Chapter I

Introduction

Look deep into nature, and then you will understand everything better- Albert Einstein

1.1 Background

Vision and colour

Vision is the ability of animals to perceive light and everything around us. It is the light that makes our life meaningful and colourful. Colour, however, is the unique characteristic of human visual system, which is perceived by the stimulation of cone cells in the eye through electromagnetic radiation [1]. Our eyes can distinguish different objects, based on the brightness, hue, saturation or purity of the object [2]. Proper functioning of the eyes has been described by Leonardo Da Vinci, long ago where he compared the eye as a perfect camera obscura [2]. The photoreceptors present in the retina of the eyes, known as 'cones' are sensitive to different colours and hence enable us to recognize light of different wavelength with different intensities. Thus, it is quite interesting to take note of the eye components and its use as a natural camera. Nobel prize winning physicist Sir CV Raman in his scientific papers had very well explained regarding light, vision and colour [2, 3, 4]. The physiology of vision, the colour of flowers has been very nicely explained in his scientific papers [5, 6, 7]. The schematic representation of the eye is shown in Fig. 1.1.

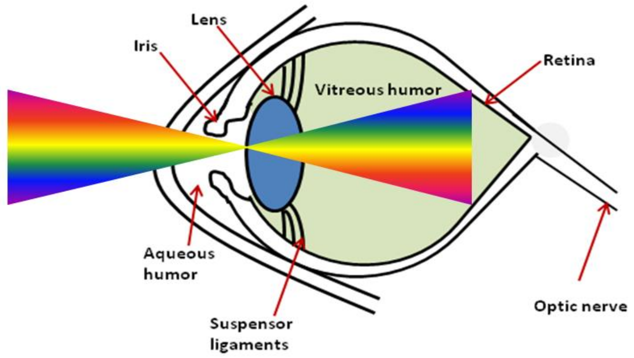

Figure 1.1: Schematic representation of eye, stimulated by em radiation.

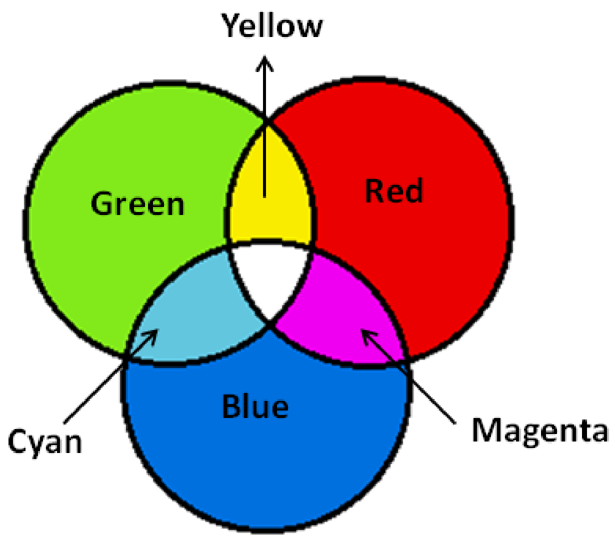

Figure 1.2: Schematic representation of the primary colours and additives.

The concept of colour can be understood from the fact that different objects interact with the incident light in different ways. Depending on the wavelength of light they reflect, absorb/transmit, one can distinguish one colour from the other, with red, blue and green recognised as primary colours. The scheme of colour circles is highlighted in Fig. 1.2.

When we talk about colour, Mother Nature is the obvious choice where beautiful patterns and colours are evolved with abundancy. And, owing to its evolutionary nature, it throws numerous questions to human minds. However, quests can be quenched by befitting, logical reasoning already existing in nature itself. Natural systems are always beautiful not only due to their structural symmetry but also numerous interesting properties that they exhibit for exploitation in different fields [1]. The two most important phenomena that are explicitly exhibited by natural systems are; namely, structural colouration and surface wettability characteristics, which can be treated on the same platform as both these phenomena are as a consequence of the morphology of the surface concerned.

Colour in nature has always attracted us and researchers and scientists are engaged over decades to unravel the underlying mechanisms at large [8]. Basically, two types of colours exist in nature: pigmentary and structural.

While pigmentary colour deals with the chemical composition of the material, structural colour, as the name suggests, indicates the outcome of the physical interaction of light with the surface microstructure and inhomogeneities present in the material [8]. By and large, pigmentary colour is defined as the colour that appears as a result of select absorption of light, and normally observable in dyes, pigments, paints and petals [9]. The pigmentary colouration results as a consequence of energy interaction between light and electronic sub-system, which is quite different from the origin of structural colour. Although study of structural colour was initiated years back, it could find its due importance only recently and particularly, in association with the fast growing field of nanophotonics. The various patterns and structures of nature have been unravelled, which leads to the evolution of structural colour. Structural colours have been observed in numerous natural systems, which include butterflies [7], insects [11], flowers [12], cephalods [13] and aquatic species [14]. For instance, *Lepidoptera* systems possess interesting colours and patterns, which have captivated the attention of researchers in recent years. Understanding these natural creatures will pave a way in fabricating such microstructures for relevant applications that rely on controlled optical and surface properties. The importance of colours in nature can be realised in the fact that it plays a vital role in the evolution of plants and animals. Back in history, the study of structural colour was made by Robert Hooke in the feathers of peacock in *Micrographia* in the year 1665 [15]. Later, Issac Newton later described the iridescent peacock feathers in '*Opticks*' where he attributed the origin of iridescence to the thin transparent parts of the feathers [16]. This was followed by Maxwell and Hertz, who gave us the theory of electromagnetic (em) waves in 1873 and 1884 [8]. Soon, after the establishment of the Maxwell's equations, the optical properties of reflection, refraction, interference and diffraction aspects were well understood both in terms of theoretical treatment and experimental validation. This was followed by a long debate by various scientists from Sir Walter to Lord Rayleigh who gave

