \tilde{H}_i\rangle = \sum_i \alpha_i(t) \left| \frac{\sqrt{\varepsilon_0 \varepsilon_r}}{\sqrt{\mu_0}} E_i^{(0)} e^{-i(\omega t - k_i \cdot r)} \right|,
\] (C.18)

where we represent the state of the field as a sum over plane wave states, each weighted by a time-dependent coefficient \( \alpha_i(t) \). Plane wave solutions in which the \( E_i^{(0)} \) and \( H_i^{(0)} \) are perpendicular to the wavevector \( k_i \) are naturally divergence-less. We take this to be true and, in doing so, satisfy the Maxwell divergence equations. We substitute the proposed state vector into Eqn. C.17 and take the inner product with a plane wave state \( |\tilde{E}_j, \tilde{H}_j\rangle \) to show
\[
i \dot{\alpha}_j(t) = \sum_i \alpha_i(t) \langle \tilde{E}_j, \tilde{H}_j | \hat{V}(r) |\tilde{E}_i, \tilde{H}_i\rangle.
\] (C.19)
At this point, we explicitly evaluate the action of the operator \( \hat{V}(r) \) on a plane wave state. We write this as

\[
\hat{V}(r)|\tilde{E}_i, \tilde{H}_i\rangle = \left( \begin{array}{cc} 0 & \frac{-i\Delta(r)}{2\sqrt{\varepsilon_0 r}} \nabla \times \frac{1}{\sqrt{\mu_0 r}} \nabla \times \frac{1}{\mu_0} \end{array} \right) \left( \begin{array}{c} \sqrt{\varepsilon_0 r} E_i \\ \sqrt{\mu_0} H_i \end{array} \right)
\]

\[= \left( \begin{array}{c} \frac{-\Delta(r)}{2} \omega_i \sqrt{\varepsilon_0 r} E_i \\ \frac{1}{2\mu_0} \left[ \Delta(r) \nabla \times E_i - E_i \times (\nabla \Delta(r)) \right] \end{array} \right)
\]

\[= \left( \begin{array}{c} \frac{-\Delta(r)}{2} \omega_i \sqrt{\varepsilon_0 r} E_i \\ \frac{-\Delta(r)}{2} \omega_i \sqrt{\mu_0} H_i \end{array} \right),
\]

where on the final line we choose to overlook the contribution of the \( E_i \times (\nabla \Delta(r)) \) term. \( \Delta(r) \) of a typical photonic crystal, quasicrystal or amorphous material is a step-like function which can take one of two possible values. Its gradient is zero everywhere except at the infinitesimally thin material interfaces where it is delta function-like. To make further progress, we neglect these singular derivatives. Substitution of Eqn. C.20 into Eqn. C.19 and evaluation of the inner product then yields the master equation for the scattering rate into a plane wave state \( |\tilde{E}_j, \tilde{H}_j\rangle \).

We see that

\[
\dot{\alpha}_j(t) = \frac{i}{2} \sum_i \alpha_i(t) \omega_i \left[ \varepsilon_0 r E_j^{(0\ast)} \cdot E_i^{(0)} + \mu_0 H_j^{(0\ast)} \cdot H_i^{(0)} \right] \int \Delta(r) e^{-i|k_j - k_i| \cdot r} d^3r,
\]

where we have asserted that the scattering is elastic \( (\omega_j = \omega_i) \). We see that the scattering rate depends on several factors. First, the alignment between the incident and scattered electric and magnetic field pairs is significant. Second, the total scattering rate is a sum over all the possible states \( |\tilde{E}_j, \tilde{H}_j\rangle \) from which photons may scatter into \( |\tilde{E}_j, \tilde{H}_j\rangle \). Third, the scattering rate depends the value of the integral \( \int \Delta(r) e^{-i|k_j - k_i| \cdot r} d^3r \) at the corresponding momentum transfer \( q = k_j - k_i \). This integral is intimately related to the structure factor \( S(q) \) of Eqn. 2.5.

To summarise, I have derived a master equation which connects the rate at which the amplitude of a plane wave state changes to the structure factor of the medium through which the plane wave is propagating. Scattering is induced by a position-dependent perturbation to the relative permittivity which takes the form \( \varepsilon_r \to \varepsilon_r[1 + \Delta(r)] \). We may expect Eqn. C.21 to be applicable in the limit where \( \Delta(r) \) is significantly less than unity and when the photon scattering is elastic.

