Nano-Optics in the Biological World: Beetles, Butterflies, Birds, and Moths

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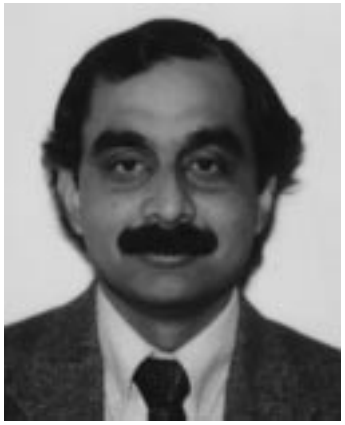

Mohan Srinivasarao was born in India in 1959. He received his B.Sc. (Applied Sciences) from the University of Madurai in 1979 and M.Sc. (Applied Chemistry) from the University of Madras in 1981. He received his M.S. (Polymer Science) in 1985 and Ph.D. in Chemistry in 1990, both from Carnegie Mellon University. He worked on flow and magnetic field induced instabilities of a rodlike polymer forming a nematic phase in solution under the supervision of Professor Guy Berry. He spent a few years as a postdoctoral fellow with Professor Richard S. Stein at the University of Massachusetts at Amherst before moving to AT&T Bell Labs where he worked on polymer-dispersed liquid crystals for display device applications. He has been an Assistant Professor at North Carolina State University since 1995. Presently, his research interests span color science including nanostructures in the biological world, physics of liquid crystals, flow properties of soft condensed matter, tracer diffusion in complex fluids, and light microscopy.

I. Introduction

In a world that is as colorful as ours, it is not surprising to find that colors produced in nature by a variety of creatures have attracted the attention of scientific giants such as Newton, Michelson, and Lord Rayleigh, just to name a few. It is perhaps somewhat surprising to find that there are still many questions remaining to be answered with regard to color produced by animals, like butterflies and beetles, and what that color means to them. This gets us into the realm of color vision and color perception in the animal world. This review will primarily focus on color production in nature purely by physical means such as diffraction, interference, and scattering but will not include those due to dyes, usually referred to as biochromes or pigments, thereby eliminating color due to absorption or emission of light.

Brilliant, iridescent colors found on the bodies and wings of many birds, butterflies, and moths are produced by structural variations and have been the subject of study for centuries. Newton was the first to suggest that such brilliant iridescent colors in birds and insects might perhaps be due to the presence of thin-film structures, as he had observed the color-producing properties of such thin films. In his "Treatise on Opticks" (London, 1704), Newton goes on to elaborate as follows:

> The finely coloured Feathers of some birds, and particularly those of Peacocks Tails, do in the very same part of the Feather appear of several Colours in several positions of the Eye, after the very same manner that thin plates were found to do... and therefore arise from the thinness of the transparent parts of the Feathers; that is, from the slenderness of the very fine Hairs, or *Capillamenta*, which grow out of the sides of the grosser lateral branches or fibers of those Feathers.

With the development of the wave theory of light, it became clear that interference phenomena played a key role in the color of bird feathers and insects. It was recognized that such colors arise from physical effects such as interference or diffraction as opposed to colors that are normally produced due to the presence of chromophores, which absorb or emit light. Such brilliant colors have been described as metallic colors due to the *saturation or purity* of the colors

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produced. Common examples of physical colors are some butterfly wings,[1] the color of Indigo snake skin,[2] hummingbird feathers,[3,4] arthropod cuticles,[5−7] gemstones such as opal,[8−11] and some crystals such as potassium chlorate.[12] While the origins of such colors are well understood, the properties of color and color specification have not received much attention.

It is worthwhile at this point to ask the question "What is color?". One can turn to *The Oxford English Dictionary* for help, which states "The particular colour of a body depends upon the molecular constitution of its surfaces, as determining the character and number of light vibrations it reflects. Subjectively, colour may be viewed as the particular sensation produced by the stimulation of the optic nerve by particular light vibrations... This sensation can be produced by other means, such as pressure on the eye-back or an electric current". In order for us to see or perceive object color, purely from a physical standpoint, three things are essential: a light source, an object that it illuminates, and the eye (and brain) to perceive the color. To specify color according to a universal standard, the eye is replaced by a photodetector for making quantitative measurements of the light that would have reached the eye. However, this color specification depends on spectral color-matching functions (spectral tristimulus values) provided by panels of human observers.

One often refers to light that is colored and we do so as well in the following pages; however, this is done with the understanding that there is no "colored" light. Newton (1730) knew that there is no such thing as a colored light. In his own words:

> And if at any time I speak of Light and Rays as coloured or endued with Colours, I would be understood to speak not philosophically and properly, but grossly, and accordingly to such conceptions as vulgar people in seeing all these experiments would be apt to frame. For the rays to speak properly are not coloured. In them is nothing else than a certain power and disposition to stir up a sensation of this or that colour.

Therefore, when we use terms such as a green-colored light or red-colored light in the following pages, we hope not to create any confusion about the colors of light.

This review mainly deals with a variety of colors produced in the biological world focusing on a variety of interesting objects that include butterfly wings, bird feathers (humming birds, peacock feathers, duck feathers), all of whose colors are due to interference, the Hercules beetle (use of color for camouflage), moths which produce color both by interference and diffraction, interference filters in the compound eyes of butterflies, and biological analogues of cholesteric liquid crystals (optically active scarab beetle cuticles). The case of cholesteric liquid crystals will serve to illustrate the elegance with which metallic colors are produced by the scarab beetles. Iridescent color has also been discovered in the fossils of the well-preserved fossil site,[13,14] Burgess Shale, in the Canadian Rockies. I will also attempt to discuss some of the issues related to the color perception of butterflies. The color space that the insects of our world use is far richer and larger than our own, since many of these insects or animals can have as many as five photoreceptors,[15] as opposed to our trichromatic visual system. The implications of such a large color space will also be discussed toward the end of the article.

A common unifying theme, in considering this diverse set of materials, is the nature of color generation. In all of these materials, color is generated in the absence of chromophores, primarily by structural variations resulting in interference, diffraction, or scattering. Since we will be interested in specifying color generated by physical means, it becomes necessary to review the language of color science. There are three main attributes that need to be considered for specifying color: *hue*, *saturation*, and in the case of nonself-luminous objects *lightness or brightness*. Knowing these, it is possible to predict (approximately) the appearance of colors to an average observer. Of course, we will run into some difficulty due to the fact that the colors human beings "see" are not necessarily the same as when these animals view those same colors!

This paper is organized as follows: a section that deals with colorimetric considerations, a brief description of color due to thin films, a section that elaborates on the structural variations that give rise to coloration of butterfly wings, beetle exocuticles, bird feathers, moths, and fossils of the Burgess Shale, and a section on selective reflection of cholesteric liquid crystals. This will be followed by a brief discussion of the visual system of butterflies, the optics of the eye (and some interference phenomena), and the "color perception" of butterflies. We include a discussion of the spreading effects of color and how then color might be perceived and why such colors are important, i.e., the biological significance. We end with certain questions that are worth asking about such methods of color production and whether such methods could be useful for any applications. Strategies for creation of such structures will be outlined when appropriate.

II. CIE Color Space

The acronym CIE stands for *C*ommission *I*nternationale de l'*E*clairage, the International Commission on Illumination. The color notation bearing this name was accepted in 1931, based on 2° observer data, and provides an international language for the science of colorimetry.[16] The system developed by CIE is psychophysical, a description of the nature of the response of "average" observers (where the field of view is limited to 2°, thus defining the 2° standard observer) to a color stimulus on which perception is based. The system is based on two premises: the Young−Helmholtz concept that all colors can be matched by additive mixing (with certain exceptions, as discussed below) of appropriate amounts of three primary lights (*with the restriction that none of the primary lights can be matched by mixtures of the other two*) and Grassman's laws for additive color mixtures. One of the latter states that the luminance of any additive mixture of lights is the sum of the

luminances of each of them, regardless of the spectral power distributions.

Additive mixing of lights occurs when two lights of different colors are combined (added together) before it reaches the eye. A common example of additive mixing occurs in stage lighting, where two colored lights are combined to produce a different color. In the case of subtractive mixing, the term refers to the removal of a part of the spectrum of light by the object (colorants, for example) before the light reaches the eyes of the observer. In either case, a physical description of the light reaching the eye of an observer, together with the measured additivity of color mixture, then provides the basis for a numerical description of perceived color.[16]

The perception of isolated color is a psychological phenomenon, and it is three-dimensional in nature.[16] The attributes that describe color in a three-dimensional space are the quantities that specify the color, which in the case of isolated colors are hue, brightness, and saturation. *Hue* is that quality we often describe by the words red, yellow, blue, green, and so on. It is what distinguishes one spectral color from another, for example, all blues differ in hue from all yellows, irrespective of other possible similarities. *Brightness* is a quality of color that can be classified as equivalent in lightness to some member of a series of gray samples ranging from white to black. *Brightness* also refers to the sensation of the overall intensity of a light, ranging from dark, through dim, to bright and dazzling. *Saturation* represents the extent to which a given color differs from a gray of the same brightness. In other words, it corresponds to the purity of a color. A very saturated color has most of the intensity of that light close to the dominant wavelength, while an unsaturated color would have contributions from many other wavelengths.

The term isolated color is used to denote the perception of color from a uniformly colored area, say of a painting, that is not influenced by the colors that surround the painting.[16] Colors are often influenced by their surroundings, leading to a psychological phenomenon known as simultaneous contrast, which artists use to achieve specific color effects. An example of an isolated color is provided by a green railway signal glowing from a distance at night in the absence of other lights. It can, however, be argued that the darkness acts as a border for the light source, thus providing a time-varying input that allows for the perception of color. It is well-known that a *truly isolated color* cannot be perceived[16a] in the absence of a time-varying or spatially-varying signal to the eyes. Kaiser and Boynton[16b,c] describe a rather simple experiment to illustrate this point. Consider the two halves of a table tennis ball placed over the open eyes which are illuminated with a uniformly colored light. At first the color is perceived, but it fades in a matter of a few seconds, reappearing on closing and reopening the eyes, only to fade once again, thus suggesting that a truly isolated color cannot be perceived. In this article the term isolated color is used only to refer to the experiment where observers are confronted with a bipartite field (or a split field), one-half of which is illuminated with the color to be matched, usually a monochromatic light of wavelength λ, with a circular black surround to determine the color-matching functions. One may choose to use the term aperture color in this context.

As we will see, hue and saturation can be represented by the chromaticity coordinates x, y on the chromaticity diagram, while the brightness (or lightness) is given by the third dimension, as shown in Figure 1. When the lightness or brightness (given by

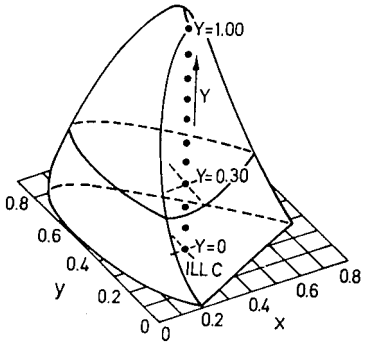


Figure 1. 1931 CIE (x, y, Y) color space (with MacAdam limits) for a nonself-luminous object illuminated by a CIE standard light source. (Reproduced with permission from ref 16. Copyright 1987 Springer-Verlag.)

Y, the luminous reflectance) is unity, the *only color* that can be perceived is the color described as white. As the brightness decreases, more colors are possible, as can be seen clearly from Figure 1. The limit of attainable color at each Y value defines the limits of possible colors, the MacAdam limit.

As can be clearly seen from Figure 1, at $Y = 0$ the MacAdam limit coincides with the spectrum locus and the colors (for all hues) are of maximum darkness—black; thus, the bottom of the diagram should be represented by a black point and not by a "range of black" as is suggested by the figure.

The perception of any color by an observer depends on the nature of the light that enters the eye (best described by the spectral power distribution) and the observer's response to that light. Thus, if the relative spectral power distribution of the light source is known [P(λ), where λ is the wavelength] and if the relative spectral reflectance of the object is also known [(R(λ)) or transmittance], the relative spectral distribution of the light entering the eye can be computed rather easily, simply by multiplying the spectral power distribution of the light source by the spectral reflectance.

An analytical description of the response of a human observer to color can be described in terms of the relative amounts of three primary colors which must be mixed additively to match each wavelength of the visible spectrum. Such descriptions have been obtained by carrying out experiments as illustrated in Figure 2, where the observer is confronted with a bipartite field (or a split field), one-half of which is illuminated with the color to be matched, usually a monochromatic light of wavelength λ. The task for an observer is to color match light of each wavelength illuminating one-half of circle with appropriate amounts of light from three different primary sources focused on the other half of the circle. The amounts of each primary required to match each wavelength

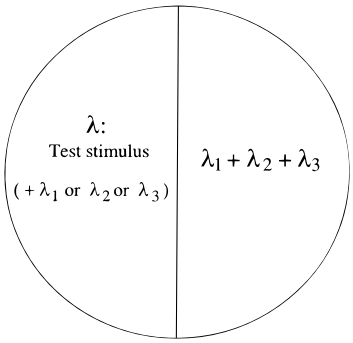


Figure 2. Illustration of the method for generating the color-matching functions.

are called the observer color-matching functions and there are three, one for each primary at each single wavelength.

Such measurements with a field of view of 2° have been made, leading to the color-matching functions plotted in Figure 3, thus defining the 1931, 2° standard observer. This can be done for all lights of all wavelengths if the human observer is sometimes allowed to add one of the primary lights to the light to be matched and that primary was assigned a negative color-matching function. To avoid using negative numbers, a special set of mathematical lights, *X*, *Y*, and *Z* lights, were created to replace the actual red, green, and blue lights. These primaries are designated *X* for red, *Y* for green, and *Z* for blue, all of which are positive numbers, and the color-matching functions are designated as $\bar{x}$, $\bar{y}$, and $\bar{z}$, respectively. The amounts of *X*, *Y*, and *Z* light needed to match a color are called the color's tristimulus values.

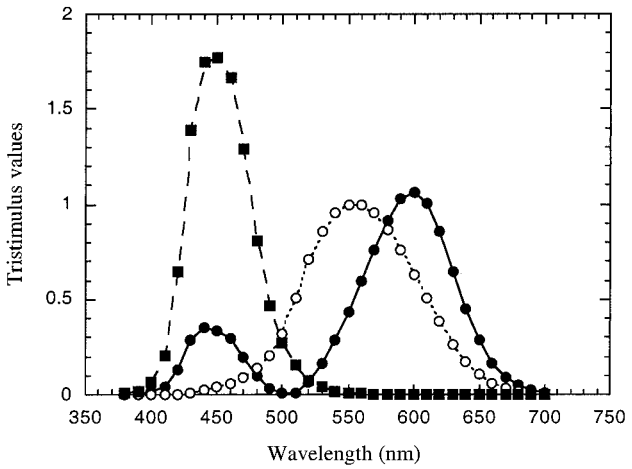


Figure 3. Color-matching functions of 1931 CIE standard 2° observer. The filled circles, open circles, and filled squares represent $\bar{x}$, $\bar{y}$, and $\bar{z}$, respectively. (Data from ref 18.)

The color perceived by an observer is then represented by the integral of the product of the color-matching functions of the standard observer, the relative spectral reflectance of the object viewed, and the relative spectral power distribution.[17] This process is illustrated schematically in Figure 4.

The magnitude of the integrated products are called the tristimulus values and is described by the following set of equations:

$$X = k \int R(\lambda)P(\lambda)\bar{x}(\lambda)\,d\lambda \quad (1a)$$

$$Y = k \int R(\lambda)P(\lambda)\bar{y}(\lambda)\,d\lambda \quad (1b)$$

$$Z = k \int R(\lambda)P(\lambda)\bar{z}(\lambda)\,d\lambda \quad (1c)$$

where *k* is a normalizing factor defined as $k = 100/\int P(\lambda)\bar{y}\,d\lambda$ and $d\lambda$ is the wavelength interval. The product of the color-matching functions and the spectral power distribution of the (standard) light sources are published as tables in many books on color science.[16,18] Hence, in order to obtain the tristimulus values, one needs to make a measurement of the reflectance (or the transmittance) of the object that one is interested in. When each of the tristimulus values for a measured color is divided by the sum of the three, a fraction attributable to each primary is obtained, and since these need to add up to 1, two fractions are sufficient to describe the "chromaticity" of the object, Figure 5. These fractions are called the chromaticity coordinates and are designated by lower case *x*, *y*, and *z*

$$x = \frac{X}{X+Y+Z} \qquad y = \frac{Y}{X+Y+Z}$$

$$z = \frac{Z}{X+Y+Z} \quad (2)$$

In principle, any two of the three chromaticity coordinates, almost always *x* and *y* in practice, may be plotted in rectangular coordinates for comparison. Plotting the pure spectrum colors in this way gives us the limit locus, called the spectrum locus, inside which all colors must fall. Such a chromaticity diagram is shown in Figure 5. The chromaticity diagram can be used to demonstrate the linearity of additive mixing of colors. Consider two colored lights

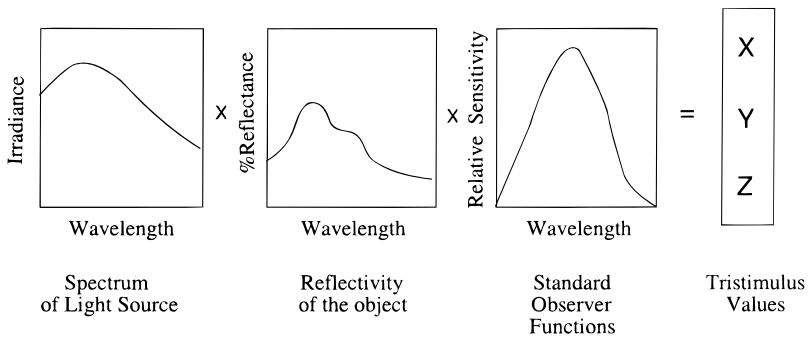


Figure 4. Procedure for calculating the tristimulus (*X*, *Y*, *Z*) values.