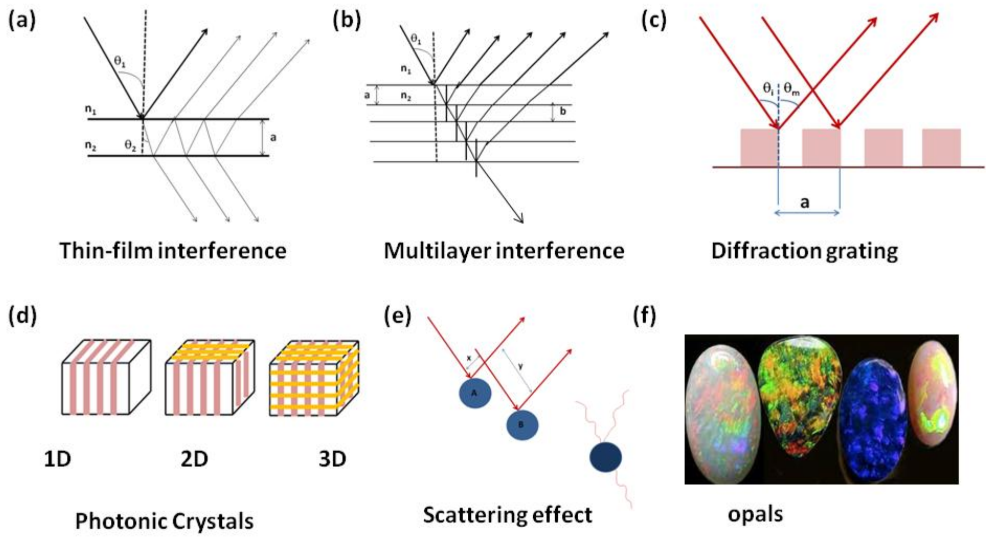

Figure 1.3: Schematic representation of different physical processes illustrating light-matter interaction.

their own views emphasizing structural colour [8]. In 1942, Anderson, Richards and Gentil have investigated the *Morpho* butterfly wing scales, which further enhanced the interest for studying structural colour in extremely tiny structures of nanometer scale [17, 18]. Nevertheless, even today the effort to understand the origin of apparent colour in different natural creatures is quite significant. The general consensus about structural colouration is that, it is purely of physical origin and is a consequence of the interaction of incident light with minute surface-structures of a given specimen of interest. The physical basis responsible for structural colouration can be either due to one or more phenomena such as, thin film interference, multilayer interference, diffraction, scattering and photonic crystal effects [8]. The schematic representation of the above-mentioned processes is depicted in Fig. 1.3.

Thin-film, or multilayer interference is the most common type of phenomenon witnessed in moths and butterflies. Multilayer interference occurs from structures that comprise of stacks of several layers, with alternating high and low refractive indices. Depending on the varying thicknesses, the light of different wavelength will either be reflected, or transmitted/absorbed. The intensity of reflected light will increase with increasing the number of layers for constructive interference. Almost every scale component contributes to the overall process. Furthermore, diffraction effects result because of the presence of parallel slits in the butterfly scales, with the separation between them of the order of wavelength. The presence of photonic crystals in colour-producing natural assemblies is known for years. These are somewhat complex structures, often come with a strong periodic arrangement and comprising of materials of alternative refractive indices. Peacock feathers are known to be the best example of photonic crystals found in nature. In natural systems, photonic crystals can be tuned for biological purposes; such as camouflage, predation, signalling and communication. Moreover, iridescence adds value to colouration principles. Typically, it is linked to the appearance of different colours, when viewed at different angles [19]. Each of the above-mentioned processes has its own importance and significance to colours exhibited by the natural systems. Most importantly, natural colour-producing systems do not exhibit colour via a single mechanism but rely on the mixed mechanisms as a combinatorial effects. Onslow in the year 1923, had observed iridescence in more than 50 animals, mainly to uncover meaningful insights as regards, surface colour and structural colour [20]. Merritt *et. al.* have studied the reflectance spectra of the *Morpho* butterfly, and described exhibition of colour in terms of thin-film interference [21]. In *Lepidopteran* scales, the origin of structural colour, was attributed to thin-film/multilayer interference. Despite the fact that *Morpho* butterflies have been studied by Kinoshita *et. al.* in great detail, still numerous issues remain untouched till date. Infact, the studies on structural colour were mostly focussed on the butterfly wings and insect covers, but its scope can be extended to aquatic animals and also to plant kingdom. To be specific, in plant kingdom, the structural colour is chiefly associated with the flowers [22-25], fruits [26] and leaves [27]. The main purpose of structural colour in flowers is to attract bees and bumble bees [23, 24]. In fruits, the intense colouration serves as a means to attract birds and animals. Although the biological function of structural colour is known to be mainly for inter-species communication, there exist numerous applications in industries, such as, paint, textile, automobile, display, cosmetics etc. [8]. Structural colours in nature have fascinated the research community for decades, however in 1940, the measurements made by scanning electron microscope (SEM) has intrigued new dimension to the study of structural colouration [8]. Understanding natural creatures with the help of scanning microscopy images, infact, have unravelled the role of miniscules of matter and nanostructures in the structural colouration process. Since then, the colour producing structures have been explored, and new ones are discovered, yet there are lot more to be done in this field. Biomimicry is an effective way for the optimisation of design of artificial structures. The potential applications of structural colouration were tracked three decades ago, with the discovery of photonic crystals in nature [28]. Morpho butterflies are not only studied in terms of structural colouration but also great efforts have been made by the researchers for their practical use through biomimicry. The combined effects of the underlying physical phenomena make it the best example of structural colouration. But it also imparts significant challenges to the researchers involved in the fabrication of artificial structures inspired from naturally occurring designs.

Wetting and de-wetting

Wettability, is an interesting, yet complex problem. Wetting phenomena can be observed almost everywhere in nature. Wetting and spreading are two important aspects which have both small and large scale relevance [29]. In large scale, the applications are in the fields of oil recovery [30], in depositing pesticides/insecticides in plants [31], along with water drainage in highways [32] and cooling of industrial reactors. On smaller scale, uses can be broadened in the field of microfluidics, nanoprinting, raincoats, painting and so on [33]. Because of the immense potential and truly with interdisciplinary nature, it has attracted research community across the globe in the field of physics, chemistry as well as biology. One of its significant use has been observed in self-cleaning and anti-fogging applications [34-36]. Speaking about wetting-dewetting, it can be broadly divided into three categories: superhydrophilic surface (0°-10°), hydrophilic surface (10°-90°), hydrophobic surface (90°-150°). Here, the values within the parenthesis represent range of contact angles and that for CA, greater than 150°, it can be termed as the superhydrophobic surfaces. Superhydrophilic state basically represents complete wetting, superhydrophobic state, on the other hand, denotes complete de-wetting (drying). It is interesting to observe the moths and insects which fly in rain, without getting wet. Wetting basically refers to the spreading of liquid on the surfaces and consequently, intrusion into the micropores present in the system. In fact, the wetting-dewetting phenomenon is pertinent to several industrial applications and the understanding of which could lead to the emergence of numerous functional materials. When a liquid comes in contact with a solid, it is governed by three phases: solid-liquid, liquid-vapour and solid-vapour. The drop shape is essentially dictated by the nature of chemical composition and surface morphology of the specimens. There are evolutionary benefits associated with the low wetting phenomena in the natural system. The water repulsion property allows cleaning the dirt from the surface along with the ability of an organism to inhibit it from being slowed down due to water/rain. The governing factors for these water-repellency properties are the surface topography and chemical composition. However, in case of rough surface structure, the surface composition plays the dominant role. In natural systems, the varied patterns are responsible for such superhydrophobic properties, which involve plants and insects and even pseudo-superhydrophobic organisms. Primarily, two main and basic models

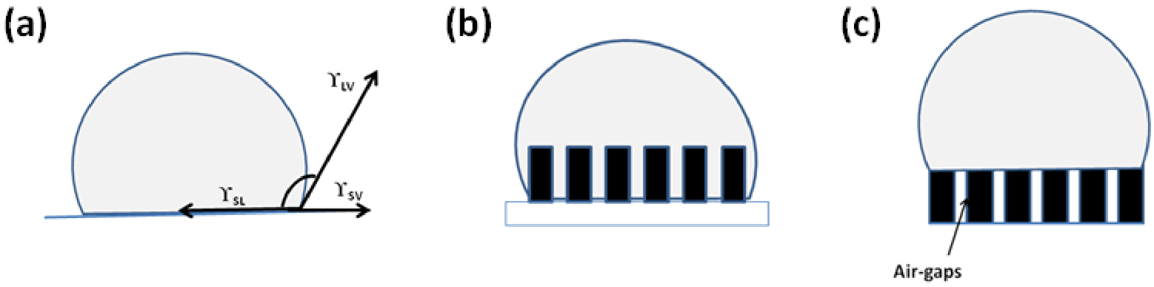

Figure 1.4: Schematic representation of water droplet on (a) smooth surface (Young's model) and rough surface highlighting (b) collapsed state (Wenzel model) (c) suspended state (Cassie-Baxter model).

which help to assess the wettability nature are: Wenzel and Cassie-Baxter models [37, 38]. For a smooth surface, the Young's equation can be applied to explain the hydrophobicity as given below [39]:

$$\Upsilon_{LV} \cos\theta_y + \Upsilon_{SL} = \Upsilon_{SV} \qquad (1.1)$$

$$\cos\theta_y = (\Upsilon_{SV} - \Upsilon_{SL}) / \Upsilon_{LV} \qquad (1.2)$$

where Υ_{LV}, Υ_{SL} and Υ_{SV} are the respective surface tension of liquid-vapour, solid-liquid and solid-vapour phases, respectively (Fig. 1.4 (a)). The Wenzel and C-B models essentially describe contact angles for diverse rough surfaces. The Wenzel model is normally applicable to surfaces where the droplet makes its way into the grooves, and therefore signifies the collapsed state (Fig. 1.4 (b)). In contrast, the Cassie-Baxter model generally describe the suspended state of a water droplet on a pillar-like rough surface, where it does not fill up the grooves and air is likely to get entrapped beneath the water drop (Fig. 1.4 (c)).

The Wenzel model can be expressed mathematically as:

$$\cos\theta_w = r\varphi \cos\theta, \qquad (1.3)$$

where θ_w and r_φ are the Wenzel contact angle and roughness factor respectively. The C-B equation can be written as:

$$\cos\theta c = \varphi(1 + \cos\theta) - 1, \qquad (1.4)$$

where, θ_c, θ and φ are the measured C-B angle, Young's angle and water-solid fraction respectively.

The collapsed and suspended states are shown schematically in Fig. 1.4 (b) and (c); respectively. Apart from these, there exist other transitional regimes of hydrophobicity/superhydrophobicity, *viz.* Lotus and gecko states and a transitional state between Cassie and Wenzel [40]. In addition to the Cassie and Wenzel states, four different wetting regimes have been proposed by Cha *et. al.*, which have been termed as: Cassie state, Wenzel state, Cassie-Wenzel, Wenzel-Cassie, Wenzel-Wenzel [41]. Schematic representation of these states is depicted in Fig. 1.5 (a), (b), (c) and (d) and the equations representing Cassie-Cassie, Cassie-Wenzel, Wenzel-Cassie and Wenzel-Wenzel are described through equations 1.5, 1.6, 1.7 and 1.8 respectively. The above states have been described based upon dual surface roughness depending upon the contact mode. Cassie-Cassie state is described by the contact mode where the liquid is suspended upon the micro and nano pillars without getting wet.

The equation is represented by:

$$\cos\theta_{CC} = \varphi_m \varphi_n(\cos\theta + 1) - 1 \text{ (Cassie-Cassie)} \qquad (1.5)$$

where, φ_m and φ_n represents the solid-water fraction for both micro and nano roughnesses. Cassie-Wenzel state depicts the contact mode where the liquid wets the nanopillars but sits on the micropillars, and is given by:

$$\cos\theta_{CW} = \varphi_m (r_n \cos\theta + 1) - 1 \text{ (Cassie-Wenzel)} \qquad (1.6)$$

where, r_n represents the roughness factor of the nanopillars

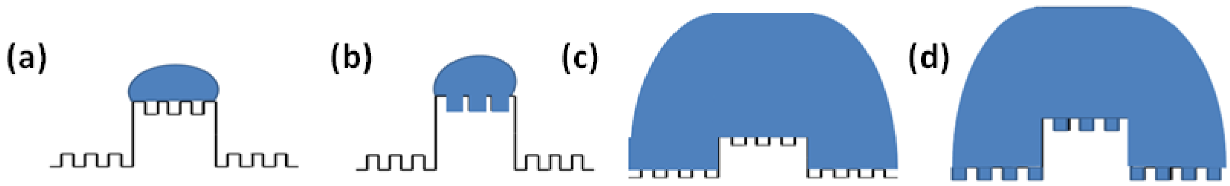

Figure 1.5: Schematic representation of water droplet on (a) Cassie-Cassie state (b) Cassie-Wenzel (c) Wenzel-Cassie state (d) Wenzel-Wenzel state.

The Wenzel-Cassie mode is determined by the state of the liquid droplet when it wets the micropillars, but sits on the nano asperities and Wenzel-Wenzel mode depicts the state of liquid drop which wets both the micro as well as nano pillars. The respective equations are given by:

$\cos \theta_{WC} = (\varphi_n - 1 + r_m) \cos\theta + \varphi_n - 1$ (Wenzel-Cassie) (1.7)

and, $\cos \theta_{WW} = (r_m + r_n - 1) \cos\theta$ (Wenzel-Wenzel) (1.8)

where, r_m represents the roughness factor of the micropillars

Because of these complexities, static CA value is not sufficient in understanding the wettability features in great detail. In this regard, analysis of contact angle hysteresis (CAH) is quite important to help visualizing the complete picture of wettability. When a liquid droplet comes in contact with a rough surface, it is apparent that it will have several equilibrium positions instead of a single value [34]. The surface energy value would exhibit adhesion hysteresis, with maximum and minimum CA values known as advancing (θ_{adv}) and receding angles (θ_{rec}); respectively. The measured CA of a sessile (immobile) drop always lies in the range, $\theta_{rec} \leq \theta \leq \theta_{adv}$. The difference between the advancing and receding CA is known as contact angle hysteresis (CAH). Adhesion hysteresis or CAH is an important parameter that explains the state of hydrophobicity/hydrophilicity. A higher CAH value indicates a higher extent of adhesion, which is referred as 'rose-petal effect', and is quite different from the 'lotus-effect'. The Lotus effect depicts the state of the water droplet, with a higher CA (>90°) but a lower adhesion. This is the reason, why a liquid droplet on the lotus leaf rolls off the surface, easily removing all the dirt from it and is the consequence of self-cleaning mechanism, which has inspired many technological applications. Different groups have made different opinions about these aspects. Li and Amarfazli did not support the fact that a surface could be superhydrophobic while displaying a higher adhesion to the liquid droplet [42]. Bormashenko, on the other hand, have reported on the transition between different wetting regimes, depending upon the morphology of the surfaces [43]. From the application point of view, superhydrophobic materials are quite in demand, chiefly because of the self-cleaning behaviour. This concept has been utilised in artificially fabricated materials, which includes, water-repellent and breathable clothing, umbrellas that are water-repellant, paints, building materials, epoxies, and silicones [44]. With more and more advancements in this field, newer products can be realized day-by-day by adopting hydrophobic/superhydrophobic principles suitably.

1.2. Insects, moths and butterflies

Odanata is an order of insects that mainly includes dragonflies (*Anisoptera*) and damselflies (*Zygoptera*). There are three main families of Dragonflies, viz. *Aeshnoidea*, *Cordulegastroidea* and *Libelluloidea* which are again divided into subfamilies. Damselflies belong to the *Coenagrionidae* family, which is further divided into several sub-families. Regarding structural colour, the dragonfly and damselfly wings have been studied in connection to wings and body [45]. Kinoshita *et. al.* have explained beautifully regarding structural colouration in distinctly different natural systems. Mason, in 1926 described the blue colour of damselfly as the Tyndall effect, and was attributed to the scattering of light by fine particles already embedded in a chitinous material make up [8]. The research started thereafter, Veron *et. al.* have investigated the electron microscopy images of several *Odanata* species [46]. Prum *et. al.* have carried out the experiment on two *Odanata* species, viz. *Enallagma civile* and *Anax junius*, and found the reflection maxima at 475 nm and 460 nm for the *E. Civile* and *A. Junius* respectively [47]. On the other hand, the *Lepidoptera* system mainly comprises of butterflies, moths and skippers, which exist as many as, 150000 species. They are not only widely distributed but also widely studied. The butterfly wings have dazzled us, through their beautifully designed colour patterns. Their complex morphologies, ecological behaviour and evolutionary optimisation have been studied by researchers in different aspects. The number of *Lepidopteran* species changes year after year, making it a large taxon divided into families and several sub-families. However, the main three superfamilies of butterfly are: *Hesperioidea*, *Papilionoidae* and *Hedyloidea* [48]. Among these large superfamilies, *Papilionoidae*, known as “true butterflies” is a large one, divided into four families: *Papilionidae*, *Pieridae*, *Lycaenidae* and *Nymphalidae*. The classification of insects and butterflies is highlighted below in Table 1.1 and 1.2 respectively [8, 49].

Kingdom- Animals

Phylum- Arthropoda

Class- Insect

Table 1.1: Classification of insect family upto 9 orders [8]

Order	**Family**
Coleoptera	Beetles
Dictyoptera	Cockroaches, mantids
Diptera	True flies
Ephemeroptera	Mayflies
Lepidoptera	Butterflies, moths
Odanata	Dragonflies, damselflies
Hymenoptera	Ants, bees, wasps
Orthoptera	Grasshoppers, Katydids
Phasmids	Stick-insets

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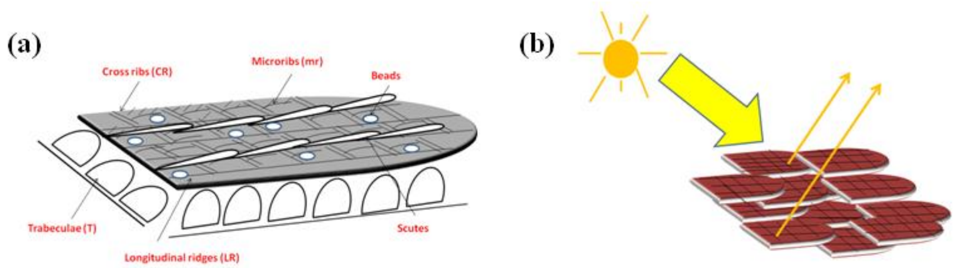

Figure 1.6: (a) Schematic representation of butterfly scale with the microscopic scale components (not to scale) (b) Schematic representation of light interaction with the butterfly scales.

Table 1.2: Classification of butterfly families along with their characteristics [49]

Family	**Common name**	**Characteristics**
Hedylidae	American moth-butterflies	Small, brown, like geometrid moths, antennae not clubbed, long slim abdomen
Hesperiidae	Skippers	Small, darting flight, clubs on antennae hooked backwards
Lycaenidae	Blues, coppers, hairstreakers	Small, brightly coloured often have false heads with eyespots and small tails resembling antennae
Nymphalidae	Brush-footed/ four-footed butterflies	Reduced forelegs, four-legged, brightly coloured
Papillionidae	Swallowtails	Have tails on wings
Pieridae	Whites and allies	White/yellow or orange
Rionidae	Metalmarks	Metallic spot on wings, coloured with black, orange and blue

The lepidopteran scales, the scale components, longitudinal ridges (LR), Cross ribs (CR), scutes, flutes and trabeculae contribute largely to the overall optical properties. The schematic diagram of the lepidopteran scale including schematic representation of interaction of light with the butterfly scale is shown in Fig. 1.6(a) and (b) respectively. Due to structural complexity and diversity, understanding of structural colour in these systems becomes a challenging task. Nevertheless, the *Morpho* butterflies are studied in great detail; owing to their availability and attractive blue-iridescent behaviour [50]. Ding et.al [51] have investigated the wings of *Morpho Peleides* butterfly and have found that the cover scales play an important role in producing structural colour. The study provided a deep insight regarding the nature of the reflection peaks in the reflectivity spectra. This study paved the way towards smart biophotonics where the functional material which are responsive to the environment, such as light, electric field, humidity and gases [48]. Apart from normal reflectance, butterflies also exhibit polarisation sensitive reflectance features. The polarised light is widely utilised by the butterflies for biological purpose. The utilisation of polarised light is important because it enhances the adaptive capability of the butterflies in extreme environments and is also favourable for navigation, signalling functions and communication purposes [50]. As a wide variety of butterflies show polarisation sensitive reflectance features, the origin and underlying mechanisms have drawn significant interest among scientists.

Dragonflies and damselflies have fascinated us by flying in the rain without getting wet. So it is interesting to take note of their wing characteristics as regards to wetting-dewetting features apart from reflectance properties. As already mentioned, the dewetting phenomenon in butterflies, dragonflies and in several other natural systems have not only fascinated us but also lead to the fabrication of artificial superhydrophobic surfaces with potential applications. There exist numerous reports on the wettability features of the butterfly wings, insect covers, birds' feathers etc. [51]. N. D. Wanasekara *et. al.* have investigated the wettability properties of four butterfly specimens, *viz. Phoebis Philea*, *Greta Oto*, *Antheraea* and *Actias Luna* with different microstructural features. The water CA of *Actias Luna* is found to be highest due to the combination of low dense fork shaped structure and tiny hair-like structure [52]. Moreover, studies have been carried out on the Namib desert beetle (*Stenocara* sp.) [53]. This can collect water from the fog-laden wind through the wax-free entity (hydrophilic) found at the top of its bumps, while the troughs on the rest of the elytra surface have a hydrophobic character [52]. It has been reported that the texture of the wing surface can enhance its hydrophobicity, but not all elytra with micro-scale features have hydrophobic characteristics. As for butterfly wings, there is a strikingly diverse array of irridescence mechanisms in beetles, and they are referred to as 'living jewels'. The structural colouring of elytra has been speculated to help with camouflage, aposematic colour and thermoregulation. Some beetles' elytra colours change with the absorption of moisture as a result of variations in humidity, temperature and environmental conditions. Studies of structural and optical property in biological systems may deepen our understanding on specific issues and offer natural solutions, thereby advancing the possibility for designing novel artificial materials.

1.3. Avian and Aquatic systems

Structural colour is also observed in avian as well as in aquatic systems. The classification of avian system is shown in Table 1.3 [54]. Among birds, structural colouration is very prominent and can be seen in a wide variety within a given class. Basically, the presence of melanin granules in the barbules of the birds' feathers is primarily responsible for structural colouration in birds. The granules arrange themselves regularly to produce structural colour [8]. Earlier, the melanin granules have been systematically classified into five types by Durrer *et. al*.[55, 56]. Peacock feathers have attracted researchers due to their beautiful colour and pattern for centuries [57]. Peacock feathers are the best example of naturally occuring photonic crystals. Despite several conflicting theories between the surface and structural colour, the colouration mechanism in peacock feathers could be understood by their sophisticated microstructural make up revealed through electron microscope, and clarified by Durrer *et.al.* [8]. Apart from peacock feathers, structural colouration is realised in other bird varieties', *viz*. pheasants, ducks, humming birds, pigeons, kingfishers, cotingas, jays etc. [57, 58, 59]. In each of these, colouration mechanism is different and likely to be caused by single, or multiple effects. Aquatic species/ marine systems also exhibit ubiquitous structural colouration. Under-water organisms, which comprise of aquatic plants, sea animals etc. exhibit brilliant colouration, and often possess iridescence characteristics. It has been found that the ventral scale surface of sprat fish contains a reflecting layer which exhibits copper-coloured reflected light and greenish transmitted light [60]. Similarly, there are other varieties of fishes and creatures which exhibit multilayer structure for facilitating multilayer interference colours. Not surprisingly, apart from structural colouration, wettability property in avian system is also quite prominent. It has been observed that there are varieties of birds (Kingfisher etc.) that can dive deep into the sea-water to prey on fish. This activity is facilitated by the de-wetting property of birds' feathers where hydrophobicity nature is attributed to the chemical composition and the microstructural topography of the feathers [61]. A water droplet on the bird feather does not wet the feather because of the reason that air is entrapped in the solid-liquid interface, which is formed within the barbules. This air gap is referred to as plastron, which restrains the feather to get completely wet, and hence contribute to the water-repellency characteristics [62, 63].

Table 1.3: Classification of birds' order and type [54]

Order	**Birds**
Passeriformes	warblers, shrikes, birds of paradise, sunbirds sparrows, weavers, bulbuls
Tinamiformes	tinamous
Galliformes	turkey, pheasants, chicken, quail
Anseriformes	ducks, geese, swans
Piciformes	woodpeckers
Trogoniformes	trogons
Coraciiformes	kingfishers, hornbills
Colliformes	mousebirds
Cuculiformes	cuckoos
Psittaciformes	parrots
Apodiformes	swifts, humming birds
Musophagiformes	turacos
Strigiformes	owls
Columbiformes	pigeons, doves
Gruiformes	cranes, bustards
Ciconiiformes	egrets, herons, hamerkop
Caprimulgiformes	nightjars
Charadriiformes	puffins, plovers
Falconiformes	eagles, falcons, kestrels, hawks
Gaviiformes	loons, divers
Pelecaniformes	pelicans, darters, cormorants,
Phoenocopteriformes	flamingoes
Procellariiformes	albatrosses
Struthioniformes	ostriches, rheas, emu, kiwis

1.4. Plant system

In nature, structural colour is typically associated with the animal kingdom, but rarely studied in plants [27]. The classification of the plant kingdom with the type of plant is shown in Table 1.4 [64].

Table 1.3: Classification of plant families with type [64]

Plant Family	**Type**
Compositae (Asteraceae)	Largest family of flowering plants
Gramineae (Poaceae)	Grass like plants
Cyperaceae	Grass like plants with sedges
Liliaceae	Group of several families
Leguminosae	Tropical trees and temperate herbs
Labiatae	Aromatic herbs and shrubs
Solanaceae	Poisonous herbs and shrubs
Malvaceae	Trees (Basswood/chocolate tree), Shrubs (cotton), Herbs (mallow)
Rosaceae	Trees (apple), Shrubs (rose), Herbs (strawberry)

Our work

Flowers are the reproductive structures of flowering plants (angiosperms) [65]. In most angiosperms, flower colouration arises from pigments [66, 67]. Changing the chemical composition of the pigments, varying their concentration and mixing them can all generate a broad colour palette. The intensity of the reflected colour however depends on the shape of the epidermal cells containing the pigments [68]. The cell shape and tissue build up focuses the light onto the pigment rich regions inside the cell and enhances scattering between neighbouring cells [68-71]. The structural color in flowers arises mainly from diffraction gratings [23,24]. The diffraction gratings are regular arrays of diffractive elements that periodically modulate the phase and/or amplitude of the incident light wave. In flowers, diffraction gratings consist of ordered striations or ridges that form on the epidermal cells. The formation of these striations during the development of the petals is not fully understood, but one possible mechanism is the buckling of the cuticle (a waxy layer that covers the surface of the plant epidermis) during the anisotropic petal growth [72].

The wettability studies in plants are known since Neinhuis and Barthlott have discovered the "*Lotus effect*" [73]. Superhydrophobic surfaces are common in plant system, which infact, led to the popular "*Rose-petal*" effect [74]. Superhydrophobic surfaces in plants have several implications that are bestowed upon these organisms. To be specific, de-wetting phenomena has relevance owing to its hierarchical microscale (> 1 μm) and nanoscale structures (below 200 nm) that offer desired surface roughness [75]. Understanding these structures help us in translating ideas for mimicking and fabricating artificial micro-structures with improved hydrophobicity. However, the works of Neinhuis, Barthlott, Bhushan and Koch have thrown light on the superhydrophobic nature of numerous plant systems [27, 32, 73, 76-78]. The waxy cuticular plant structure that is responsible for dewetting features is classified into two main categories. The first category describes the films and layers, which form a smooth homogenous layer [36]. The second category of the plant system is more relevant to superhydrophobic surfaces, which consist of different waxy morphologies, like platelets, tubules, rodlets etc. [36]. However, the superhydrophobic surfaces in plants have been attributed to the hierarchical morphology, which consists of dual composition, both nano and micro-scale features. The lotus-leaf exhibits superhydrophobicity, with microscale papillae covered with nano wax tubules [36].

1.5. Motivation

After an extensive literature survey on naturally occurring systems of biological origin, it has been realised that, along with specific applications, fundamental insight can be profoundly enriched in the area of biophotonics and soft matter physics. Both these aspects have attracted the attention of researchers and scientists across the globe largely in artificial systems. However, biophotonic structural colouration and wettability features in delicate natural systems need intensive investigation, which is presently lacking. Yet, there is a lot to explore in this upcoming field, which is coined as 'softonics' that would selectively bridge soft matter physics and photonics. The work can be expanded by choosing systems from animal kingdom, insects to aquatic and avian systems and also other colourful butterflies. Fabrication of artificial structures with such controlled microstructural features can be a reality by mimicking and understanding natural systems ensuring structure-property relationship. A detailed knowledge of these fantastic structures would greatly help in possible in mimicking and fabricating components to meet technological and industrial needs and to benefit society at large.

1.6. Thesis objective and structure

We have concentrated on the two important and interesting properties of natural systems, namely, structural colour and wetting-dewetting phenomena. From insect kingdom, we opted to explore different orders of animalia; *Anisoptera*, which includes dragonfly (*Gynacantha Dravida*) and damselfly (*Pseudagrion Microcephalum*), *Lepidoptera*, which includes butterflies, belonging to *Nymphalidae*, *Pieridae*, *Papilionidae* family. Each of these specimens has different physical structure and activity. Among plants, we have chosen multicoloured flowers, *viz*. three varieties of rose flowers belonging to *Rosacea* family, namely, White rose (*Rosa chinensis var spontanea*), Light Pink rose (*Rosa chinensis var minima*) and Dark Pink rose (*Rosa chinensis var minima*); three varieties of Hibiscus flowers belonging to *Mallow* family (*Malvaceae*) viz. Red, Pink and yellow (*Hibiscus rosa sinensis*).

This thesis is a collection of facts, phenomena and experimental analysis as regards structural colouration and wettability properties of several natural systems, spread over seven chapters and followed by appendices. The *Chapter I* essentially deals with the background, literature survey and motivation behind the work, along with the thesis objectives highlighted at the end.

Chapter II discusses the physical characterisation tools and techniques executed in various studies. As for the microstructural and morphological analyses, optical and scanning electron microscopy (SEM) technique is employed for viewing at different magnifications. Moreover, normal and variable incident angle dependent reflectance features have been studied using Shimadzu and PerkinElmer UV-Vis-NIR spectrophotometers, with integrating sphere attachment whenever desired. Since, numerous natural systems are sensitive to polarized light, therefore, it is important to take note of the polarisation dependent reflectance features. In this regard, we have investigated the polarisation dependent features using a set of polaroids (Holmarc optics), to acquire s and p-polarisations for certain systems. The degree of polarisation for various specimens has also been estimated. The reflectance curves have also been illustrated through the use of 1931 CIE diagram/ chromaticity diagram. In this colour space, the reflected wavelength is converted to chromaticity coordinates (x, y), which could help us locating colour spread in a more precise manner. Apart from the optical studies, we have carried out the wettability studies both in terms of static contact angle (CA) as well as dynamic CA features as per requirement. In this regard, a custom-made and advanced contact angle meter set up (Kyowa Interface Science Co. Ltd.) have been employed.

In *Chapter III*, we have discussed bifunctional reflectance features and hydrophobic properties of the dragonfly and damselfly wings belonging to same, *Odanata* order. To be specific, each part of the wing, viz. basal, middle, distal and edge parts have been worked out. The data acquired have been analysed in conjunction with simple treatment. At equilibrium, the Wenzel and Cassie-Baxter modes have been considered on equal footing and theoretically limiting hydrophobic response which has been predicted for a maximum change of CA, $\Delta\theta \sim 10.1°$. On the other hand, empirical formulae derived from the experimental data sets have been provided. Moreover, the reflectance features have been interlinked with the surface roughness of the wings. The study paved a way for correlating optical with the surface microstructure and roughness of the natural systems, which has immense value while fabricating artificial make-ups and designs meant for specific uses.

In *Chapter IV* we highlight the optical and wettability features of three distinctly different white appearing butterfly wings (*Lepidoptera* order but different sub-families) emphasizing on the angle dependent and polarisation features. To be specific, in this chapter, we discuss the evaluation of structural color and surface wettability features of the white admiral (WA) (*Limentis Camilla*), large white (LW) (*Pieris Brassicae*) and dark blue tiger (DBT) (*Tirumala Septentrionis*) butterfly wings on a comparative basis. Prior to comparing white parts of all the wing-types, white and brown parts of the admiral butterfly wing were considered independently as regards imaging and reflectance measurements. Despite the fact that the brown part is seen to be structurally ordered, the white part offered a higher reflectance response owing to the presence of irregular scales and micro-beads that are mainly responsible for coherent multi-scattering events. While sharing a common optical trend, however, both the white and brown wings have displayed an improved reflectance feature after adequate ethanol uptake. The rough surface of the wing is believed to be optically smooth after insertion of ethanol into the tiny air gaps of the scale microstructure. On comparing white parts of the three butterfly specimens, we ascertained that the micro-beads are not necessarily responsible for the white coloration in each case. Moreover, the butterfly specimens have substantial pigmentary components, which possessed periodic arrangement of scales but differed in microstructural makeup and distribution. While reflectance response is increased for the WA butterfly wing, it is repressed for the LW and DBT wing after ethanolic treatment. Furthermore, the role of ethanol uptake to structural coloration has been visualized through the chromaticity diagrams, which are apparently altered for different specimens. Apart from the normal reflectance measurements, angle-dependent and polarisation-sensitive reflectance features of the three specimens are assessed. The de-wetting responses of the three specimens are exploited and consequently, roughness and solid-water fractions have been noted. Amongst the three specimens, the LW butterfly specimen exhibited a lower static CA of 100°.

In *Chapter V*, the surface wettability features and optical properties of three varieties of *Rosacea* have been discussed. This section deals with the extensive studies of microstructure-based wettability and reflectance responses of three varieties of Indian *Rosaceae* (*Rosa*) cultivars, *viz*. white (W) rose (*Rosa chinensis var spontanea*), light pink (LP) rose (*Rosa chinensis var minima*) and dark pink (DP) rose (*Rosa chinensis var minima*). As for wettability, static and dynamic (advancing and receding) CAs have been measured, for each type of the matured rose petals. The surface roughness factors (r_{φ}), which are largely dependent on the micro-papillae assembly within the rose petal, are estimated to be, 2.74, 2.27 and 2.94 in case of W, LP and DP petals; respectively. Whereas, the respective contact angle hysteresis (CAH) values are measured as, 42°, 27° and 59°. In order to exploit structural colouration through the reflectance characteristics, the specimens were dipped in three types of media of different refractive indices (*RI*), *viz*. ethanol (*RI*=1.36), propanol (*RI*=1.39) and glycerine (*RI*=1.47) for about 24 h. Upon ethanol and propanol adsorption, light pink (LP) and dark pink (DP) roses showed unusually similar reflectance patterns over a wide range of wavelengths, thus indicating a common microstructural share and structural colour contribution. The discolouration effect due to liquid immersion has also been discussed. The wetting-dewetting and structural colouration in natural systems, to a great extent, are dictated by the surface structure and solid-liquid and liquid-air interfaces, not only offer fundamental interest but also give ample scope for mimicking in artificial designs of specific interest.

Chapter VI explains the reflectance features of the three varieties of Chinese rose specimens, *viz.* red, pink and yellow appearing Hibiscus flower, belonging to *Mallow* family. It is known that, the optical properties can be manifested in two ways either by changing the R.I. or by changing the dimension of the structural parameters. In this regard, here we have attained this by modifying the refractive index (R.I.) of the petals, or changing microstructure as a result of aging/natural drying which is largely caused by physiological processes. The overall R.I. has been changed inserting the petals in methanol (R.I.=1.32), ethanol (R.I.=1.36), propanol (R.I.=1.39) and glycerine (R.I.=1.47). Next, petals were allowed to dry for four days, so as to cause micro-morphological changes in the petals, causing wrinkles and cracks on the petal surfaces. Assessing the wettability properties of the fresh petals has led to some interesting features of the hibiscus flowers. Amongst the three flowers, the red hibiscus petals showed a higher static water CA of 110.7° and a low CAH value of 25.13°. The structural colouration and surface-wettability properties are elaborated.

Chapter VII discusses the conclusions drawn from the present study, limitations, potential applicability and future scope of the research work.

The significance of structural color and wettability features in natural systems is expected to deliberate numerous scope for generating and mimicking artificial designs which have immense potential in the field of softonics.

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