### C.6 Solution in the Born Approximation

To proceed further with the solution of Eqn. C.21 is challenging. At this point, I make some significant approximations in order to tease out the important qualitative behaviour of the scattering.
Let us simplify the system under consideration by stating that the $xy$ plane is a mirror plane of the structure. The structure is then projected infinitely along the positive and negative $z$ directions. The electromagnetic fields separate into uncoupled transverse electric (TE) and transverse magnetic (TM) polarisation states everywhere in the plane. We consider specifically the case of TE polarised light, in which the $H$ field is polarised along the $z$ axis, and the $E$ field lies in the $xy$ plane.

Consider the scalar products between field polarisation states in Eqn. C.21. For TE polarised modes, the term $H_j(0) \cdot H_i(0)$ may be equated with a constant. The term $E_j(0) \cdot E_i(0)$ depends on the relative orientation of the incident and scattered electric field vectors. For now, let us neglect this directionality entirely and set the scalar product equal to a constant.

Finally, let us apply the Born approximation, and take the initial state of the light field as the driver of any scattering processes. To implement this, we assert that any coefficient $\alpha_i$ that is not associated with a momentum component of the initial light field is negligible. Further, the scattering is weak such that the initial state of the light field is itself unaffected by the perturbation. The summation over $\alpha_i(t)$ in equation C.21 is therefore written as an integral over the coefficients $\alpha_i(k_i; t=0)$ which describe the momentum state of the light field at time zero.

Subject to these approximations, time integration of Eqn. C.21 shows

$$|\alpha_j(t)|^2 \propto |\omega_j K \int \alpha_i(k_i; t=0) \left[ \int \Delta(r)e^{-i[k_j-k_i] \cdot r} d^2r + \alpha_j(k_j; t=0) \right]|^2,$$  \hspace{1cm} (C.22)

where $K$ is a constant and the double integral may be interpreted as the convolution of the initial state of the radiation field with the structure factor.

### C.7 Illustration

I now illustrate that my approximate solution to the Bragg scattering problem reflects the generalised dispersion relation of a low refractive index patterned structure. I show this by numerically calculating the momentum distribution of the light field, as predicted by Eqn. C.22, for an example low refractive index hyperuniform network structure.

To begin, let us specify the initial state of the radiation field at time zero. Let the initial state be a bath radiation of frequency $\omega_0$ in which all plane wave states are equally excited. The radiation satisfies the dispersion relation $\omega_0 = c|k|/\sqrt{\bar{\varepsilon}_r}$ and so we specify the values of the plane wave expansion coefficients at time zero as $\alpha_i(0) = \delta(|k| - \sqrt{\bar{\varepsilon}_r} \omega_0/c)$. The momentum distribution of the radiation field is therefore circular and corresponds to the homogeneous medium case (Fig. 4.2).

Using Eqn. C.22, we now numerically compute the distribution of coefficients $|\alpha_j(t)|^2$ for an illustrative case. We define $\Delta(r)$ to represent the dielectric distribution of a unit vertex density $\chi = 0.49$ hyperuniform network architecture (Fig. 4.7). This structure comprises a mixture of air.
and connected dielectric network of relative permittivity $\varepsilon_r = 2.25$. Its dielectric fill fraction is 55%. We shrink the network to optical lengthscales through multiplication by a scaling parameter $a = 270\text{nm}$. For each frequency $\omega_j$, we generate the coefficients $\alpha_j(t = 10\text{fs})$ by convolution of the initial state of the radiation field $\alpha_i(0)$ with the structure factor-like term. The resulting set of coefficients $\alpha_j(t)$ is azimuthally averaged in the momentum space for comparison with generalised dispersion relations calculated using the spectral function method.

Fig. C.1 presents the result of this calculation. We observe that the predicted momentum distribution models the essential features of the hyperuniform network’s generalised dispersion relation (Fig. 4.9). The effective medium band, which we specified as the initial state of the light field, is visible as a bright diagonal slash from bottom left to top right. The approximate solution predicts the branching of the effective medium band into two around $(ak/2\pi, af/c) = (0.54, 0.42)$; this is in good agreement with the generalised dispersion relation. It is clear that this branching is a result of scattering of the effective medium states by the momentum transfers of the structure factor. Specifically, the set of momentum transfers associated with significant values of the hyperuniform network’s structure factor (Fig. 4.7) defines a relatively narrow annulus. Momentum states of the effective medium are therefore predominantly scattered by a narrow range of momentum transfers; this generates a well defined scattered band.
Bibliography


Bibliography