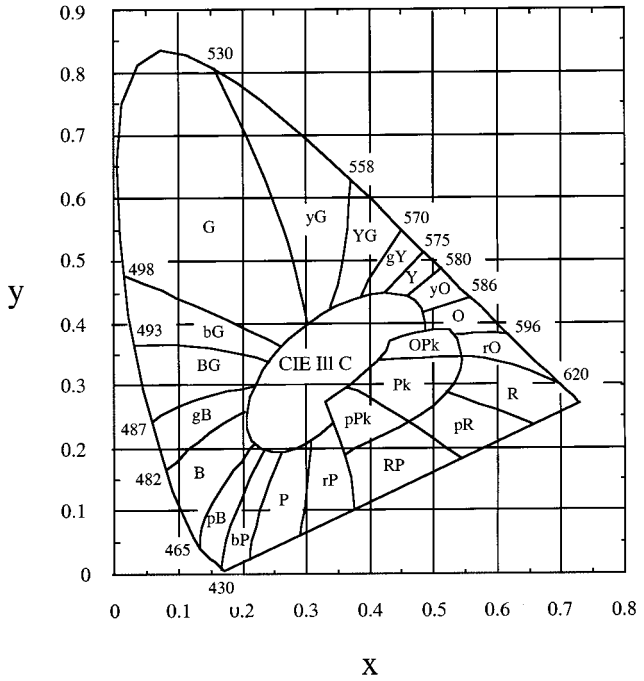


Figure 5. Various colors are represented in the CIE chromaticity diagram. (Adapted from ref 16.) The various colors are abbreviated as follows. pB: purplish blue; B: blue; gB: greenish blue; BG: blue green; G: green; yG: yellowish green; YG: yellow green; gY: greenish yellow; Y: yellow; yO: yellowish orange; O: orange; OPk: orange pink; rO: reddish orange; Pk: pink; R: red; pR: purplish red; pPk: purplish pink; RP: red purple; rP: reddish purple; P: purple; bP: bluish purple.

that are mixed to produce a third color. The *x*,*y* values for the mixture color will lie on a line joining the chromaticity coordinates of the two colors that were mixed. When three colored lights are mixed additively, all the colors that can be produced using those three colors must lie within the boundaries of the triangle connecting the *x*,*y* coordinates of the individual colors. This triangle defines the *color gamut* that is available using these three colored lights. When calculating the chromaticity coordinates for a given color, the closer the value to the spectrum locus, the more saturated the color is. It will be shown below that colors produced by cholesteric liquid crystals are saturated colors and lie close to the spectrum locus.

The above discussion of the quantitative description of color is applicable to animals that have a trichromatic visual system, like the standard human observers. In this review, we will have occasion to discuss the color space for animals that have more visual pigments than do humans. In the case of animals, like butterflies, it is hard to describe what color vision means. Our own experience of this colorful world tells us that to have color vision is to see colors. The problem now becomes one of extending and translating this operational definition to other animals. We will return to this topic later in this review [see section VI].

III. General Methods of Color Production

In this section, we describe briefly the various methods of color generation that use primarily physical optics. The discussed methods are the following: (a) interference, (b) diffraction, (c) dispersive refraction, (d) scattering, and a combination of the above. We will see examples of all of these methods with the exception of dispersive refraction which, therefore, will not receive a detailed discussion. However, the reader is referred to a delightful book by Nassau.[19]

A. Colors Due to Interference

Interference colors are observed in a variety of situations having to do with thin films. A common example is the colors of soap films seen in sunlight. Such colors are produced by light waves interfering after reflection from the two surfaces of the soap film. Such interference colors are quite prevalent in the animal kingdom.

In this discussion, we will primarily deal with coherent light. Although the light source under consideration might be incoherent in comparison to a laser light source, however, the coherence length of such incoherent sources are on the order of a few micrometers.[20] We shall be interested in reflection of light producing colors only from films that are a few micrometers thick, and therefore, one can use the theory of interference developed for coherent sources.

It is well-known that interference of light from two incoherent beams, as in the case of two headlights of a car, does not occur. This is due to the fact that there is no phase relationship between the two sources of light waves, since their phases change so rapidly. However, it is a common observation that soap films produce quite beautiful colors.[21,22] This is due to the fact that the sunlight reflected from the two surfaces interferes constructively, thus behaving as two independent coherent sources. One sees interference colors when the film thickness is on the order of the wavelength of visible light. Therefore, to manipulate colors, one changes the film thickness or the viewing angle. The theoretical foundation necessary for understanding the interference phenomena that is observed from thin film structures is provided by the Fresnel equations.[20] For a detailed discussion of the subject pertaining to optical effects from submicrometer structures, see the article by Pfaff and Reynders in this thematic issue.

Consider the situation displayed in Figure 6, where

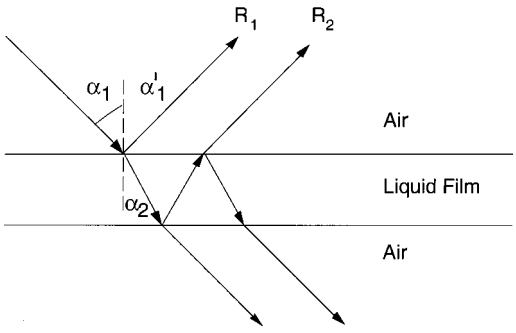


Figure 6. Interference produced by reflection at a liquid (soap film) air interface. R_1 and R_2 are the reflectivities with α_1 as the incident angle, α_1' the reflected angle, and α_2 the angle of refraction.

the film thickness can be varied. When the reflections from the two surfaces add in phase or constructively interfere, a large net reflection is created that the

observer "sees" as certain colors. Constructive interference occurs due to the following reasons: The Fresnel reflection coefficient is positive for a light beam reflected from a soap film (liquid) at the liquid−air interface and is negative for reflection from the air−liquid interface. A negative reflection coefficient can simply be thought of as a beam undergoing a 180° phase shift between the incident and reflected light waves. Therefore, the 180° phase shift suffered at the air−liquid interface together with the 180° phase shift suffered in a round-trip through the quarter-wave plate (the thickness of the film is $\lambda/4$, with λ being the wavelength of the light beam) leads to perfect constructive interference for all the reflected waves.

The optical path difference experienced by the two rays that interfere constructively is simply equal to the extra distance the light beams had to travel in the medium. Making reference to Figure 6, this turns out to be $2n_2d \cos \alpha_2$, where n_2 is the refractive index of the film and α_2 is the angle of refraction. In addition to the optical path difference of $2n_2d \cos \alpha_2$, there will be an additional path difference of $\lambda/2$ due to the additional phase difference π that occurs at the air−film interface whenever an incident light beam is reflected by a medium of higher refractive index than the initial medium. Thus, the effective path difference between the two rays is $2n_2d \cos \alpha_2 + \lambda/2$. Consequently, if $2n_2d \cos \alpha_2 + \lambda/2 = n\lambda$, where n is an integer, the two rays will interfere constructively and give an intensity maximum. On the other hand, if $2n_2d \cos \alpha_2 + \lambda/2 = (n + 1/2)\lambda$, one has destructive interference resulting in zero intensity. Since by implication we have assumed the amplitudes, A, of the two beams to be equal, the resulting amplitude of the reflected wave will be given by A_r, where $A_r = A + Ae^{i\delta}$ with the phase difference, δ, given by $\delta = (2\pi/\lambda)(2n_2d \cos \alpha_2 + \lambda/2)$. The total reflected intensity is $I_r = A_rA_r^*$, and is equal to $4A^2 \cos^2 \delta/2$. This equation can be rewritten in terms of the reflectivity R to have the following form $4I_iR \sin^2\{(2\pi/\lambda)n_1d \cos \alpha_2\}$, where I_i is the incident light intensity. One can, of course, rather easily eliminate the angle of refraction from the above formula to show the dependence of intensity on the incident angle.

Making reference to Figure 6 and to quantify the above discussion leads us to the task of deriving expressions for the reflected and transmitted light intensity. Fresnel equations predict the amplitude (r) of the reflected light from thin-film structures and can be written as[23]

$$r_s = \left[\frac{n_1 \cos \alpha_1 - n_2 \cos \alpha_2}{n_1 \cos \alpha_1 + n_2 \cos \alpha_2}\right] \quad (3)$$

$$t_s = \left[\frac{2n_1 \cos \alpha_1}{n_1 \cos \alpha_1 + n_2 \cos \alpha_2}\right] \quad (4)$$

where n_1 and n_2 are the refractive indices of the two media in which light propagates and r_s and t_s are the amplitudes of reflection and transmission for S-polarization of the incoming light beam. Here, polarization is defined with respect to the plane of incidence of the light; S-polarization implies the polarization is perpendicular to the plane of incidence, where the plane of incidence is defined as that plane which contains both the incident and reflected light beams. Similar expressions can be derived for P-polarization. The reflected intensities for both the polarizations are related to the amplitudes in a simple manner and can be written as $R_s = r_s^2$ and $R_p = r_p^2$. The propagation of the light waves can be traced simply by realizing that the beams obey Snell's law, $n_1 \sin \alpha_1 = n_2 \sin \alpha_2$, and that the incident angle is equal to the reflected angle.

In the case of normal incidence, that is, $\alpha_1 = \alpha_2 = 0$, we have $r_p = (n_1 - n_2)/(n_1 + n_2)$ and $t_p = (2n_1/(n_1 + n_2))$. The results for S-polarization are, of course, indistinguishable from those for P-polarization at normal incidence. When using unpolarized light, the intensity is the sum of the intensities of the two polarized components. The reflected intensity for normal incidence is then given by the well-known expression[20]

$$R = \{(n_1 - n_2)/(n_1 + n_2)\}^2 \quad (5)$$

Equations 3−5 relate the amount or fraction of incident light reflected or transmitted as a function of (i) the angle of incidence α_1, (ii) the angle of refraction α_2, and (iii) the refractive indices. One can eliminate the angle of refraction using the laws of refraction and obtain expressions that are a function of incidence angle. The desire to have expressions as a function of incidence angles is motivated by the fact that the colors from a butterfly wing are angle dependent. The Fresnel formulas for S-polarizations can be written as[23]

$$r_s = \frac{\cos \alpha_1 - (n_2/n_1)\sqrt{1 - [(n_1/n_2) \sin \alpha_1]^2}}{\cos \alpha_1 + (n_2/n_1)\sqrt{1 - [(n_1/n_2) \sin \alpha_1]^2}} \quad (6)$$

The above equation reduces to eq 5 when the incident angle is equal to zero, which is gratifying. In the above discussion, we have taken into account only the two waves that are most important. In principle, there will be an infinite number of waves producing interference which can be represented by R_1, R_2, R_3,... and similarly for transmitted waves T_1, T_2, T_3,... (see Figure 7)

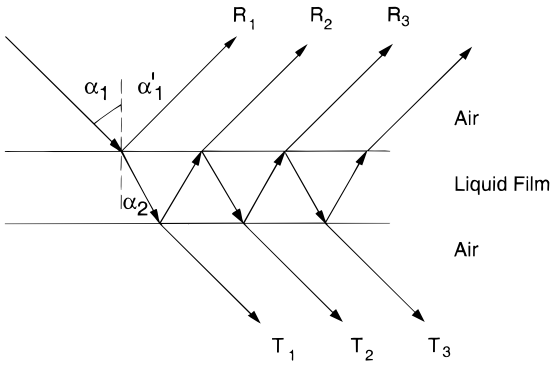


Figure 7. Schematic diagram of interference produced by multiple reflections (and transmissions) of a single incident wave.

To get the angular dependence one can easily eliminate the angle of refraction and write the optical

path difference in terms of the incident angle. The wavelength of maximal reflectance can then be easily shown to be given by

$$\lambda_{max} = \left(\frac{4n_2 d}{2n+1}\right)\left(1 - \frac{{n_1}^2}{{n_2}^2}\sin^2 \alpha_1\right) \quad (7)$$

This expression clearly shows that the reflectance is shifted to shorter wavelengths with increasing angle of incidence, consistent with all the interference colors, including those due to butterfly wings.

B. *Colors Due to Diffraction*

When a propagating beam encounters an obstruction, part of the energy of the incident beam is scattered. However, when the dimensions of the obstruction become comparable to the wavelength of the propagating beam, the effects of scattering become more easily observable since the beam is scattered at larger angles with respect to the direction of incident beam. If the obstruction is periodic or for that matter if periodic variation of any parameter that affects the propagation of a light beam (or wave) exists, energy is scattered into various discrete directions or diffracted orders. A structure that functions in this fashion is referred to as a "diffraction grating". Each of the diffracted orders that have been diffracted by the grating has a direction, and the amount of deviation from the incident beam depends among other things on the periodicity of the grating and its relation to the wavelength. In this way, a grating disperses a variety of wavelengths to form a spectrum. It is as if a grating performs the same function as a prism, but in many respects it does so better and far more conveniently. There are many examples in nature where the interaction of light with matter is used to produce brilliant colors for a variety of purposes, which include for colorful displays, warning predators, or courtship, among others. Often in the examples we will consider the periodicity approaches that of the wavelength of visible light and, therefore, leads to interference among waves so that such gratings produce color. We will have the opportunity to deal with gratings where the periodicity is of the order of the wavelength of visible light, thus giving rise to gratings called a "zero-order diffraction grating" (see section IVB).

In its simplest form, a diffraction grating consists of a large number of parallel grooves drawn on a sheet of transparent material like glass or a polymer film. The diffraction of a light beam passing through a grating is analogous to the case of double-slit interference. Figure 8 schematically depicts diffraction from a series of slits of width s and separated by a distance d. The diffraction angle is given by the *grating equation* which can be written as $d \sin \theta = m\lambda$, where $m = 0, 1, 2,...$ Here, m is the order of the diffracted beam. When light is incident at some arbitrary angle α, then the grating equation can be written as $d(\sin \theta - \sin \alpha) = m\lambda$.

When one considers the case of multiple slits, as is necessary when considering diffraction from a grating, the intensity distribution due to interference

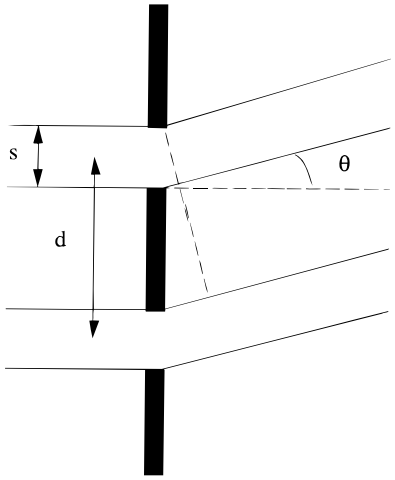


Figure 8. Schematic diagram of a diffraction grating showing slit width s, slit separation d, and the diffraction angle θ.

of the diffracted beams can be written as[24]

$$I_\theta = I_0 \frac{\sin^2(N(\pi/\lambda)d \sin \theta)}{\sin^2((\pi/\lambda)d \sin \theta)^2} \quad (8)$$

where N is the number of slits. The total intensity distribution of the diffracted beams is given by the product of the contribution due to diffraction (not shown) and that due to interference and can be written as[24]

$$I_\theta = I_0 \frac{\sin^2((\pi/\lambda)s \sin \theta)\sin^2(N(\pi/\lambda)d \sin \theta)}{((\pi/\lambda)s \sin \theta)^2 \sin^2((\pi/\lambda)d \sin \theta)^2} \quad (9)$$

It should be noted that the intensity is proportional to $\sin^2(N(\pi/\lambda)d \sin \theta)$, so that the intensities in the principal maxima are proportional to the square of the number of slits. As the number of slits increase, the principal maxima become higher and higher and narrower, thus separating the light source into its component spectrum. Such colors produced by fine gratings will lie on the spectrum locus of the chromaticity diagram shown in Figure 1. Not so surprising is that the principal use of diffraction gratings is in spectroscopy, where they are used to analyze the spectrum of a light source. It should be obvious by now that the blues are nearer to the optic axis of a system (or the direction of the incident beam) and the reds farther away from it. The zeroth order retains the composite color of the source. We will have occasion to discuss this particular situation in detail. When the spacing of structures of interest become comparable to the wavelength of visible light, the transmitted light (zero-order diffraction) becomes a function of wavelength, thus having implications for color production in biological systems where one often finds submicrometer structures are responsible for the color. We will in such cases have occasion to discuss reflection gratings as opposed to transmission gratings.

C. *Colors Due to Scattering*

Many of the blues found in nature, like the blue feathers of a blue jay, are due to scattering and not

to pigmentary colors. It is then useful to discuss how scattering can produce the "perception" of a blue color. One needs to look no further than to read the papers by John William Strutt, later Lord Rayleigh, published in the late 1800s. "It is now, I believe, generally admitted that the light which we receive from the clear sky is due in one way or another to small suspended particles which divert light from its regular course. On this point the experiments of Tyndall with precipitated clouds seem quite decisive" starts the paper published in *Philosophical Magazine* in 1871[25,26] by John William Strutt. It was common wisdom that such small particles were composed of water or ice. However, Lord Rayleigh was somewhat skeptical of the nature of small particles in the atmosphere responsible for the blue sky. He wrote in 1871 "If it were at all probable that the particles are all of one kind, it seems to me that a strong case might be made out for common salt. Be that as it may, the optical phenomena can give us no clue".[25] After an interval of 28 years, Lord Rayleigh wrote "I think that even in the absence of foreign particles we should still have a blue sky". This implies that the air molecules themselves are sufficient to provide the blue sky. The arguments that Lord Rayleigh put forward in 1871 based purely on dimensional analysis is worth pointing out in the following for the production of color due to scattering.[26]

Consider a particle that is small compared to the wavelength of light in the path of the illuminating beam. The scattering from such a particle is proportional to its volume V. This amounts to saying that the elementary oscillators into which the particle may be subdivided scatter waves that are in phase with one another primarily due to the small size of the particles, when illuminated by a light beam. The total scattered electric field E_s is, therefore, proportional to the particle's volume. Since the scattered field (E_s) is due to the excitation beam with an amplitude E_i, E_s must be proportional to E_i. Since the particle is small, the scattered field must drop with distance from the particle in a way that energy is conserved. To see how this might occur, consider a sphere of radius r centered on the particle with a surface area of $4\pi r^2$. The total energy scattered across this spherical surface must then be independent of r. This will be the case if the irradiance or the radiant flux density decreases as $1/r^2$. Since the irradiance is proportional to E_s^2, E_s must therefore be proportional to $1/r$. Dimensional considerations will quickly make it obvious that the scattered field must be inversely proportional to the square of the wavelength λ, the only relevant quantity with dimensions of length, and can be written as

$$E_s = \frac{KE_iV}{\lambda^2 r} \tag{10}$$

where K is a dimensionless constant. However, the scattered irradiance or the intensity is proportional to the square of the scattered field and can be written conveniently as

$$I_s = \frac{K^2 I_i V^2}{\lambda^4 r^2} \tag{11}$$

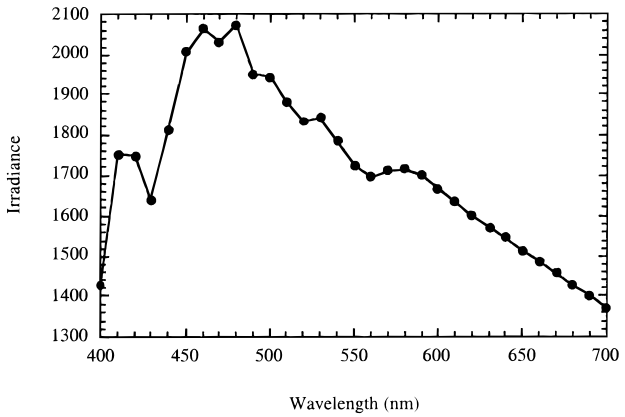


Figure 9. Spectrum of sunlight outside the earth's atmosphere (data from ref 18).

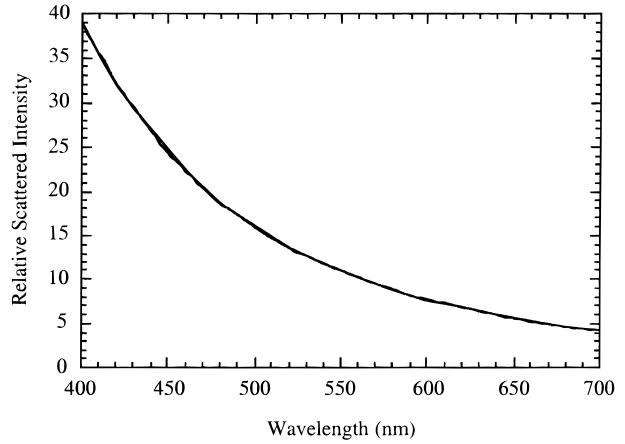


Figure 10. Wavelength dependence of scattered intensity by molecules in the atmosphere.

where I_i is the incident light intensity. A cautionary note about the constant K: it depends on the refractive index of the particle. Equation 11 is often referred to as Rayleigh scattering. Equation 11 also shows the now famous relation $I_s \propto 1/\lambda^4$, which is usually cited for the blue sky. However, knowing that the wavelength of violet is shorter than that of blue, the question of why the sky is not violet is never asked by any student.

What is often omitted in most textbooks that deal with scattering is that the perception of a particular color is not determined only by the optical properties of the medium being observed but depends on how we see things. As discussed in section II, the perception of a color is determined by the product of three functions: the amount of light reaching the detector, the light that is illuminating the object, and the spectral response of the eye. So the blue color that is perceived by the brain is a product of the solar spectrum (Figure 9), the scattering from the molecules in the atmosphere (Figure 10), and the spectral sensitivity of the eye (Figure 11). Even though violet is scattered more than blue, the effect of the eye being less sensitive to violet and the solar spectrum being somewhat depleted in violet provides a combined signal processed by the brain to yield the sensation we call blue.

Many of the noniridescent blues in the animal kingdom are a result of scattering, and the greens of

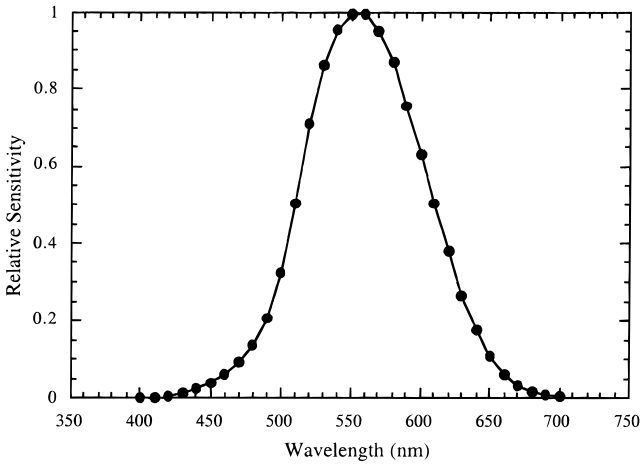


Figure 11. Spectral sensitivity of the human eye (data from ref 20).

parrot feathers are due to a combination of pigmentary colors combined with the blue resulting from scattering. The barbules of the parrot feathers have a yellow colorant, and this combined with the blue from scattering gives the perception of a green color.

IV. Color Generation on Wings

A. *Butterfly Wings*

It was pointed out earlier that some of the wings of butterflies and the cuticles of beetles produce rather remarkable colors using arrays of precisely fabricated structures, providing a striking example of pattern formation in biological systems. These elaborate architectures lead to *structural colors* that are seen in various insects and birds. Most of the colors are produced by either thin-film interference or diffraction or, as in the case of some beetles, by selective reflection of light. In the case of thin-film interference (which is known as thin-film reflectors), coloration is due to alternating layers of high and low refractive index materials. Such assemblies are usually referred to as Bragg reflectors in the physics literature. Such multilayer stacks or Bragg reflectors have been considered for use in optical limiting and switching applications, using the terminology of photonic band gap (PBG) crystals.[27]

The beauty and the variety of patterns one finds on the wings of butterflies and moths are hardly ever matched by other organisms in nature, perhaps with the exception of hummingbirds. However, this order of insects—the Lepidoptera—consisting of about 100 000 species can be identified solely by the color patterning of its wings. Such magnificent colors (and patterns) are even more remarkable when one considers how they are produced.[28−31] The lepidopteran wing is made of scales that are quite small and form (generally) two or more layers over the wing membrane. Each scale is about 100 μm long and 50 μm wide. The scales cover the membrane and when viewed under a microscope appear to overlap like roof tiles.

When one looks at the wing, it becomes evident that on a given patch of wing there are typically two

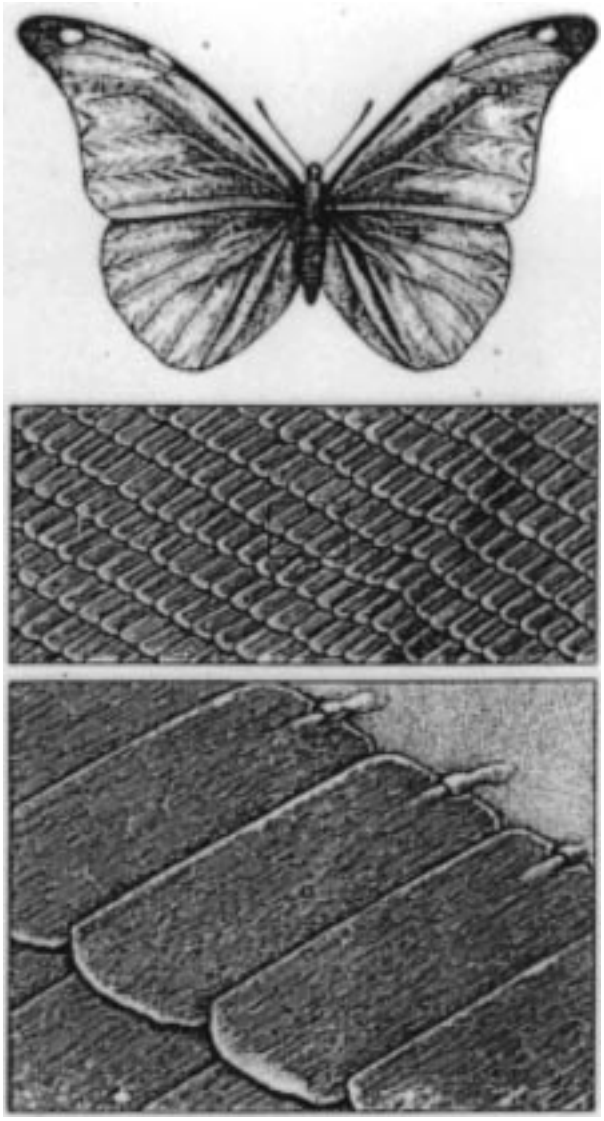


Figure 12. Structure that gives rise to the beautiful colors of *Morpho rhetenor*, a South American butterfly, is depicted at an increasing magnification. The horizontal ridges support the microribs, which produce a brilliant blue due to constructive interference. (Adapted from ref 29.)

and sometimes three types of scales, which alternate positions on a roof-tiles-like arrangement. The larger "cover" scales and the smaller "ground" scales are arranged in an alternating fashion. In most cases, the cover scales tend to be architecturally more elaborate, although oftentimes the ground scales may show a similar architecture. The form of both cover and ground scales can change from a given patch of the wing to the next. The density of the scales varies from about 200 to 500 scales per square millimeter. The scales making up the color pattern that is seen on the wings are quite delicate. Anyone who has handled a butterfly by its wings would have noticed that the scales rub off easily along with the color pattern.

At high magnification it becomes evident that the color pattern is a result of a finely tiled mosaic, with each tile of the pattern being made up of a single wing scale containing structural features which is responsible for color. This is schematically shown in Figure 12, where the butterfly and its wing structure

are shown at increasing magnification.[29] The entire color pattern is then made up of single colored tiles, often comprising between three and five colors, and the unique variations in color and hue are created just by varying the number and density of the different colored scales on the wings.

The various colors are due mainly to two types of color production mechanisms: pigmentary and structural. Even in the case of colors produced by structural variations, one often finds that there are colorants involved—the membrane of the wing usually contains the colorants, either melanins or pterins. The primary purpose of these colorants is to accentuate the color effects due to structural variations, as discussed below.[29]

As an example, the spectacular metallic color of the tropical *Morpho* butterfly has been attributed to interference brought about by the elaborate structural features on the wings of these animals. Depending on the species, interference colors arise from structural variations on a theme that produces constructive interference to yield the observed color. Such structures frequently also contain colorants, usually a dark melanin, which is there primarily to absorb the light that is not reflected, so that the reflected colors will appear particularly bright. It may also function as a way of regulating the body temperature of these animals.[32]

In the context of structural colors, the work of Mason[33−36] remains one of the most complete accounts of the origin and diversity of color in insects. Among the most common colors observed is white, and Mason pointed out that white is observed when a colorless cuticle has many small, irregular surfaces that reflect light. He demonstrated that white is a structural color by immersing a white portion of the wing in xylene (which almost matches the refractive index of the cuticle). The only color left is a pale brown of the cuticle. On drying, the white of the wing would reappear.

Mason examined a variety of butterfly wing scales and beetle scales; he came to the conclusion that the colors must be due to interference and wrote[34]

> The properties of scales presented in... need hardly be compared item by item with those of gratings or selectively reflecting substances to eliminate these from further consideration; their whole behavior is definitely at variance with either of these explanations. On the other hand, in spite of the efforts of the writer to avoid introducing the terminology of thin-film colors, the reader can scarcely have missed the rather striking resemblance between the behavior of the scales and that of thin color-producing films. That this resemblance is more than superficial is substantiated by detailed comparison of their optical properties.

He also went on to say,[34] "The criteria enumerated... indicates the very close similarity between iridescent scales and thin film colors as regards their optical properties. Quantitative optical studies by Rayleigh and by Merritt also emphasize this resemblance". Since the work of Mason, there have been a multitude of studies, primarily using electron microscopy as a tool,[37−41] that have essentially confirmed the conclusions reached by Mason based on his impeccable light microscopy studies.

Virtually all iridescent colors and most of the blues and greens are due to structural variations on the wing. Ghiradella[42] surveyed the diversity of the structures that produce colors due to interaction of light with matter that is periodic in nature. She categorized at least six distinct variations that produce coloration. She noted that three different structural components of a scale can be modified and elaborated into self-assembled arrays repeating themselves to produce the brilliant colors. Figure 13 shows the different possible structural variations of a generic wing scale. The diversity and complexity of the fine structure makes the butterfly wing scale among the most complicated extracellular structures manufactured by a single cell.[28]

Figure 14, a light micrograph of the scales of two different butterfly wings, *Ornithoptera priamus* with green scales and *Necyria duellona* with blue scales, demonstrates the precision with which the individual tiles are placed on the wing membrane. The individual wing scales are clearly seen, and it is apparent that each scale is a monochrome color. Figure 15 represents the reflectance spectrum of the individual wing scales measured with a Zeiss microspectrophotometer with a measurement spot size of about 20 μm. It is quite clear that the spectrum reflects the blue or green color that is perceived by the observer. Figure 16 shows a part of another scale (*Papilio daedalus*) at high magnification which reflects in the blue part of the visible spectrum, but the ultrastructure giving rise to the blue is quite different in appearance in comparison to the scales of *Necyria duellona*. The figure also shows the reflectance spectrum from an individual wing scale. Even though the reflectance at the peak is not as high as one might expect, however, the *dominant wavelength* in the reflectance spectrum is in the blue, as can be seen from Figure 15 and also from the chromaticity coordinates (see Figure 36).

It is interesting to note that the membrane that holds the individual scale is visible against the bright green or the blue color of the individual scales (see Figure 14). A phenomenon known as assimilation or the Bezold spreading effect[43,44] can occur when such intricate patterns, as the ones found on the wing scales, are present. Assimilation occurs when a background and an interlaced pattern of color fail to oppose each other but seem to blend together. An example is shown in Figure 17, where one can see the effects of assimilation with four different colors or hues that have black or white crosshatched patterns superimposed on the colors. Even though the background hue is the same within each hue, it appears different depending on whether it is superimposed with black or white crosshatches. Assimilation is used well by artists to produce different color effects for the observer. It should be mentioned that the phenomenon is not well understood even for human observers.

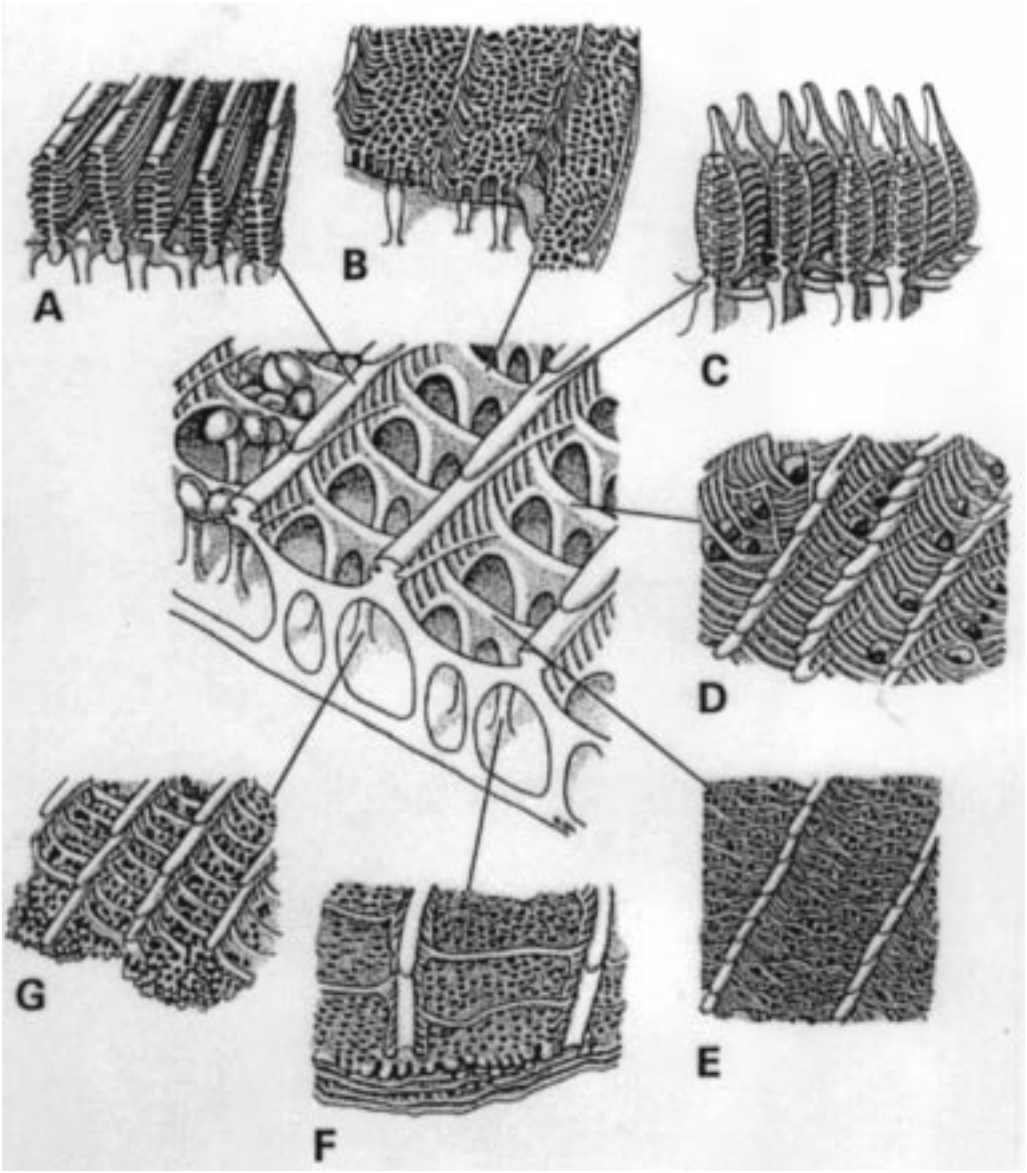


Figure 13. Structural variations that give rise to the beautiful colors of butterfly wings. In the center is a schematic cut-away view of a scale fragment showing the upper and lower layers, ridges, crossribs, ridge-lamellae, and microribs. (A) Ridges that produce thin-film reflectors giving rise to the colors. (B) Flats between the ridges may have an elaboration that gives rise to color due to scattering. (C) Lamella/microrib system now becomes the structure producing color. (D) Structure where the microribs fills the space and are the structural elements. (E) Flats may be filled with plates and pores pattern. (F) Interior of the scale may be filled with body-lamellae that now become the elements of a thin-film reflector. (G) Scales may be filled with a crystalline lattice that produce diffraction colors and *may* behave as zero-order gratings. (Reprinted with permission from ref 42. Copyright 1998, Wiley-Liss.)

It is, however, known that it cannot be explained due to the light scattered from one region to another region of the image. When the crosshatched pattern is fine relative to the diameter of the individual receptors, additive mixing of light occurs but the crosshatches themselves are not visible. If, on the other hand, the elements making up the hatches are small relative to the postreceptoral elements that sum inputs from the cones, assimilation can occur. So varying the viewing distance, thus varying the relative size of the pattern, allows one to observe mixing of light or assimilation. It is interesting to ponder the color vision of the butterfly visual system since the intricate pattern must in some way affect the color that is perceived by the butterfly. Since color is used for a variety of purposes, this would form an interesting and much less studied aspect of color vision of the butterflies. Does assimilation in fact occur in butterflies? What might be the advantages of such optical effects? These are questions that will not be addressed here but are, however, worth pointing out. Answers to these questions will not be easy to obtain since one must design experiments that can probe for such effects.

In the iridescent areas of the wing, each of the individual wing scales is well-known to produce structural colors, and the study of these individual scales has shown that there are three parts of a scale—the ridges, the flats between the ridges, and the interior lumen—that may be modified to produce changes in the color of the scales. The ridge−lamellae form stacks with as many as 5−10 per stack, de-

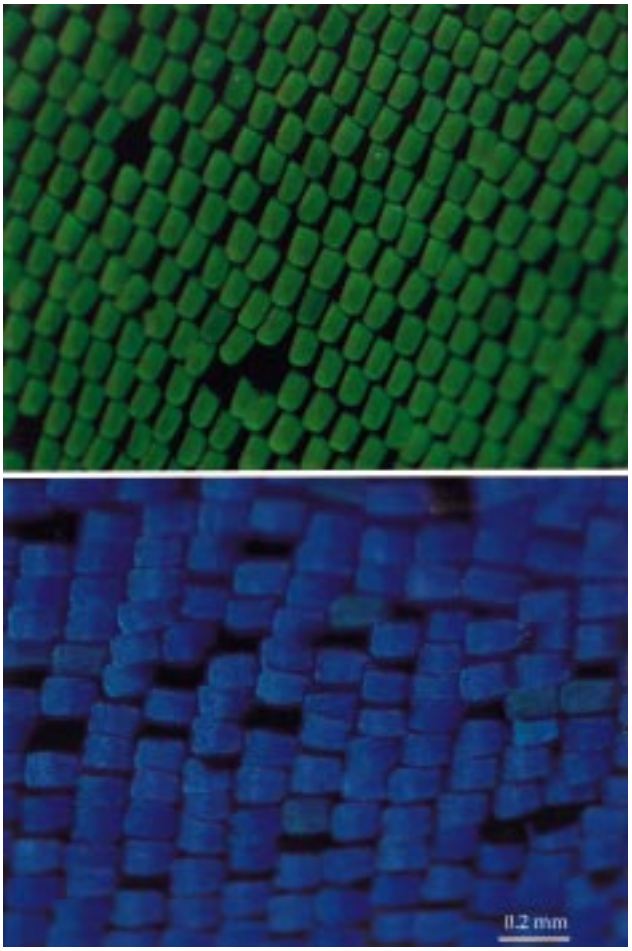


Figure 14. Light micrograph of the scales of two different butterfly wings, *Ornithoptera priamus* with green scales (top) and *Necyria duellona* with blue scales (bottom).

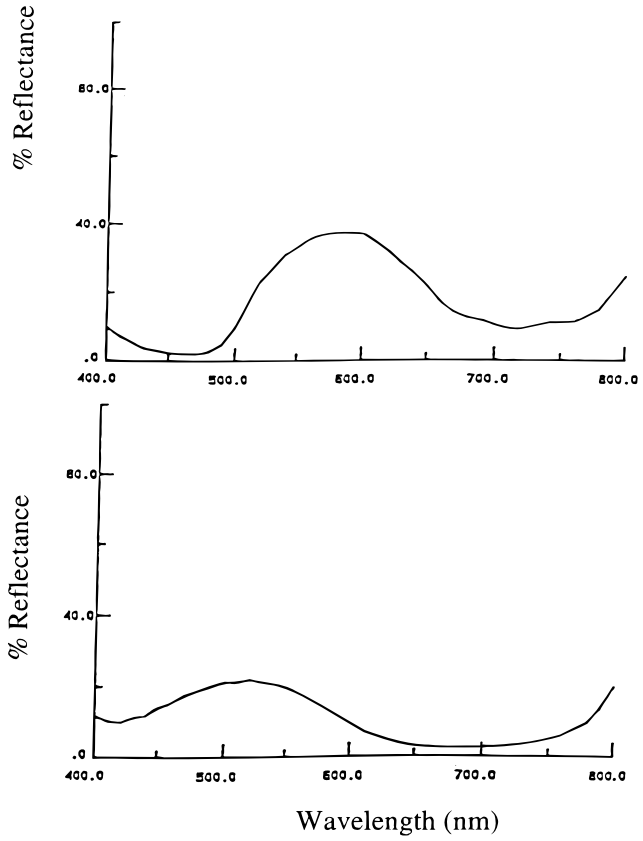


Figure 15. Reflectance spectrum of individual wing scales from the wings of the butterflies shown in Figure 14.

pending on the species of the butterfly and the reflectivity of the wing scale. These ridge−lamellae then act as thin films, and together with the air spaces between the lamellae, they form a quarter-wave interference filter that reflects light that meets the condition for constructive interference.[42]

It is usually necessary to have multiple layers of thin films to produce brilliant colors, so that the reflectivity can approach unity, for a given wavelength. While the reflectivity of an individual wing scale does not reach unity, however, it can be significant enough to produce the sensation of a particular color to be perceived by the observer. It is the dominant wavelength of reflection that matters for a particular color to be perceived and not a reflectance that reaches a maximum attainable reflectivity of one. For example, the blue of the sky cannot exceed a purity of about 42%—in other words, there are other wavelengths in the observed spectrum of the sky; however, because the dominant wavelength is blue (476 nm), the sky appears blue to the observer.[26]

Figure 18A is a light micrograph which very clearly shows the transparent cover scales and the ground scales, both of which are iridescent. Figure 18B is an electron micrograph of a part of a *Morpho* wing, showing the individual scales which are about 100 μm long. Figure 18C shows the cover scale at a higher magnification which reveals the fine structure responsible for the color generation. The structure is created using insect cuticle, a complex biopolymer, and air as the building materials, with the cuticle held apart by vertical spacers. While the precise chemical composition of the scales are not known, it is, however, known that an insect cuticle is a composite containing chitin microfibrils and various other substances that may include proteins such as *resilin* or *scleretin*.

A dramatic example which shows that a wing color is a structural color can be demonstrated, as shown in Figure 19, where the top figure shows several blue scales and the bottom figure shows the same set of scales when filled with acetone. Acetone replaces the air in the ridge−lamellae, thereby increasing the optical path that the light beam has to travel, thus shifting the color of the blue scale to the green part of the spectrum. On evaporation of acetone, the blue of the wing scales returns and provides the original reflectivity spectrum, shown in Figure 18D.

As can be seen from Figure 18B and C, the thin-film structure of these scales comes in the form of stripes. Between the stripes one can see the color of the body of the scales or, as is the case sometimes with transparent scales, the color of the scales underneath. So in this case we see the two colors, a structural color from the ridges and a pigmentary color from the main part of the scales or from a neighboring ground scale. This essentially will form a pattern of color, whatever the color may be, with dark stripes due to the pigmentary colors. This in principle can lead to assimiliation, as discussed

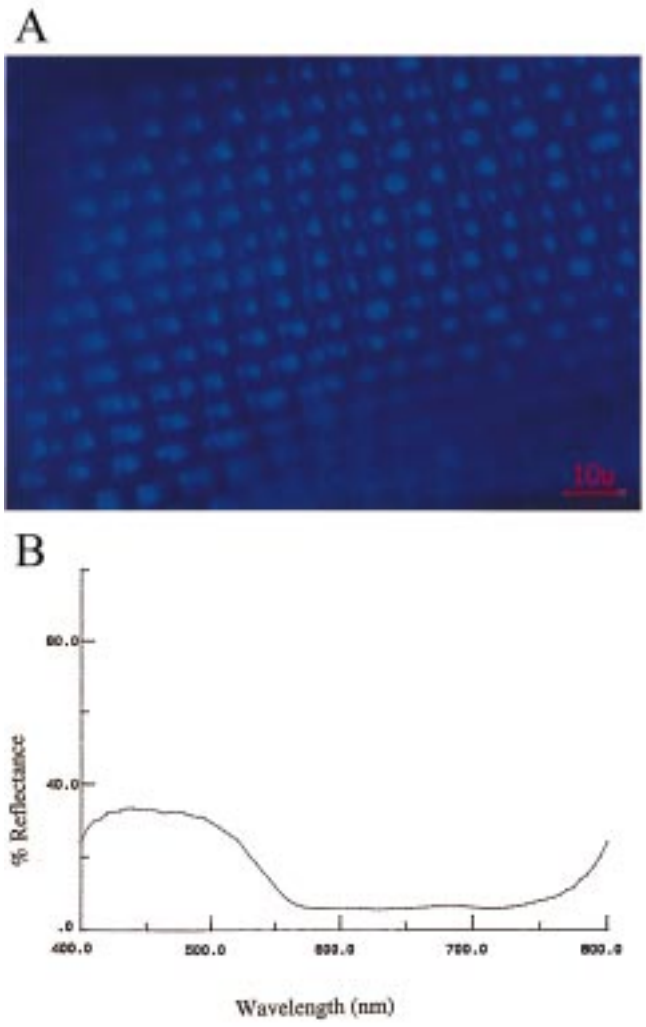


Figure 16. (A) Another blue wing scale, *Papilio daedalus*, which also reflects in the blue part of the visible spectrum but with different ultrastructure (see Figure 13F). (B) Reflectance spectrum of individual wing scales from the wings of the butterflies shown in Figure 16A.

above. It is not known if such processes occur in butterfly vision. Should assimilation occur in butterflies, the obvious next question is what are the implications (if any) of assimilation for insect (color) vision. To the best of my knowledge the question of assimilation has had no discussion in the literature.

In the examples of the blue *Morpho* butterflies, the deep blue comes from the melanized ground scales while the transparent iridescent cover scales provide a shimmery appearance. There are several examples of such interaction between pigmentary and iridescent colors.[42]

The base structure of the wing is also made of cuticle but contains some melanin which absorbs the light that is transmitted through the thin-film structure responsible for the iridescent color, and at grazing incidence, the wing looks almost a dull shade of dark gray, characteristic of melanin. In attempting to understand the color formation, models based on thin-film structures have been constructed by several authors,[3,43−46] and they have all assumed that the complex structure can be modeled by taking plane-parallel sheets of cuticle separated by air, simplifying

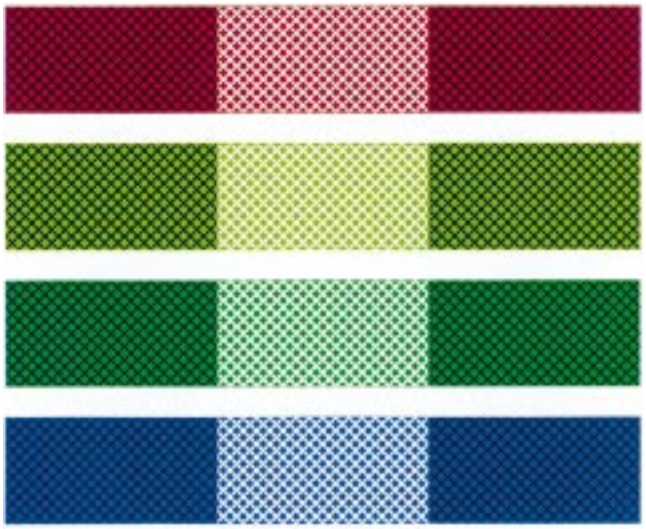


Figure 17. Illustration of assimilation or the Bezold spreading effect. The background color (hue) is identical within a panel, however, it appears darker when interlaced with black hatchings in comparison to the regions with white hatchings. (Reprinted with permission from ref 43. Copyright 1998 De Gruyter.)

the structure considerably. We will have occasion to ponder if such simplified assumptions are valid; however, they have been successful in predicting the trends in the reflectivities observed.[1,45,46]

Structural color can also reside in the flats between the ridges. One of the modifications that will give rise to the colors is due to microribs that extend across from one ridge to the next. One can conceive of other modifications of the flats between the ridges. It is not uncommon to find regularly spaced crossribs that might produce colors due to diffraction. The scales of the moth, *Trichoplusia orichalcea*, are an example of such diffraction grating structures, as shown in Figure 20. Diffraction of incident light by the structure shown in the figure (Figure 20) is responsible for the metallic yellow and the specular reflection and polarization properties of the scattered/diffracted light.[47] In some butterflies, the network of crossribs or microribs is transformed into a set of periodic pores (with a diameter of roughly 200−400 nm), which produces a blue color due to scattering often referred to as Tyndall blue.[48]

The origin of structural colors can also reside, as pointed out by Ghiradella,[42] within the lumen of the scale. It is known that in at least three lepidopteran families, the Lycaenidae, the Papilionidae, and the Uranidae, the quarter-wave plates that are responsible for the interference colors lie within the body of the scale.[1,42] These body-lamellae generally seem to occupy the lumen of the scale, rendering it opaque and highly reflective, thus hiding any of the scales beneath it. The first two of these three families also possess another kind of structural color-producing element, a three-dimensionally ordered lattice of air pockets embedded in a soft polymer matrix,[1,42] producing a sparkling green color. The lattice constant for such a structure is about one-half the wavelength of visible light (taking visible light to be 520 nm or so) and thus falls under the category of submicrometer structures that produce zero-order diffraction

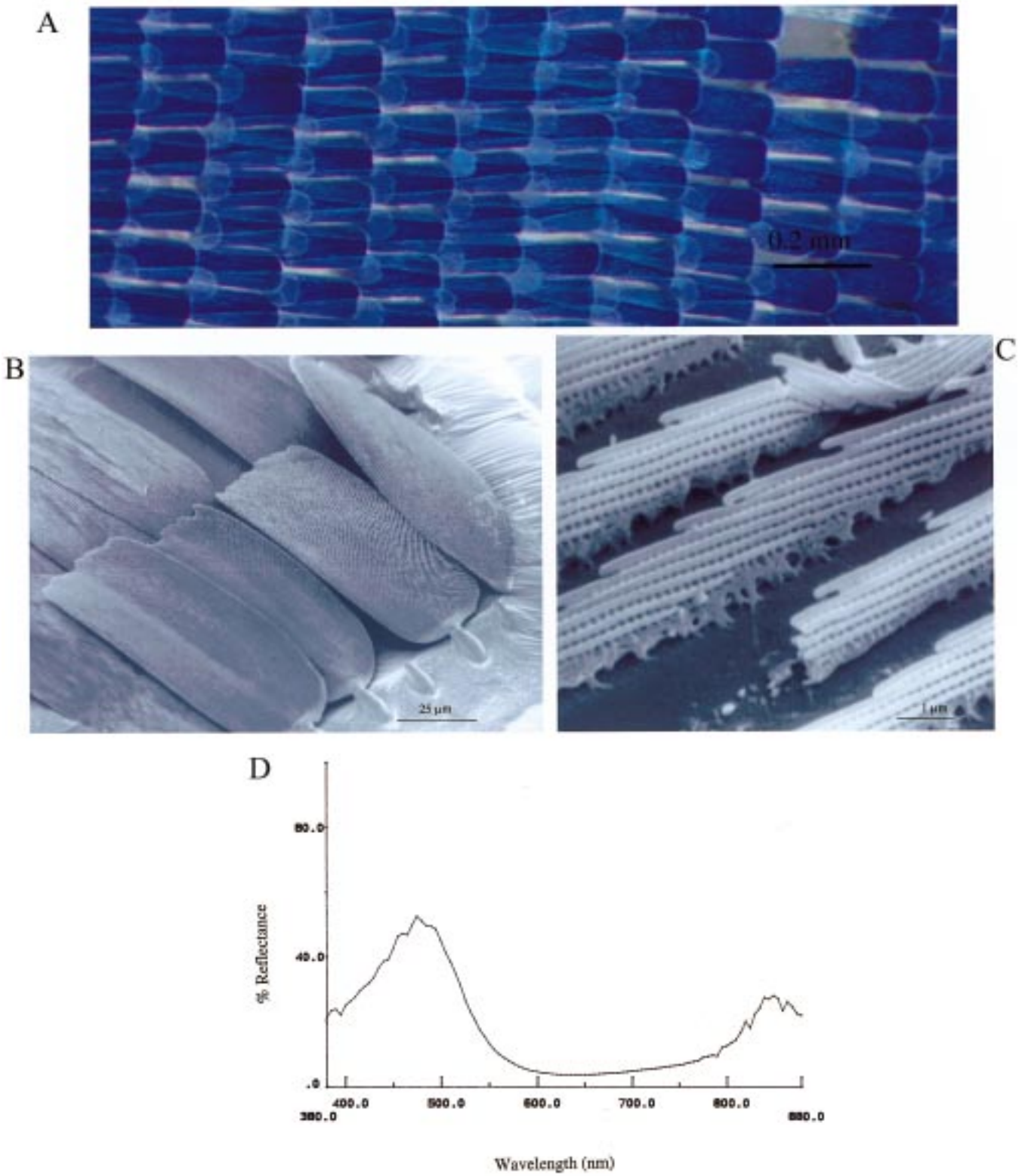


Figure 18. (A) Wing scales of a Morpho (*Morpho menelaus*) butterfly at low magnification, where both the cover scale and the ground scales are clearly visible. (B) Electron micrograph of several wing scales. (C) Electron micrograph showing the ridges and lamellae responsible for the brilliant blue color of the wings (B and C; Courtesy of Prof. Helen Ghiradella.) (D) Reflectance spectrum of an individual wing scale shown in Figure 18A.

gratings, since the higher orders become evanescent and are thus nonpropagating beams.

Many of the structures that have been discussed in the above are schematically represented in Figure 13, and this demonstrates how the various modifications of a generic wing scale can yield a multitude of structures through self-assembly, a process under much investigation for decades. Despite these investigations into the self-assembly process, we are still far from reaching the precision with which a single cell produces the multitude of structures that give rise to the beautiful colors and patterns on the ever so fragile wings of butterflies. One is then faced with the issue of how such structures are produced, a topic

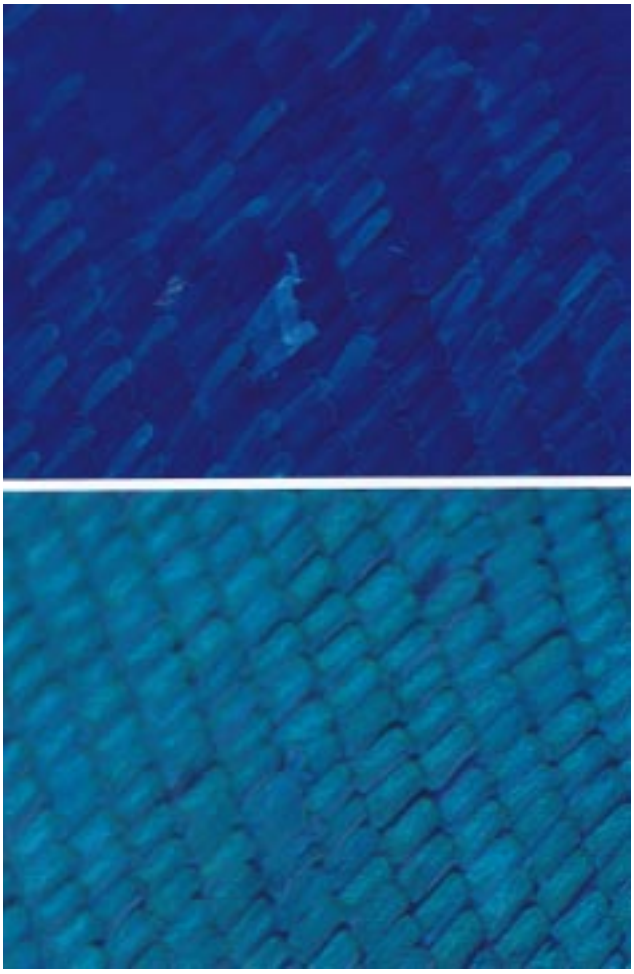


Figure 19. Photograph showing the effect of changing the refractive index of the medium between the spaces in the lamellae of the wings. Top figure is when filled with air, and the bottom one shows the dramatic color change by the addition of acetone. On drying, the original blue color returns.

that has been studied for a long time and will not be discussed here, as it is beyond the scope of the article and the expertise of the author. The interested reader is referred to a beautiful review by Ghiradella[42] and to a book by Nijhout.[28]

An example of color produced by diffraction can be found on the wings of Lycaenidae (Lepidoptera). The Green Hairstreak, *Callophrys rubi*, a member of Lycaenidae, displays a very uniform green iridescence over the whole of the underside of the wing. Morris[49] examined the structure responsible for the color using a light microscope and found that each scale was composed of a mosaic of irregular polygonal grains. He also used an electron microscope to study the structure in detail and found the lamellae within each of the grains to be perforated with a high degree of ordering. Upon study of a number of grains, Morris came to the conclusion that the structure could be represented as a cubic network of perforations, as depicted in Figure 21. The lattice parameter or constant was estimated to be $0.257 \pm 0.025\ \mu$m, with individual grains with a diameter of 5.4 μm. Figure 22 shows the reflectance curve showing a maximum in the green part of the spectrum with a theoretical curve[49] calculated using a function with the form $I/I_0 = (\sin x/x)^2$, where $x = 2\pi t/(\lambda - \lambda_\theta)$, with t the

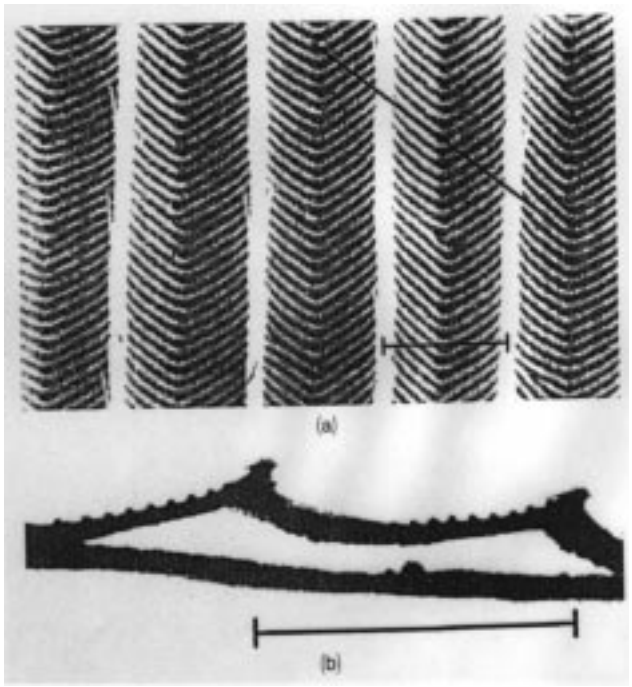


Figure 20. (a) SEM micrograph showing a top view of part of a scale from the moth *Trichoplusia orichalcea*. The length of the marker is 1.6 μm. (b) Oblique section of a wing scale. The length of the marker in b is 2 μm. (Reprinted with permission from ref 47. Copyright 1996 Optical Society of America.)

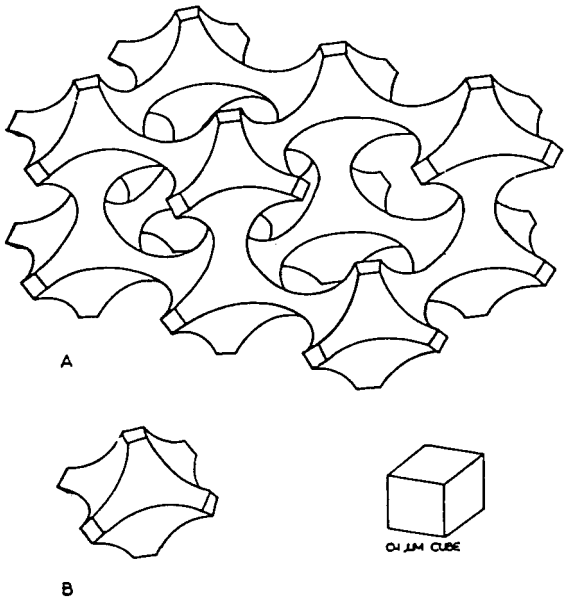


Figure 21. (A) Model of the wing scale of *Callophrys rubi*, a cubic network. (B) Unit cell that forms the cubic network. (Reprinted with permission from ref 49. Copyright 1975 Royal Entomological Society of London).

thickness of the walls of the structure shown in Figure 21. Here, the parameter λ_θ is defined as $(2/g)\sin\theta$, where g (μm^{-1}) is a reciprocal lattice parameter for the optical path and 2θ is the angle between the incident and diffracted beams. The optical path (g) will be slightly larger than the physical dimension by a fraction that is dependent on the scale material in the path of the light beam. It is clear that the shape of the calculated and the experimental curves agree quite well, except for the magnitude.

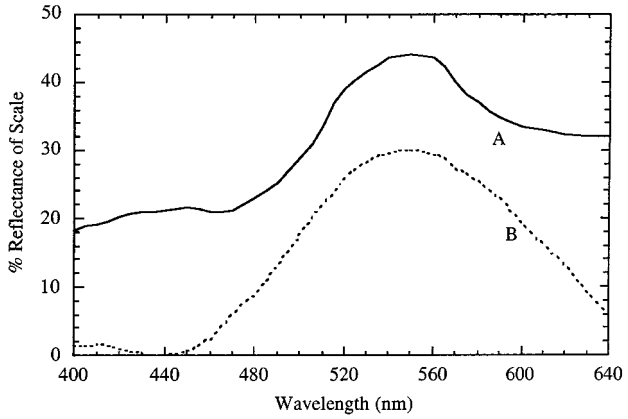


Figure 22. Plots of the reflectance: (A) from the green iridescent scales; (B) theoretical reflectance for the iridescent scale (redrawn with data from ref 49).

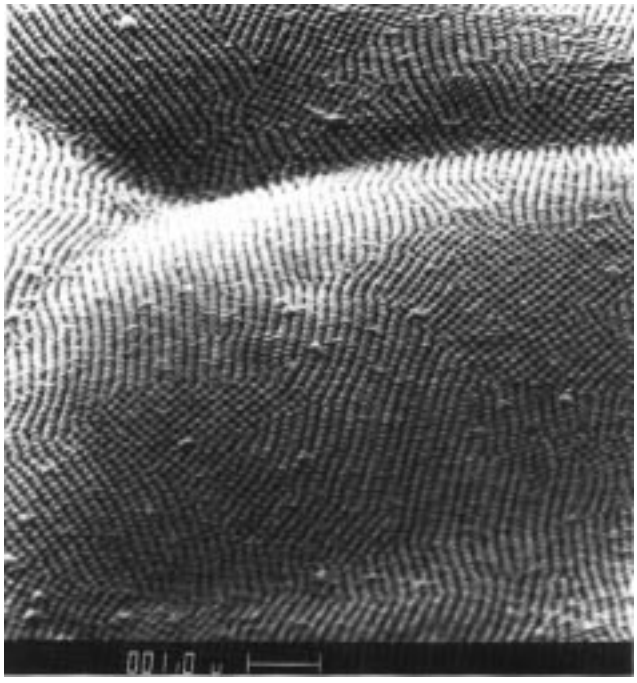


Figure 23. Scanning electron micrograph of the front surface of a sulfur butterfly cornea. (Reprinted with permission from ref 61d. Copyright 1979 Springer-Verlag.)

B. *Zero-Order Gratings*

A diffraction grating having dimensions comparable to that of the wavelength of visible light or finer is referred to as a zero-order grating. This is due to the fact that a light beam travelling through such a structure is diffracted in a way that the first and higher orders of diffraction become evanescent, thus becoming nonpropagating waves, and therefore do not contribute to the observed reflectance. Such subwavelength structures are ubiquitous in nature.[37−42,49] However, their optical properties have not been studied from the point of view of subwavelength structures, although references to such structures have been made in the context of zero-order gratings for color production using surface relief gratings[50−53] and for creating antireflection coatings with various subwavelength architectures.[50,51−60]

Consider a one-dimensional surface relief profile, also known as surface relief grating, with a period p and a profile height d (see Figure 24). If the grating is composed of two materials of refractive index n_1 (in this case air) and n_2, for normal incidence no light will be diffracted into transmitted (and reflected) higher orders, when $p < \lambda/n_1$ (and λ/n_2). Such a condition implies that for the scale of *Callophrys rubi*, the submicrometer structure giving rise to zero-order diffraction will fall below 0.3 μm. The size of the perforations on the scales of *Callophrys rubi* fall in this range, and hence, it might behave as a zero-order grating. The color that is reflected (or transmitted) will then be determined by the refractive index, the depth of the relief structure, and the wavelength of the incident beam. At the present time, there are no reports of color generation in nature from such subwavelength structures. However, it must become obvious from the micrograph in Figure 18, and from the model for *Callophrys rubi* scales (Figure 21), that such subwavelength structures will contribute to the color of the wings.

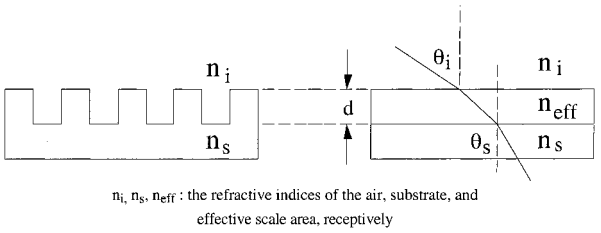


Figure 24. Model of a butterfly wing taking account of the zero-order structures showing how one might include the effects using an effective medium theory.

It would be interesting to study the reflectance and transmittance of many of the subwavelength structures that are found in nature. For example, from Figure 18C it is obvious that the dimensions of air pockets between the ridge lamellae are on the order of about 0.1−0.2 μm. Most of the models that have been used to calculate the reflectance of such structures have assumed that the structures can be simplified to a stack of thin plates alternating in refractive index. The effects of zero-order diffraction have hardly been taken into account. It should be pointed out, however, that in studying the optical properties of these intricate structures, interaction of light with subwavelength structures will play a very important role. To what extent such structures lead to the observed colors on the wings of butterflies is unknown.

In recent years, interest in subwavelength structures has increased due to the fact that many of these structures have rather interesting optical properties.[50−60] In particular, submicrometer structures having surface relief features have been constructed due to their unique optical properties. Such surface relief structures function as good antireflection coatings, and as an example, Figure 23 depicts the protrusions on the cornea of a moth, discovered by Bernard and Miller,[61] who noted its function in antireflection. Subsequently, the optical properties of the so-called "moth eye" antireflection surfaces have been studied extensively (ref 58 and references therein, also Yoshida et al., ref 61a).

Clapham and Hutley[62] prepared an array of protrusions similar to that depicted in Figure 23 using

photolithography and demonstrated that the reflectances of such surfaces were in fact lower than unstructured surfaces. The measured reflectance (using a D65 standard illuminant) at normal incidence was reduced from 5.5% to about 0.2% while the transmittance increased, though not by the same amount, and the difference was attributed to absorption losses due to the photoresist used to make the structures. The reason for the reduction in reflective losses is due to the fact that a light beam propagating through a subwavelength grating experiences approximately the same behavior as if it were traveling through a homogeneous medium. The effective medium theory (EMT) relates the parameters of a subwavelength grating to those of an effective homogeneous medium.[63,64] It is beyond the scope of this article to delve into the details of the effective medium theory (EMT) for subwavelength structures. However, the interested reader is referred to several well-written articles on this topic.[65−67] Continuously tapered and discrete multilevel subwavelength grating structures have also been designed and their antireflection properties studied extensively.[68−70]

Looking at the magnified view of the butterfly wings (see Figure 18C), it becomes clear that the reflection properties of such structures can be affected by the subwavelength structures that are present on an individual wing scale. The modeling of such structures have been hampered partly due to lack of measurements of the optical properties of the wing scales. Also, as already mentioned, much of the modeling done to understand the reflectance of the scale structures have used a thin film with alternating refractive index as a model. A more accurate model must take account of the subwavelength structures that are present. Such a model is being formulated, by the author, using the structure shown in Figure 24 as an analogue of the scale structure.

C. *Eyeshine Of Butterflies*

So far, we have discussed color on the wings of butterflies and the structures that are responsible for the observed colors. The eyes of many insects contain structures that are comparable in dimensions to the wavelength of light, and therefore, it seems relevant to provide a few examples of such structures. Many of the optical effects discussed are also present in the eyes of these insects. Much of the discussion in the following pages draws heavily from the work of Bernard and Miller.[61]

The compound eye of an insect consists of many little eyes, called *ommatidia*, close-packed on the surface of the insect's head. Each of the ommatidium views only a small part of the scene, typically a few degrees centered about the axis of the ommatidium. Each possesses the optics necessary for detection and processing of the light that it receives; these optical elements include a photodetector composed of about eight retinular cells.[61] The output (due to the excitation by light) from the retinular cells is processed by the neural part of the visual system. The butterfly eyes are sensitive to wavelengths ranging from about 0.3 to 0.65 μm, which includes the part of the spectrum invisible to humans, the near-ultraviolet, from 0.3 to 0.4 μm. While the butterflies are sensitive in the UV part of the of the spectrum, they are not sensitive to longer wavelengths (0.65−0.70 μm) that humans are sensitive to. Their sensitivity to shorter wavelengths is due to the presence of photoreceptors, some of which are sensitive in the ultraviolet region of the electromagnetic spectrum. It is known that these insects can have as many as five photopigments/photoreceptors.[15,71,72]

Figure 25 represents the optical elements making

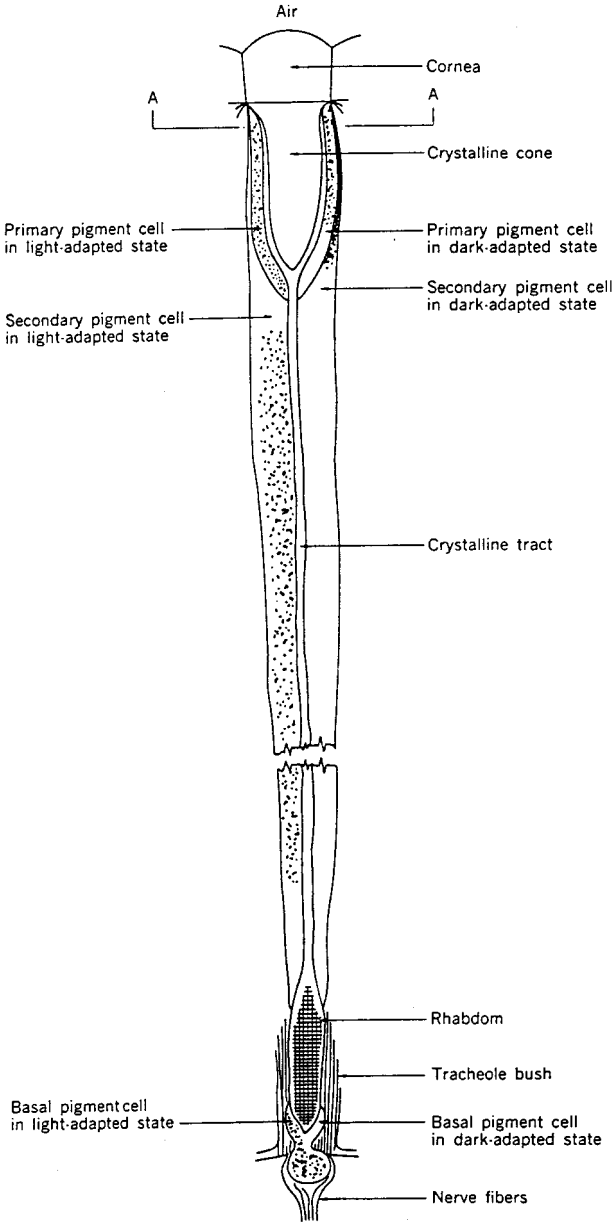


Figure 25. Schematic of the optical components of a typical insect ommatidium (little eye). The left side depicts the eye in the light-adapted state, while the right side shows the dark-adapted state. (Reprinted with permission from ref 61a. Copyright 1970 The Institute of Electrical and Electronics Engineers, Inc.)

up the eyes of a typical nocturnal insect, where the section shown is perpendicular to the eye's surface. The optical characteristics of the eye then determine the kind of signal delivered to the neural part of the visual system. The refractive index of both the tract

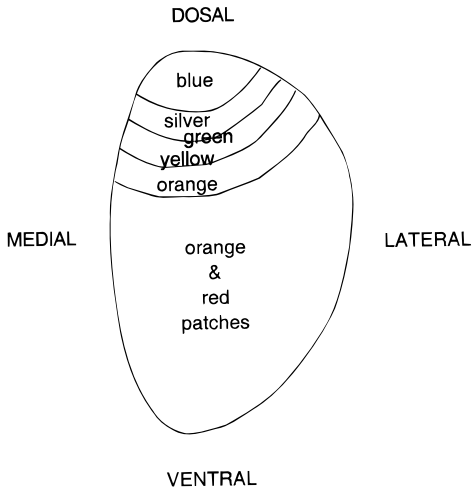


Figure 26. Schematic diagram of the distribution of butterfly glow over the compound eye of the monarch butterfly. (Adapted from ref 62.)

and rhabdom being greater than the surrounding medium, the crystalline tract and rhabdom function as optical waveguides. The crystalline tract is a long transparent cylinder, hundreds of micrometers long and a few micrometers in diameter, and functions as a waveguide, while the rhabdom functions as a photodetector as well as a waveguide. The light carrying the information propagates down the tract and delivers the information into the rhabdom, the photodetector. The crystalline tract can function as a lossless waveguide or as a lossy waveguide depending upon the interaction with the secondary pigment. When the secondary pigment is activated by a higher intensity of light (in comparison to the dark-adapted state in the dark), the secondary pigments move down the tract, making the tract lossy, due to the evanescent waves being siphoned away from the waveguide, and thus being converted to propagating waves outside of the tract. This implies that less information about the image is sent to the photodetectors, thus compromising the daytime vision of the insects. We will not worry about the evolutionary aspects that seem to have taken care of this problem.[61] However, we will discuss a phenomenon called the eye shine. This is visible at night when moths or butterflies attracted to a light source are found to possess brightly glowing eyes. This eye shine is caused by a reflecting layer or an interference filter, the tapetum, that in a moth is part of the tracheole bush (see Figure 25). The tracheole bush is a densely packed collection of tubes filled with air which serves as a reflecting layer, the tapteum, which causes the eye shine. Another example of eye shine that is most familiar is the reflection from a cat's eye viewed in a

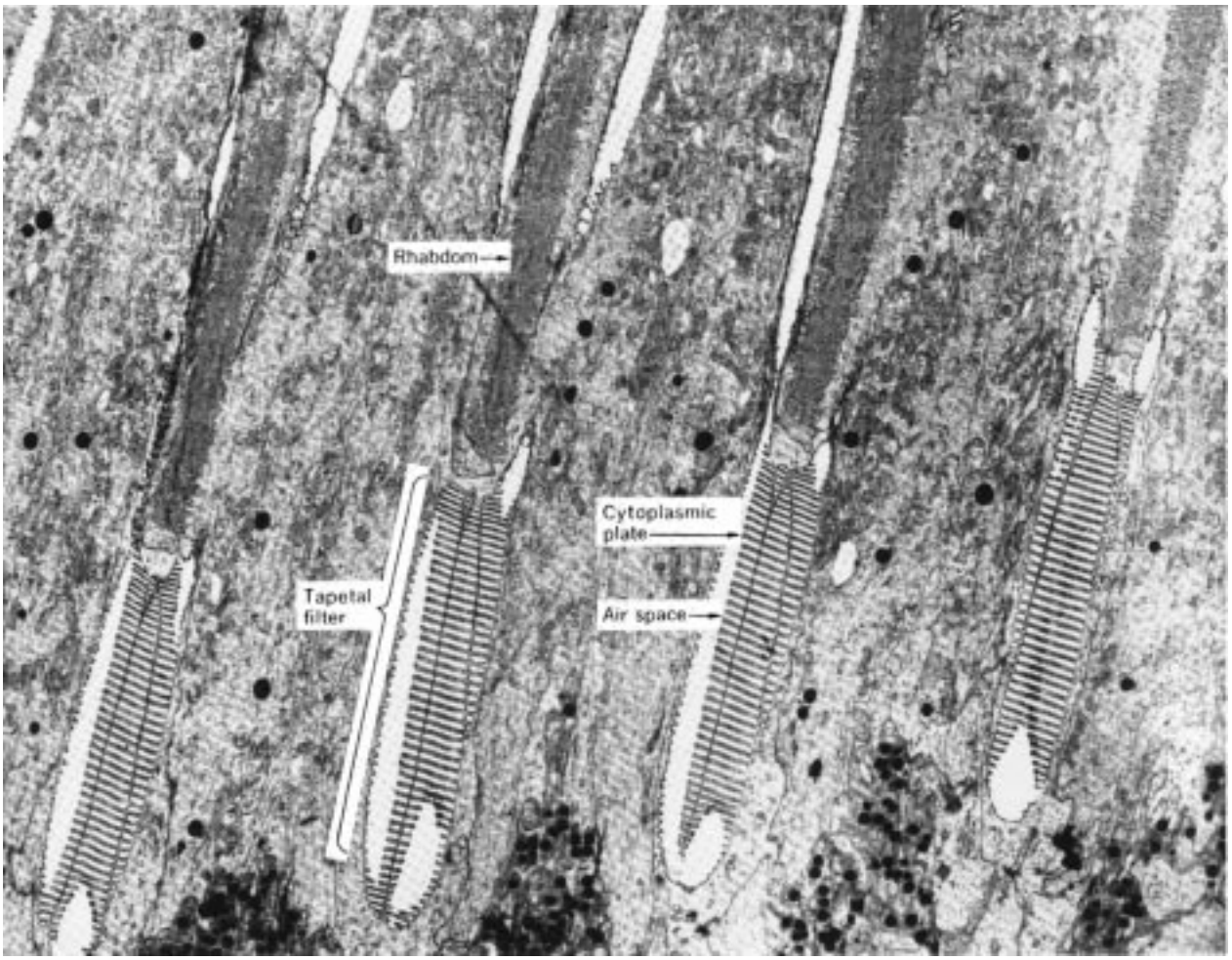


Figure 27. Electron micrograph of a section parallel to the ommatidial axis from a Buckeye butterfly eye. The periodicity of 0.23 μm of the cytoplasmic plate leads to constructive interference, giving rise to the butterfly glow. (Reprinted with permission from ref 61a. Copyright 1970 The Institute of Electrical and Electronics Engineers, Inc.)

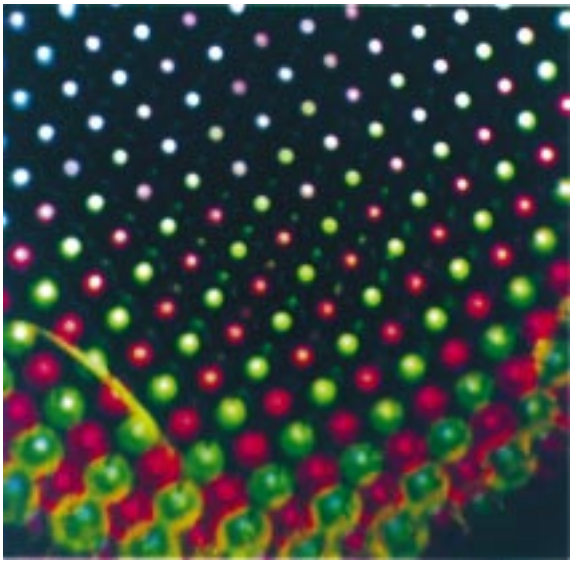


Figure 28. Eyeshine from the cornea of a long-legged fly that contains four types of interference filters. (Reprinted with permission from ref 61a. Copyright 1970 The Institute of Electrical and Electronics Engineers, Inc.)

car's head lights. The butterfly also has a tapetum, which apparently is unusual for a diurnal (daytime) animal.

The eye shine seen from a monarch butterfly is schematically represented in Figure 26.[61] This is due to the fact that most butterfly eyes have a band rejection (interference) filter located at the bottom of each rhabdom.[61] This is shown in an electron micrograph, Figure 27, illustrating an almost longitudinal section of several ommatidia from a butterfly eye. The rhabdomes and the tapetal filters are shown in the figure. It is remarkable that the butterfly tapetum is periodic in refractive index due to the periodic set of cytoplasmic plates that alternate with air spaces. This produces a quarter-wave plate, giving rise to an interference filter that reflects a band of visible light that propagates up the rhabdom and out of the eye where it is observed as the colored eye shine. Wavelengths in the band-pass filter simply propagate down the filter stack only to be absorbed in the basal pigment. An unusual aspect of the butterfly filter system is that each rhabdom's mirror has its own filter characteristics, which could be entirely different from that of the neighboring rhabdomeres, and such a display is shown in Figure 28. It is clear that there are a variety of interference filter sets in the butterfly visual system. The micrographs were obtained by Bernard and Miller[61] by illuminating the living eye with white light and observing the eye shine from the direction of illumination. These are visible if the directions of illumination and observation are within a few degrees of each other.

D. *Bird Feathers*

Many birds feathers display iridescent colors whose origin has been a puzzle at least since the time of Newton. Experimental evidence for iridescent colors primarily came from the usual clues for thin-film colors: absence of colored pigments, shift of the reflection maximum or the color to shorter wavelengths with increasing angle of incidence, and change of color toward the red end of the spectrum on immersing the feathers in a medium with a higher refractive index than air. On the basis of these observations, Lord Rayleigh[73] and Mason,[34] among others, refuted earlier suggestions by Michelson[74] that such colors are "surface colors" similar to those seen from reflecting metallic surfaces.

While the physical origin of color in feathers was recognized early on, it remained until the early 1960s before the structural features producing the colors of bird feathers were determined. The work of Greenwalt stands as an outstanding example of the study of the iridescent color of bird feathers, in particular hummingbird feathers. The interested reader is referred his fascinating book.[4] In this article, I simply want to point out the structure responsible for the brilliant colors of hummingbird feathers, drawing primarily from the work of Greenwalt.[4,75]

Figure 29 is a light micrograph of a typical iridescent platelet mosaic of a hummingbird feather from *Heliangelus viola*, the blue gorget. The micrograph shows that elliptical platelets, about 2−3 μm in length and 1−1.5 μm in width, are packed into a beautiful mosaic, almost like a tiled floor. The platelets are clustered into cells that are separated by diagonal lines crossing the width of what are termed as barbules. The platelets are embedded in a dark matrix, and it is apparent that the platelets are responsible for the iridescent color. It was found by measuring the reflectivity as a function of incident angle that the refractive index of various feathers (for different colors) varied from about 1.85 for red feathers to 1.5 for blue feathers. Now the question is "how is this refractive index variation accomplished?"

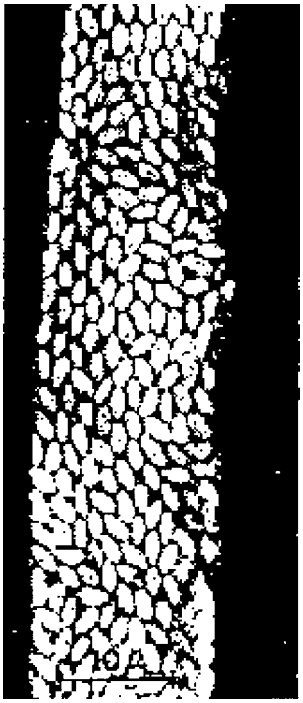


Figure 29. Typical mosaic of platelets of hummingbird feathers (*Heliangelus Viola*, blue gorget). (Reprinted with permission from ref 75. Copyright 1960 Optical Society of America.)

Such variations can be accomplished either by producing materials with different refractive indices for every color or by noting that different colors can be produced by making the interference films from two different materials, one of high and the other of low refractive index, and varying the average index simply by varying the composition of the two substances. It is rather ingenious of nature to produce the variety of colors found simply by varying the proportion of the two substances, air and keratin. This is demonstrated in Figure 30 which shows the

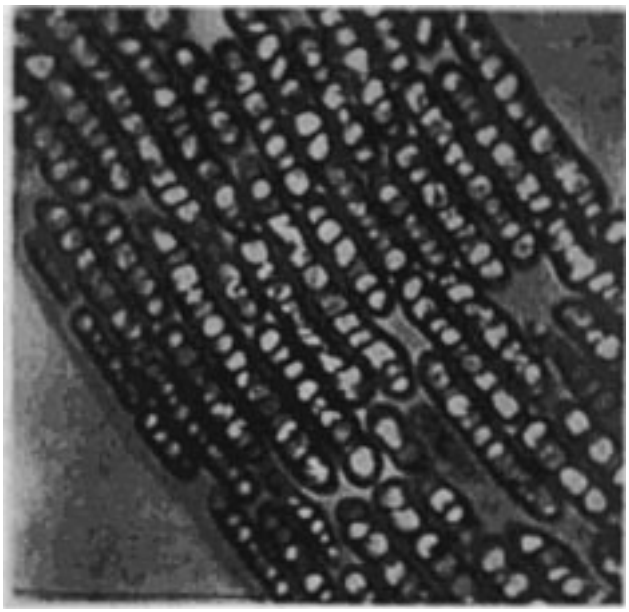


Figure 30. Cross section of iridescent feather surface at high magnification (*Clytolaema Ruricauda*, red gorget). (Reprinted with permission from ref 75. Copyright 1960 Optical Society of America.)

section of a platelet taken using an electron micrograph. The platelets consists of tiny air pockets embedded in keratin with as many as eight layers forming them. This structure is responsible for the thin-film interference and the color of the hummingbird feathers. The measured reflectivity curves agree with the calculated curves. Details of the optical model can be found elsewhere.[75] Many of the iridescent bird feathers have similar morphologies which produce color. The simplicity with which colors are produced in bird feathers is simply astounding.

V. Color of Beetles

A. Color of Scarabaeid Beetle Exocuticle: Selective Reflection

Neville and Caveney[5−7] studied the colors of many beetles and found that the exocuticles of these beetles had remarkable optical properties, such as selective reflection of left circularly polarized light, high optical rotation of transmitted light, and a brilliant metallic appearance. All of these optical properties bear remarkable similarity to the optical properties of cholesteric liquid crystals (CLCs), which have been studied extensively[76−78] since the discovery of liquid-crystalline phases.[79,80] Neville and Caveney[5] concluded that the exocuticles behaved as optical analogues of the cholesteric liquid crystals. In this section, we will discuss some of the results that have been reviewed by Neville and Caveney,[5,7] pointing out the ingenious ways that nature uses such structures for a variety of purposes. I will primarily discuss only the color aspects of this topic. The structure of the exocuticle has other implications, which will not be addressed here, but the interested reader is referred to an excellent monograph by Neville.[7]

Many species of beetles, all *Scarabaeidae*, were examined[5] in a simple, yet brilliant study of the optical properties of these beetles. One of the first observations was that these metallic-looking beetles reflected circularly polarized light, and in most cases studied, the reflected light was left circularly polarized. This can be studied using right circular analyzers which extinguish left circularly polarized light. When the beetles were viewed with right circular analyzers, the beetles appear dark with no color. When the beetles were viewed at increasing angles of incidence, the colors of the cuticle shifted to lower wavelengths, as observed by many earlier researchers.[73,74,81] This is a clear indication that the colors are due to the phenomenon of interference. We have already dealt with such interference colors in detail. However, reflectivity from the structures discussed in the earlier part of the paper does not lead to circular polarization of the reflected beam. Neville and Caveney also made observations of the light transmitted by the exocuticle and found that the transmitted light had a color different from the reflected colors and that the transmitted light was also circularly polarized but in the opposite direction. In other words, the colors in transmission did not correspond to colors due to birefringent objects with uniaxial symmetry, since such materials would extinguish light under crossed polarizers on rotation.

Onslow, in 1921, suggested that the layered structures responsible for the colors are located in a surface layer of $\lambda/2$ thickness.[82] The experimental results of Neville and Caveney[5] clearly demonstrate that such an interpretation is quite incorrect. In working with several species of beetles, Caveney found an exception to the rule of all the beetles reflecting only left circularly polarized light. For the species, *P. resplendens*, the reflected light consisted of both left circular and right circular polarization.[6] The beetle, gold in color, has a peak reflectance at around 560 nm for left circularly polarized light and a broad reflectance peak for right circularly polarized light between 575 and 624 nm, with little reflectance in the blue part of the visible spectrum. Much of this optical behavior of the beetles is due to the (solidified) cholesteric nature of the exocuticle. Therefore, we first discuss the properties of a cholesteric phase and return to the reflectivity of beetles.

Of the many thousands of organic compounds that have been synthesized, a significant fraction exhibit a liquid-crystalline phase.[79,80] Liquid crystals are a state of matter that have order between an isotropic liquid and a crystalline solid. These are fluid phases but possess molecular order, leading to some unusual physical and optical properties. Depending on the nature of molecular ordering, these phases can be classified as nematic, cholesteric, or smectic phases.[79,80] In the case of a cholesteric liquid crystal, the rodlike molecules that comprise this fluid phase have long-

range orientational order and form a layered structure. In each successive layer the direction of the long axis is rotated by an angle of 10−20 arc min; this gives rise to a helical arrangement of the rodlike molecules. The spacing between layers differing by 360° is called the pitch, p, of the helical structure.

Cholesteric liquid crystals (also known as chiral nematics) whose pitch is in the visible region selectively reflect light with a peak at $\lambda_{max} = 2np$, where n is the average refractive index,[79,80] with the peak width given by $\Delta\lambda = p\Delta n$, where Δn is the birefringence of the fluid phase. In principle, the peak at λ_{max} can be made quite small by tuning the birefringence of the fluid. Selective reflection occurs when the optic axis of the liquid crystal is parallel to the bounding surfaces, known as the Grandjean texture. Such an alignment orients the helical axis normal to the bounding plates. As a result of the periodicity in molecular orientation, reflections from all layers separated by $p/2$ interfere constructively, giving rise to a reflection band of a wavelength that is relatively narrow and steep. The color so produced appears highly saturated and metallic in nature. The reflected light, of course, has the same handedness as that of the cholesteric phase. If the cholesteric phase is left-handed, then the reflected light is left circularly polarized.

In our studies the CLCs were formed by adding appropriate amounts of an optically active material to a commercial nematic liquid crystal. Nematic liquid crystals are materials that have long-range orientational order, with the molecules oriented more-or-less parallel to one another, and addition of an optically active dopant gives rise to the cholesteric phase. Appropriate amounts of CB15 (a chiral dopant) was added to E48 (a commercial nematic fluid, from E. Merck) to obtain the cholesteric phase. Well-aligned cells, with planar alignment (the helical axis normal to the glass surfaces), about 3 μm thick were prepared for reflectance measurements. Reflectance measurements were made for materials with pitch covering the entire visible regime. An example is shown in Figure 31 for four different concentrations

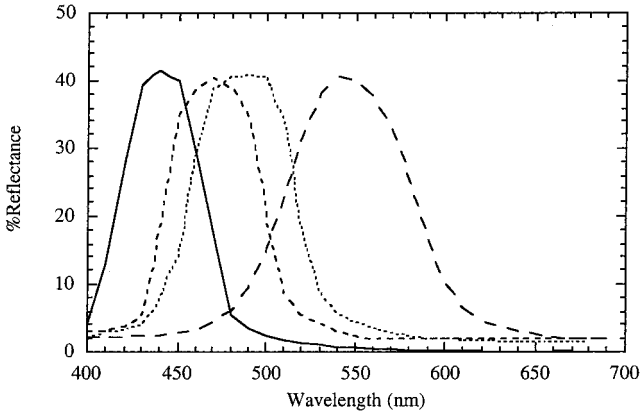


Figure 31. Reflectance curves for cholesteric liquid crystals with four different pitches.

of the chiral dopant.

Notice that the reflectivities are close to the maximum theoretical limit of 0.5. The theoretical maximum is 50% due to the fact that a CLC selectively reflects light of the same handedness.[80] Unpolarized light can be considered as a superposition of left circularly and right circularly polarized light, and therefore, light of the same handedness (∼50%) is reflected while the rest is transmitted. It should also be emphasized that there is very little absorption loss.

It is this ability of selective reflection that gives rise to the additive color mixing properties for CLCs while producing a color gamut greater than those attainable with dyes, inks, and pigments. The color due to selective reflection by cholesterics is quite saturated and pure; thus, the color points (x,y coordinates or the chromaticity coordinates) in the CIE chromaticity diagram lie very close to the spectrum locus, as demonstrated in Figure 32. One of the

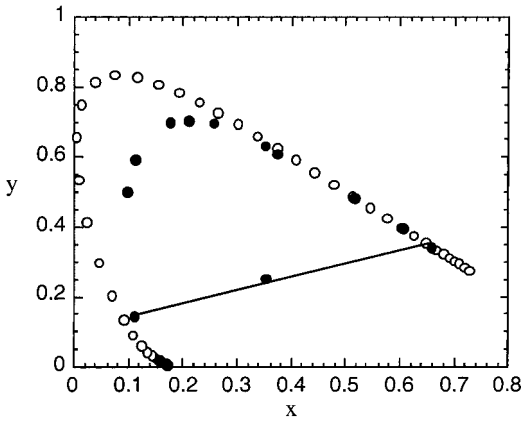


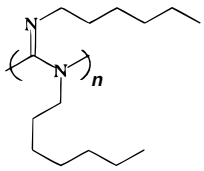
Figure 32. Plot of the CLCs showing the wide color gamut that can be produced using cholesteric liquid crystals. The filled circles are due to the CLCs.

problems, however, is that the maximum reflectance is only ∼50%. However, one can use an optical trick to get almost 100% reflectance, as demonstrated by Makow.[83,84] The trick is to use a half wave plate that is sandwiched between the liquid-crystal samples of the same handedness. The half wave plate converts the transmitted right circularly polarized light beam to left circular polarization, which is then reflected at the bottom interface. As the beam travels through the $\lambda/2$ plate, it is reconverted to right circular polarization and is transmitted through the top layer.

Having discussed the properties of a simple neat cholesteric fluid, we can return to the case of the optically active beetles. The gold beetle, *P. resplendens*, which was found to have both left and right circular polarization in its reflected light, has perfected the optical trick of using a $\lambda/2$ plate that functions as a half wave plate reasonably well for the wavelengths between 520 and 640 nm. The chitin layers, which are at the heart of the helical or helicoidal arrangement of the exocuticle, give rise to the selective reflection of circularly polarized light, which produces the brilliant metallic iridescence of this family of beetles. The gold beetle, *P. resplendens*, has a unidirectional layer sandwiched between the helical (left-handed) chitin layers and was found to contain uric acid. An obvious question arises: How does the beetle manage to create layers that are cholesteric and nematic, using more or less the same materials as the building block? The unidirectional

layer is quite analogous to nematic ordering of the chitin crystallites. The role of uric acid in this cholesteric to nematic transition is not known. It is quite remarkable to find such a beautiful analogue of the optical properties of the cholesteric phase in nature.

In the following, I offer a suggestion for how the cholesteric to nematic transition may be brought about. I would like to warn the reader that this amounts to no more than a speculation on my part. Recently, Schlitzer and Novak[85] reported on some experiments that were designed to study chiral amplification. They started with a chiral homopolymer made from *N*-(*R*)-2,6-(dimethylhexyl)-*N*′-hexylcarbodiimide and found that the polymer had trapped kinetic states because the optical rotation took sometime to achieve its equilibrium value. This led them to conclude that the molecule must be a dynamic helix. They then proceeded to remove the chiral center from the starting monomer so that one can, in principle, have a dynamic helix (the structure of the polymer is shown below) which, when protonated with (*S*)-camphorsulfonic acid, gave rise to large



Poly-(di-n-hexylcarbodiimide)

optical rotation signaling the formation of a single helical sense for the molecule.

Control of chirality or the helical sense through protonation and complexation is likely to be very important in biological systems. As we have seen in the case of scarab beetles, the exocuticle is made of chitin and is a multilayer superstructure with alternating cholesteric and oriented layers of chitin.[6] The question of how does the beetle grow structures such as that can be answered by making the following hypothesis. On the basis of the knowledge that the oriented layer (nematic) contains uric acid, it is perhaps plausible that some kind of ion pairing may lead to the unwinding of the cholesteric helix. This is only a hypothesis which may turn out to be completely incorrect. However, it might be worthwhile to think about this mechanism as a possible way of producing such multilayered structures.

B. *Color Changes in Beetles*

There are not many examples of rapid color change in insects, apart from the well-known examples of migration of pigment granules in the iris cells.[86] Hinton and Jarman, in the early 1970s, discovered that the Hercules beetle, *D. hercules*, changed color rather rapidly from greenish-yellow to black and back to yellow, all in a matter of a few minutes. This is shown in Figure 33A, where two live Hercules beetles are shown. In one the elytra are in the yellow phase and the other in the black phase. It has been noted that the only other insects that can change color reversibly and rapidly are some chrysomelid beetles (subfamily of Cassidinae) that change the color of

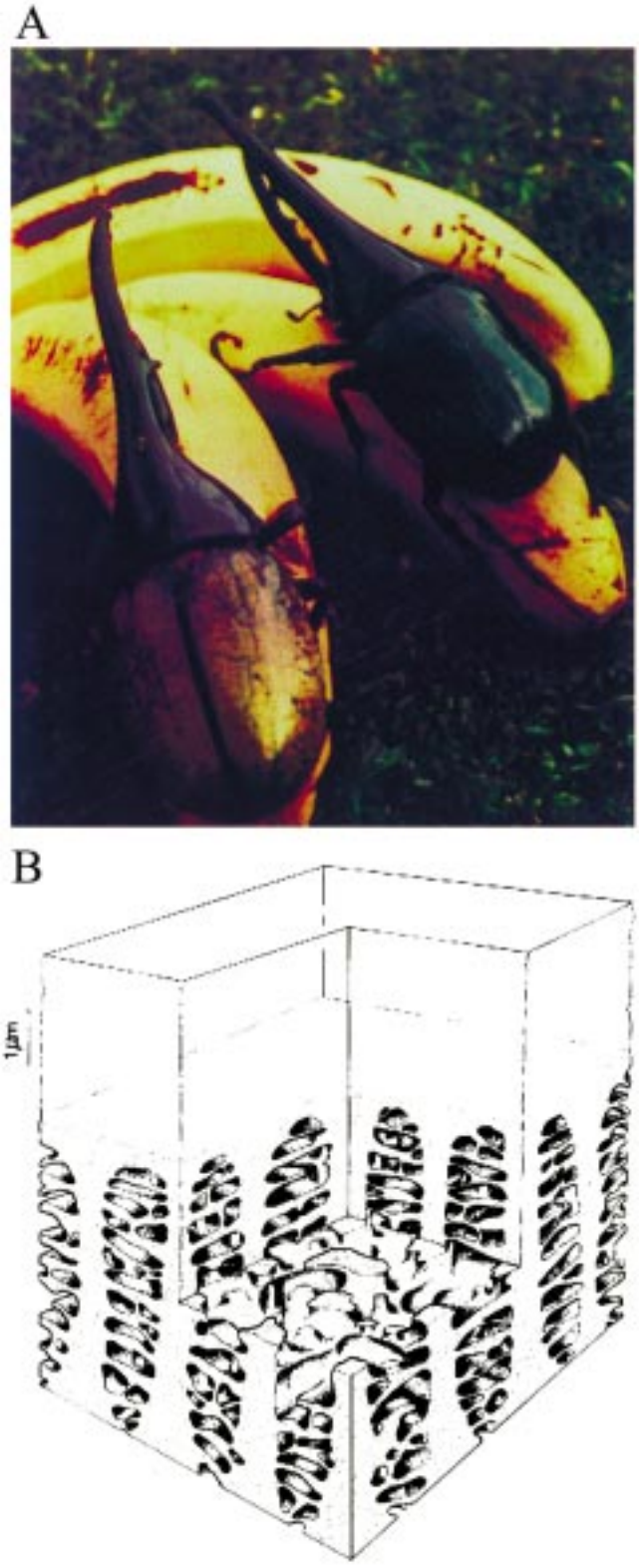


Figure 33. (A) Live Hercules beetles, *Dynastes hercules*. The beetle on the left is in the yellow phase (when the spongy layer is filled with air), and the beetle on the right is in the black phase (when the spongy layer is filled a liquid). (B) Schematic of the yellow spongy layer of the elytra beneath the transparent epicutilce. (Reprinted with permission from ref 87. Copyright 1972 Macmillan.)

their elytra by varying the level of hydration. The iridescent colors of these beetles arise from multilayer reflection due to interference, a phenomenon that has

been discussed at length. Changes in the level of hydration cause a variation in the thickness of the multilayer stack, leading to a color change that is in accordance with predictions.

The outermost layer of the cuticle of the Hercules beetle is found to have a transparent layer, about 3 μm deep, below which is a yellowish spongy layer that is about 5 μm deep. Below the yellowish spongy layer of the cuticle there exists a black layer (in reflected light). Hinton and Jarmin did electron microscopy[87−89] of the spongy layer and found that the spongy layer consists of columns or pillars normal to the plane of the cuticle, usually about 0.5−1 μm thick, which are connected to each other by irregular branches normal to their major axes (see Figure 33B). The cuticle appears yellow when the spongy phase is filled with air, and it appears black when filled with water. This is due to the fact that when filled with water the material is homogeneous in refractive index, thereby exposing the black area underneath the yellowish spongy layer. The selective advantages of such color change have been discussed by Hinton and Jarmin.[88]

C. *Diffraction Colors in Beetles and in Burgess Shale Animals*

Diffraction gratings produce color. The finer the grating, the more efficient it is in providing a spectrum of the white light. Many of the exocuticles of beetles are found to have grating structures on them as do some snakes, like the Indigo snake.[2] Figure 34 shows the diffraction color produced by a ground beetle, *Iridagonum quadripunctum* (Figure 34a), *Loxandrus lucidulus* (Figure 34b), and stridulatory file of the mutillid wasp, *Mutilla europaea* (Figure 34c), respectively.[90] Only the grating structure responsible for the color of the ground beetle *Iridagonum quadripunctum* is shown in Figure 35. It is clear from the electron micrograph (Figure 35) that the grating is far from perfect. Hinton and Gibbs identified a whole host of beetles that possess such grating structures[91] and discussed the advantages that such colors might have. It is not apparent that the polarization properties of the reflected (diffracted) colors have been studied, but it is quite conceivable that they will have interesting polarization effects.

Hinton[91] suggested that such colors might have several purposes. Such brilliant colors are usually taken as warning colors by the predators. In the case of such brilliant metallic colors, it is possible that the predator is startled by the appearance of such bright colors which change color rapidly with small changes in the viewing angle. It has been noted that when variations in appearance (its reflectance or both reflectance and color or hue) occur, it becomes difficult to estimate the distance,[91] size, and shape of the object that is being viewed, which certainly is an advantage when one wants to avoid being consumed by a predator!

This review would not be complete without the inclusion of some recent, exciting, results that have been presented by Parker.[13,14,92] To a large extent, much of the iridescent colors that one has dealt with so far can be categorized into two classes: those that are a result of thin-film interference and those that

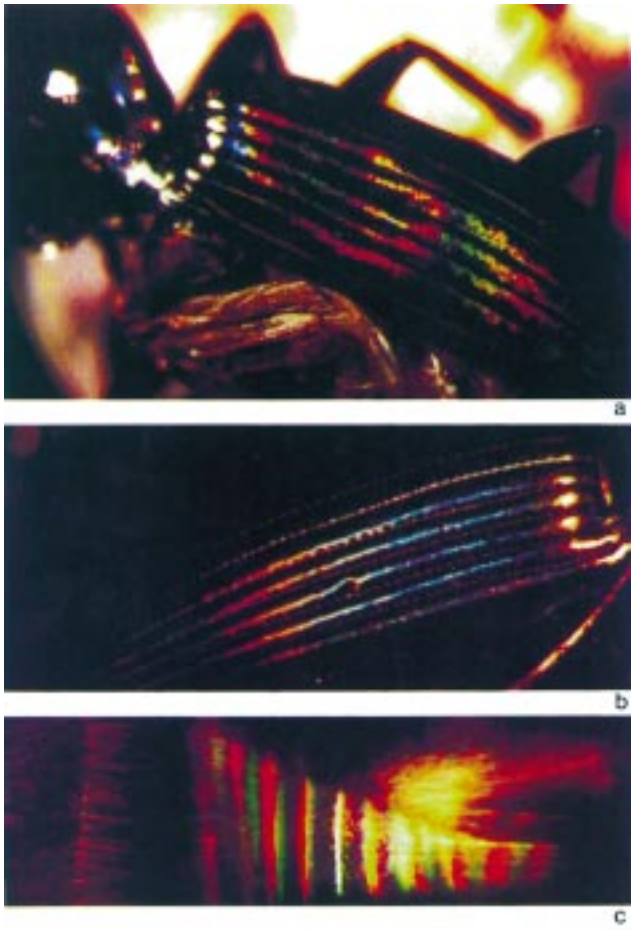


Figure 34. Color produced by diffraction gratings: (a) ground beetle, *Iridagonum quadripunctum*. (b) ground beetle, *Loxandrus lucidulus*, (c) Stridulatroy file of the multillid wasp, *Mutilla europaea*. (Reprinted with permission from ref 90. Copyright 1973 Charles Scribner and Sons.)

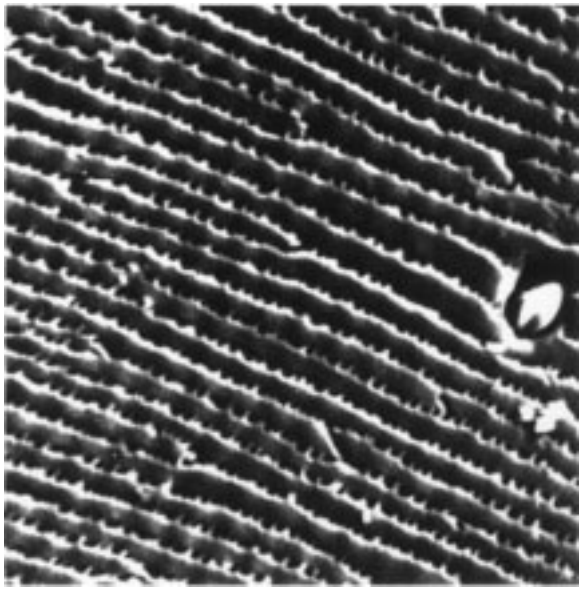


Figure 35. Grating structure responsible for the diffraction color of the ground beetle, *Iridagonum quadripuntum*. (Reproduced with permission from ref 90. Copyright 1973 Charles Scribner and Sons.)

are due to scattering (Tyndall blues). Although there has been some discussion of colors produced by

diffraction, for beetles in particular, by and large much of the discussion in the biological literature deals with colors produced by thin-film interference or by scattering.

Recently Parker[92] identified a variety of creatures that possess surface gratings, which include diffraction gratings and Bragg gratings. Here, surface gratings are those structures on the surface of animals that produce iridescent color due to splitting up of the incident light beam into its component wavelengths, the direction of which is governed by the grating equation (see section IIB). The series of papers by Parker[93,94] identified the existence of surface gratings producing color in Burgess Shale animals. This implies that the animals (*Wiwaxia corrugata*, *Canadia spinosa*, and *Marrella splendens*) from Burgess Shale (Middle Cambrian (515 million years), British Columbia) displayed iridescent color in their natural environment. This is perhaps the first report of "color" in the animals of Burgess Shale. The implications of such color production will not receive any discussion in this review. However, the interested reader is referred to the beautiful papers by Parker.[90−94]

VI. Color Specification and Color Vision

We have discussed at length the kinds of structures that produce beautiful colors on the wings of butterflies, beetles, and birds. It is clear that the precise control of the wing structure is the key element in producing the color that we perceive. The purposes of such an elaborate display of patterns and colors are severalfold, which include warning, camouflage, courtship, species recognition, and perhaps in regulation of the body temperature.[1,42,95−99] In the discussion so far we have not said much about how to specify the color that is displayed by the wings. In terms of specifying color, we deal only with the color of butterfly wings, in particular, the blue *Morpho*. It is apparent to the human observer who views the color of the wings of this family, in particular, *Morpho menelaus*, that it appears to possess an intense blue which shifts in color (or hue) to lower wavelengths depending on the angle at which it is viewed. The color shifts from blue to violet as one increases the angle. This is characteristic of most wings that possess color due to thin-film interference. It is often said that the wings reflect a pure blue color, however, with little quantification of color specification to back up the statement.

Figure 36 displays a plot of the chromaticity coordinates of a *Morpho* wing, with the coordinates computed for three different illuminants. Each of the illuminants has a different spectral power density, thus giving rise to the perception of different colors of the same butterfly wing under different illuminants. The calculations are done in accordance with the procedure outlined in the earlier sections (section II), taking the product of the standard observer function together with the spectral reflectivity of the wing and the spectral power density of the incident light source used to observe the object. It is clear from the figure that the *purity* of the blue color is not very high, the *purity* of a color being defined as the ratio

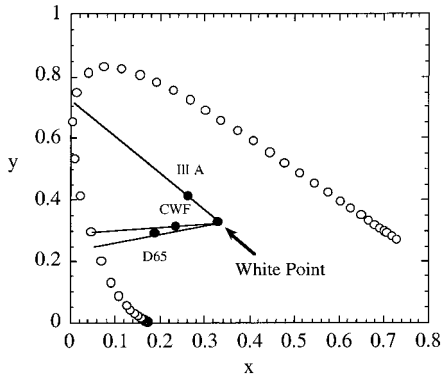


Figure 36. CIE coordinates for a Morpho wing with three different illuminants: iluminant A, cool white fluorescence (CWF), and D65.

of its distance from the illuminant point to the total distance of the illuminant point to the spectrum locus. It is, however, clear that the calculated chromaticity coordinates for daylight (approximating to illuminant C or D65) fall in the range of blue colors. It is often said that the iridescent wings of a *Morpho* possess a pure blue color, but color measurements show that this is not so. The blue of the *Morpho* wing appears pure for a reason similar to the "pure" blue sky, in that the blue of the sky is viewed against a dark background, while the blue wing of the *Morpho* is viewed against the dark melanin in the body scales.

One has to remember that the computations of the color points done here are based on the response function of a standard human observer. One does not know how the color appears to a butterfly, since butterflies have more than three photopigments or photoreceptors, and therefore, the color perceived by the butterflies would be quite different, to say the least. Attempts to study how certain colors might appear to insects have been studied in the past, and we refer the reader to a delightful book by Barth.[100]

This issue of specifying the color based on a "standard human observer" raises a serious, very important question: what do we mean by color vision[101] when the question pertains to color vision of butterflies, since the colors on the wings are far more important to the butterfly than to the human beings who marvel at the beauty of such colors and take pleasure in understanding how this color is produced. It should come as no surprise that a prerequisite for color vision is the existence of at least two spectrally different classes of photopigments or receptors and the presence of appropriate neural connections that can process the input from the receptors.[101]

Let us assume that a retina contains more than two kinds of receptors that differ in their spectral sensitivity. The presence of multiple receptors alone does not entail color vision. This is so because an argument can be made that such multiple receptors are there primarily to broaden the spectral region to which an animal is sensitive. Therefore, the presence of multiple receptors alone is not a sufficient condition or sufficient demonstration for the existence of color vision. A conclusive way to demonstrate that an animal has color vision is to establish its presence by *appropriate* behavioral tests. This criterion runs

into problems as well, since it is hard to establish what is *appropriate*.[101]

Traditionally, this problem has been formulated as a need to demonstrate that an animal can process wavelength and intensity separately or as independent variables. Our own experience of this colorful world tells us to have color vision is to "see" colors. The trouble that we run into with this working definition of color vision is the following: how does one translate this into an operational definition that can be applied to animals? The most common procedure is to train animals to do a particular task, like pushing a bar when it sees the "correct" stimulus. In such an instance, the success of this approach to color vision of animals relies on the capacity of the animals to learn, but this does not necessarily mean that the ability to learn is a prerequisite for color vision. It should be recognized that such abilities allow the (human) experimenter to probe the animal's sensory competence. For more details on the evolution of vision the interested reader is referred to an excellent review by Goldsmith.[101]

One can approach the problem of color vision from a different perspective, relying more on theory rather than on the behavioral tests. It is well-known and accepted that color vision is achieved by comparing the response of two or more spectrally different classes of receptors to a stimulus. This idea goes back to the days of Maxwell and his theory of trichromatic vision.[102,103] In animals the spectral distribution of receptors can differ greatly from our own, and the neural pathways in animals may manipulate the signals in different ways compared to our own. However, the spectral characteristics of the pigments (λ_{max} and their widths) must impose their signatures on the color vision system. Some of the characteristics of color vision can be explored by color mixing and color-matching experiments, and this has been done extensively, other than for humans, only in the case of primates and honeybees.[100]

One can approach the problem of color vision from the other direction, by studying the color vision system using the knowledge gleaned from the spectral characteristics of the pigments. It should be recognized that this does not provide a substitute for behavioral measurements; however, it certainly can highlight what might be expected. Several species of butterflies have now been documented to possess color vision based on behavioral responses.[104,105]

We have seen what the color space looks like for human observers (with trichromatic vision, see Figure 5, for example). Since the butterflies are tetrachromatic (or pentachromatic[101,105]), it is of interest to speculate what the color space might look like should the animals have color vision as we know it, which is to say that they see colors. One could explore the implications of the observation of tetrachromatic or pentachromatic observation using graphical means. Just as in the case of trichromatic vision, where three quantum catches of light can be plotted on the surface of a triangle, it is not unreasonable to expect that four values can be plotted in the volume of a tetrahedron, as shown in Figure 37, a conclusion reached by both Goldsmith[101] and Neumeyer (cited in Burkhardt, 1989[106]) independently. It is then clear that each vertex of the tetrahedron represents a particular photoreceptor. Should one of the photoreceptors be absent, then the diagram reverts back to that of a trichromatic visual system to form a color triangle.

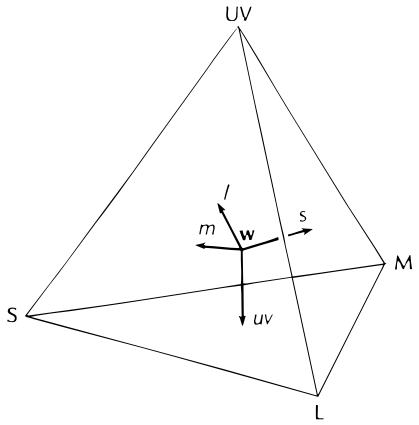


Figure 37. Tetrachromatic system can be represented with the use of color tetrahedron. Any color can then be represented as a point in such a system; in the example shown, the point w signifies that the color is white, representing equal absorptions of all the four pigments (L, M, S, and UV). The relative absorptions are given by the lengths of the normals from the point to the four sides of the tetrahedron. (Reprinted with permission from ref 101. Copyright 1990 Stony Brook Foundation.)

To carry the analogy further, Figure 38 shows the spectrum locus (the tongue-shaped curve in Figure 5, for example) for an animal with visual pigments with λ_{max} at 620 (L), 520 (M), 450 (S), and 370 nm (UV).[101] L, M, S, and UV denote long, medium, short, and ultraviolet wavelengths, respectively. This way of representing the color space leads to a rather intriguing and interesting conclusion. It says that if the color space looks like that shown in the figure (Figure 38), then the color space must possess two additional nonspectral sequences or hue along the UV-M and UV-L trajectories. It would be interesting to learn if such nonspectral colors are perceived. Psychophysical measurements to demonstrate the perception of nonspectral hues in these animals have not been performed. It is quite clear from this exercise that the color points plotted for colors (based on human visual system) *must be incorrect* for color perception of the same colors by the animal!

VII. Concluding Remarks

In this review I have attempted to point out color effects found in nature that are truly fascinating. There has been no attempt to be comprehensive, but rather I have chosen to provide a flavor of the kinds of phenomena that occur in nature to produce these beautiful colors that we take delight in viewing. There is a whole host of questions that are relevant to ask with regard to the color effects that I have touched upon in this article. These range from the more routine questions of how does one make structures such as the ones that have been discussed to the deeper questions of color perception and the implications of color on the behavior of these animals.

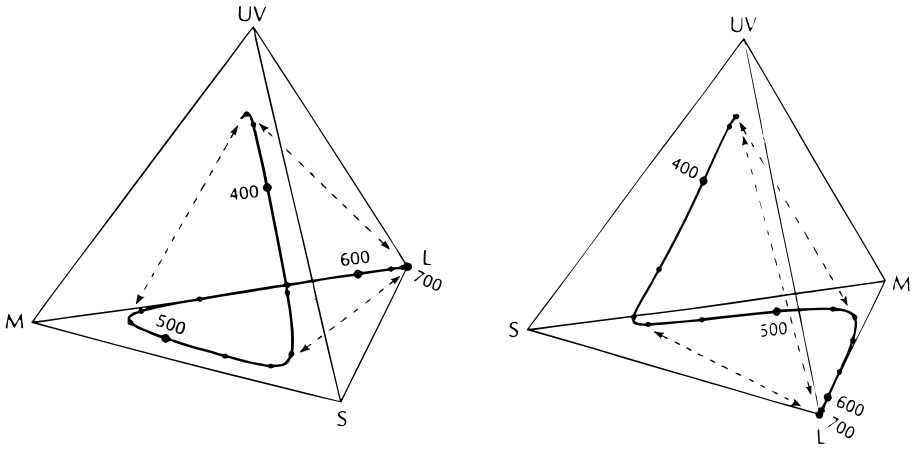


Figure 38. Two views of color space for insects with four visual pigments with λ_{max} at 370, 450, 520, and 620 nm; the spectrum locus is shown as a solid line with wavelength marks at 20 nm intervals. The nonspectral colors are shown as dotted lines. (Reproduced with permission from ref 101. Copyright 1990 Stony Brook Foundation, Inc.)

In particular, we know that the scarab beetles produce a bright, brilliant, metallic color which is in many cases circularly polarized. The obvious questions are what might be the purpose behind such elaborate methods of producing color and what, if any, is the use of circular polarization of the light that is reflected by the exocuticle of the beetles? The next obvious question is can the beetles detect circular polarization? If so, how is the detection accomplished? Are there advantages to circular polarization in comparison to other modes of polarization? The list of questions is primarily limited only by the imagination of reader and the writer alike.

It is the intent of this article to provide a summary of the various intriguing optical phenomena that have attracted the attention of scientific giants such as Newton, Rayleigh, and Michelson in the context of color science. It is my hope that the collection of optical phenomena discussed here and the structures responsible for them lead to renewed interest in creating such intricate structures and to an understanding of their optical properties in much greater detail.

VIII. Acknowledgments

It is a great pleasure to thank Prof. Ralph McGregor for many, many illuminating discussions on the topic of color science. I can find no words that I feel are adequate to thank Prof. Helen Ghiradella of the Biology Department at SUNY, Albany. Since becoming interested in biological color, Prof. Ghiradella has a been a constant source of encouragement, not to mention a great resource for the beautiful butterfly wings that I have used in this study. It is also a great pleasure to thank Prof. Nina Allen in the Botany Department at NC State University for being a source of encouragement and for making her excellent microscopy facilities available for my use and Mr. Dana Moxley for helping me make the color prints that are used in this manuscript. It is a pleasure to thank Dr. Carl Chiulli of Polaroid Corp. for the use of the microspectrophotometer. It is a delight to thank Dr. Gary Bernard, now at Boeing Aircraft, for sending me various reprints that I was not aware of and for the wonderful conversations about the interference filters in biological systems. I thank the referees for many useful and thoughtful suggestions, in particular, Dr. Kurt Nassau for many educational discussions on color science. Last but not least, I thank Prof. Alan Tonelli and Dr. Ed Chandross for many discussions dealing with various aspects of the problem and for being a sounding board for my ideas.

IX. Note Added in Proof

The color of many avian feather barbs has been attributed to the scattering of light by the keratin−air matrix, in this article and in many others. We have learned recently that the widely accepted "Rayleigh scattering" mechanism for the production of color is still being debated.[106−107] The essential argument has to do with the fact that many of the avian feather barbs have a peak in their reflectance spectrum, while a Rayleigh scattering mechanism (incoherent scattering) would argue against a peak in the visible region. An alternative model has recently been proposed, the constructive interference model, which takes account of the phase interactions among the light waves scattered by the keratin−air matrix to produce the structural colors of avian feather barbs.[108,109] Such a model was proposed in 1935 by Raman.[109] For further details, the reader is referred to a number of recent papers on this topic.[106−109]

X. References

(1) Ghiradella, H. *Appl. Opt.* **1991**, *30*, 3492.
(2) Monroe, E. A.; Monroe, S. E. *Science* **1967**, *159*, 97.
(3) Greenwalt, C. H.; Brandt, W.; Friel, D. D. *Proc. Am. Philos. Soc.* **1960**, *104*, 249.
(4) Greenwalt, C. H. *Hummingbirds*; Doubleday & Co.: New York 1960; pp 183−200.
(5) Neville, A. C.; Caveney, S. *Biol. Rev.* **1969**, *44*, 531.
(6) Caveney, S. *Proc. R. Soc. London B* **1971**, *178*, 205.
(7) Neville, A. C. *Biology of Fibrous Composites: Development Beyond the Cell Membrane*; Cambridge University Press: London, 1993.
(8) Saunders, J. V. *Nature* **1964**, *204*, 1151.
(9) Murray, C. A.; Grier, D. G. *Am. Sci.* **1995**, *83*, 238.
(10) Sanders, J. V. *Philos. Mag. A* **1980**, *42*, 705.
(11) Murray, M. J.; Sanders, J. V. *Philos. Mag. A* **1980**, *42*, 721.
(12) Rayleigh, J. W. S. *Philos. Mag.* **1888**, *26*, 256.
(13) Parker, A. R. *J. Exp. Biol.* **1998**, *201*, 2343.

(14) Parker, A. R. *Proc. R. Soc. London B* **1998**, *265*, 967.
(15) Arikawa, K.; Inokuma, K.; Eguchi, E. *Naturwissenschaften*, **1987**, *74*, 297.
(16) (a) Agoston, G. A. *Color Theory and Its Applications in Art and Design*; Springer-Verlag: New York, 1987; Chapters 2, 6, 7. (b) Avant, L. L. *Psychol. Bull.* **1965**, *64*, 246. (c) Kaiser, P. K.; Boynton, R. M. *Human Color Vision*, 2nd ed.; Optical Society of America: Washington DC, 1996. (d) Krauskpof, J. In *Color for Science, Art and Technology*; Nassau, K., Ed.; Elsevier: New York, 1998.
(17) Billmeyer, F. W.; Saltzman, M. *Principles of Color Technology*, 2nd ed.; John Wiley & Sons: New York, 1981; Chapter 2.
(18) Wyszecki, G.; Stiles, W. S. Color Science: Concepts and Methods, Quantative Data and Formulae, 2nd ed.; John Wiley: New York, 1982.
(19) Nassau, K. *The Physics and Chemistry of Color: The Fifteen causes of color*; John Wiley: New York, 1983.
(20) Born, M.; Wolf, E. *Principles of Optics*, 6th ed.; Pergamon Press: New York, 1980.
(21) Frankel, F.; Whitesides, G. W. *On the Surface of Things: Images of the Extraordinary in Science*; Chronicle Books: San Francisco 1998.
(22) Isenberg, C. *The Science of Soap Films and Soap Bubbles*; Dover Publications: New York, 1992.
(23) Heavens, O. S. *Optical Properties of Thin Solid Films*; Dover Publications: New York, 1991.
(24) Meyer-Arendt, J. R. *Introduction to Classical and Modern Optics*, 4th ed.; Prentice Hall: New Jersey, 1995.
(25) Lord Rayleigh (J. W. Strutt), *Philos. Mag.* **1871**, *107*, 274. (Reprinted in *The Collected Optics Papers of Lord Rayleigh*, Optical Society of America: Washington DC, 1994); Parts A&B.
(26) Bohren, C. F.; Fraser, A. B. *Phys. Teach.* **1985**, *23*, 267.
(27) Scalora, M.; Dowling, J. P.; Bowden, C. M.; Bloemer, M. J. *Phys. Rev. Lett.* **1994**, *73*, 1368.
(28) Nijhout, H. F. *The Development and Evolution of Butterfly Wing Patterns*; Smithsonian Institution Press: Washington, DC 1991. Meinhardt, H. *Models of Biological Pattern Formation*; Academic Press: New York 1982.
(29) Nijhout, H. F. *Sci. Am.* **1981**, *245*, 140.
(30) Nijhout, H. F. In *Advances in Insect Physiology*; 1985; Vol. 18, p181.
(31) Nijhout, H. F. *J. Expl. Zool.* **1978**, *206*, 119.
(32) Tada, H.; Mann, S. E.; Miaoulis, I. N.; Wong, P. Y. *Appl. Opt.* **1998**, *37*, 1579.
(33) Mason, C. W. *J. Phys. Chem.* **1923**, *27*, 201, 401.
(34) Mason, C. W. *J. Phys. Chem.* **1926**, *30*, 383.
(35) Mason, C. W. *J. Phys. Chem.* **1927**, *31*, 321.
(36) Mason, C. W. *J. Phys. Chem.* **1927**, *31*, 1856.
(37) Allyn, A. C.; Downey, J. *Bull. Allyn. Mus.* **1977**, *42*, 1.
(38) Ghiradella, H. *J. Morphol.* **1974**, *142*, 395.
(39) Ghiradella, H. *Ann. Entomol. Soc. Am.* **1984**, *77*, 637.
(40) Greenstein, M. E. *J. Morphol.* **1972**, *136*, 23.
(41) Ghiradella, H. *Ann. Entomol. Soc. Am.* **1986**, *78*, 252.
(42) Ghiradella, H. *Microsc. Anat. Invet.* **1998**, *11A*, 257.
(43) Werner, J. S. In *Color Vision: Perspectives from Difference Disciplines*; Backhaus, W. G. K., Kliegl, R., Werner, J. S. Eds.; De Gruyter: New York, 1998.
(44) de Weert, C. M. M. In *From Pigments to Perception: Advances in Understanding Visual Processes*; Valberg, A., Lee, B. B. Eds.; NATO Series 203; 1990.
(45) Land, M. F. *J. Exp. Biol.* **1966**, *45*, 433. Huxley, A. F. *J. Exp. Biol.* **1968**, *48*, 227.
(46) Ghiradella, H.; Aneshansley, D.; Eisner, T.; Silberglied, R. E.; Hinton, H. E. *Science* **1972**, *178*, 1214. Heilman, B. D., Miaoulis, I. N. *Appl. Opt.* **1994**, *33*, 6642.
(47) Brink, D. J.; Lee, E. M. *Appl. Opt.* **1996**, *35*, 1950.
(48) Huxley, J. *Proc. R. Soc. London B* **1976**, *193*, 441.
(49) Morris, R. B. *J. Entomol. Ser.* **1975**, *A49*, 149.
(50) Peng, S.; Morris, G. M. *J. Opt. Soc. Am.* **1996**, *13*, 993.
(51) Grann, E. B.; Moharam, M. G. *J. Opt. Soc. Am.* **1996**, *13*, 988.
(52) Magnusson, R.; Wang, S. S. *Appl. Phys. Lett.* **1992**, *61*, 1022.
(53) Gale, M. *Phys. World* **1989**, 24.
(54) Petit, R.; Suratteau, J. L. *Opt. Commun.* **1993**, *45*, 75.
(55) Kern, S.; Yaghmour, S. *Opt. Acta* **1983**, *30*, 167.
(56) Gale, M. T. *Opt. Commun.* **1976**, *18*, 292. Gale, M. T.; Kane, J.; Knop, K.; *J. Appl. Photogr. Eng.* **1978**, *4*, 41.
(57) Flanders, D. C. *Appl. Phys. Lett.* **1983**, *42*, 492.
(58) Wilson, S. J.; Hutley, M. C. *Opt. Acta* **1982**, *29*, 993.
(59) Haidner, H.; Kipfner, P.; Stork, W.; Streibl, N. *Optik* **1992**, *89*, 107.
(60) Knop, K. *Opt. Commun.* **1976**, *18*, 298. Knop, K. *Appl. Opt.* **1978**, *17*, 3598. Dammann, H. *Appl. Opt.* **1978**, *17*, 2273.
(61) (a) Bernard, G. D.; Miller, W. H. *IEEE Student J.* **1970**, *8*, 3. (b) Miller, W. H.; Bernard, G. D.; Allen, J. L. *Science* **1968**, *162*, 760. (c) Yoshida, A.; Motoyama, M.; Kosaku, A.; Miyamoto, K. *Zool. Sci.* **1996**, *13*, 525. (d) Miller, W. H. In *Handbook of Sensory Physiology*; Autrum, H., Ed.; Springer-Verlag: New York, 1979; Vol. VII/6A, Chapter 3.
(62) Clapham, P. B.; Hutley, M. C. *Nature* **1973**, *244*, 281.
(63) Lalanne, P.; Lemercier-Lalanne, D. *J. Opt. Soc. Am. A* **1997**, *14*, 450.
(64) Raguin, D.; Morris, G. M. *Appl. Opt.* **1993**, *32*, 1154.
(65) Xu, F. *Opt. Lett.* **1995**, *20*, 2457.
(66) Lalanne, P.; Lemercier-Lalanne, D. *J. Mod. Opt.* **1996**, *43*, 2063.
(67) Rytov, S. M. *Sov. Phys. JETP* **1956**, *2*, 466.
(68) Rayleigh, L. *Proc. R. Soc. London A* **1907**, *79*, 399.
(69) Enger, R. C.; Case, S. K. *Appl. Opt.* **1983**, *22*, 3220.
(70) Southwell, W. H. *J. Opt. Soc. Am. A* **1991**, *8*, 549.
(71) Burkhardt, D. *Naturwissenschaften* **1982**, *69*, 153.
(72) Stavenga, D. G.; Schwemer, J. In *Photoreception and Vision in Invertebrates* NATO Series A, Ali, M. A., Ed.; Plenum Press: New York 1982; Vol. 74, pp 11−61.
(73) Rayleigh, L. *Proc. R. Soc.* **1923**, *A103*, 233.
(74) Michelson, A. A. *Philos. Mag.* **1911**, *21*, 554.
(75) Greenwalt, C. H.; Brandt, W.; Friel, D. D. *J. Opt. Soc. Am.* **1960**, *50*, 1005.
(76) Adams, J.; Haas, W.; Wysocki, J. *Phys. Rev. Lett.* **1972**, *22*, 92.
(77) Ritcey, A. M.; Gray, D. G. *Macromolecules* **1988**, *21*, 1251.
(78) Sackmann, E. *J. Am. Chem. Soc.* **1971**, *93*, 7088.
(79) de Gennes, P. G. *The Physics of Liquid Crystals*; Clarendon Press: Oxford, 1974; Chapter 6.
(80) Chandrasekhar, S. *Liquid Crystals*; Cambridge University Press: Cambridge, 1992.
(81) Michelson, A. A. *Studies in Optics*; Dover Publications: New York, 1995; p 167.
(82) Onslow, H. *Philos. Trans. R. Soc. B* **1921**, *211*, 1.
(83) Makow, D. M. *Appl. Opt.* **1980**, *19*, 1274.
(84) Makow, D. M.; Sanders, C. L. *Nature* **1979**, *276*, 48.
(85) Schlitzer, D. S.; Novak, B. M. *J. Am. Chem. Soc.* **1998**, *120*, 2196−2197.
(86) Key, K. H. L.; Day, M. F. *Aust. J. Zool.* **1954**, *2*, 309.
(87) Hinton, H. E.; Jarman, G. M. *Nature* **1972**, *238*, 160.
(88) