Chapter VII

Conclusions and future directions

Comprehensive conclusions

Natural systems are found to exhibit two distinct, yet important phenomena: structural colouration and de-wetting property. It is important to understand these two properties simultaneously, because of their potential applications in various fields apart from fundamental interest. Structural colouration finds applications in sensing, light emitting sources, paints and in several other areas [1-3]. Efforts have been made by researchers to visualize these properties for decades, and eventually utilize them for fabricating artificial structures as per requirement keeping in mind next-generation demands. Although substantial progress has been made, there are lot to be explored. Moreover, de-wetting phenomena exhibited largely by the natural systems have many applications in various fields [4]. However, to mimic such structures, it is of utmost importance to first take note of the already existing structures quite precisely, as regards chemical composition and their distribution over a surface.

The thesis is an outcome of the investigation of natural systems, which include dragonflies, damselflies, butterflies and flowers. Care has been taken to address the above mentioned properties in the considered systems. The dragonfly and damselfly wings are transparent and the specimens are special in the sense that, dragonfly wings are kept fully extended and stay flat away from the body when at rest, while the damselfly wings are held back together across the body crossed. Unlike many other insects, a dragonfly is fully dependent on its wings for movement since it cannot walk with the help of legs. Usually, the time of flight of a dragonfly is comparatively larger than that of a damselfly species. Our work demonstrates an attempt to connect surface roughness with dewetting and reflectance responses after evaluating a simplified model on roughness factor and water-solid fraction in dragonflies and damselflies. We noticed that, r_φ and φ tend to follow a linear relation that gives r_φ = 1.47 in the limit, $\Delta\theta < 10.1^\circ$, latter being recognized as the difference in angle between the measured CA over a surface to that of the CA (~105°) known for a smooth surface [5]. Our experimental data, however, revealed empirical relations which predicted higher r_φ values, particularly when $\Delta\theta$ is large. Experimentally, we observed that while moving from the basal to the distal region, the microstructural parameter tends to decrease (and nanostructure roughness increase) [6,7], as a result of which a higher r_φ, and water CA can be witnessed. While the overall reflectance response of the distal segment was believed to be stronger than that of the basal part, the edge parts of the dragonfly and damselfly wings exhibited exponential associated growing trends with increasing wavelength. The relative reflectance response, corresponding to ~494 nm and 370 nm peaks, gets nearly doubled for the edge specimen as compared to the distal and basal parts. The edge- specimen, which comprises of rectangular shaped, periodic microstructures, displayed carotenoid based, two broad peak maxima at ~422 nm and ~494 nm. The surface roughness which arises through the distribution of oblate-shaped nano-fibrils was believed to be the basis of sub-surface volume scattering.

Whiteness in butterflies have been rarely discussed in literature, we have made a study in three butterflies with white stripes, complete white and white-spotted wings, namely; white admiral (WA) (*Limentis Camilla*), large white (LW) (*Pieris Brassicae*) and dark blue tiger (DBT) (*Tirumala Septentrionis*). We have evaluated structural color in the 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 multi-scattering events. While sharing a common optical trend, however, both the white and brown wings displayed an improved reflectance feature after 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 white coloration in each case. Moreover, the butterfly specimens which have substantial pigmentary components, possessed periodic arrangement of scales but differed in microstructural makeup and distribution. The incident angle dependent reflectance spectra of WA, LW and DBT specimens suggest that the LW has virtually no dependency on the incident angle due to the presence of *pterin* pigments. Finally, the role of ethanol uptake in structural coloration has been visualized through the chromaticity diagrams, which essentially depict apparent spread of reflectance points in colour space. Polarised spectra, to a great extent, showed a uniform degree of polarisation for the DBT specimen. We have also studied the hydrophobicity response in these specimens. The WA butterfly shows higher hydrophobic response, with high WCA value and high CAH. This indicates wetting effect which can be linked to the *rose-petal* effect.

We have reported 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 advancing and receding contact angles have been measured, for each type of 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. Moreover, the respective contact angle hysteresis values are measured as, 42°, 27° and 59°. In order to exploit structural colouration through the reflectance characteristics, the specimens were dipped in three different 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 have displayed unusually similar reflectance patterns over a wide range of wavelengths, thus indicating a common microstructural share and structural colour contribution.

Apart from rose petals, we have explored the bifunctional properties of the three varieties Hibiscus flowers (*Malvaceae*) viz. red, pink and yellow appearing belonging to *Mallow* family. The optical properties can be manifested in two ways either by changing the R.I. or by changing the dimension of the structural parameters. Here, we have evaluated them employing two different conditions: by changing the refractive index (*R.I.*) of the petals, which has been done by dipping the petals in methanol (*R.I.*=1.32), ethanol (*R.I* =1.36), propanol (*R.I* =1.39) and glycerine (*R.I* =1.47) and secondly by allowing petals to dry for four days. The natural drying in conjunction with physiological changes result in morphological change in the petals, causing wrinkles and cracks on the surface. It may be noted that the petal is made up of cuticular layer, which undergoes compressive stress and strain as a result of drying, and because of its visco-elastic nature [8]. We have also studied the angle dependent and polarisation sensitive reflectance features. The angle dependent spectra showed wavy patterns for all the specimens, when the incident angle varies in the range 15°-75°. All the three samples show unusually similar patterns for corresponding to an incident angle of 15° and more specifically for the red and pink hibiscus. At an incident angle of 30°, the overall reflectance feature is maximum for all the specimens. For yellowish hibiscus petal, we observed a linear rise in reflectance in the range 400-600 nm. In consistency with the general rule, from the spectral feature, the *s*-polarised light shows higher reflectance response relative to p-polarised one for all the three specimens. The degree of polarisation is greater for pink than red and yellow hibiscus. The degree of polarisation also shows a constant value, thereby, indicating uniform polarisation characteristics over the complete (visible) wavelength range, unlike butterfly specimens (*Chapter IV*). Assessing the wettability properties for the fresh petals has led to some interesting features of the hibiscus flowers. Amongst the three flowers, the red hibiscus petals showed higher static water CA of 110.7° and a lower CAH value of 25.13°. Through the extensive studies spread over 6 chapters, now we arrived at the following conclusions.

- ✓ A theoretical relation between r_φ and φ has been derived which is found to be valid for $\Delta\theta<10°$.
- ✓ The reflectance response and the hydrophobic features of the wings are correlated via surface roughness. The surface roughness which arises

through the distribution of oblate-shaped nano-fibrils was believed to be the basis of sub-surface volume scattering.

- ✓ Three butterfly specimens with different impressions of white colour are analysed and each of these possess different surface morphology which result in different optical features, in terms of normal reflectance, angle dependent response as well as polarisation dependent reflectance response..
- ✓ Also, the wettability features in the butterfly specimens have been analysed in conjunction with the different wetting modes.
- ✓ Among flowers, *Indian Rose* and *Chinese Rose* have been analysed, in terms of reflectance response and de-wetting phenomena. Both these specimens exhibit different characteristics due to their different morphologies.

Future scope and direction: There is lot to explore in this upcoming field, leading to a new area called 'softonics' that connects soft matter physics and photonics. The work can be further enhanced by choosing 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. Possible fabrication of these would contribute significantly in several technological and industrial applications. The moth-eye structure is known to be the most advanced field of biomimicry due to their low reflection response in a wide range of wavelengths and angle of incidence. Nanoimprint lithography (NIL) is the frequently applied technique for fabricating such structure [9, 10]. Similarly, artificial superhydrophobic surfaces are fabricated mimicking *rose* and *lotus effect*. There are recent reports of fabrication of self-cleaning polymer by mimicking leaf microstructures [11].

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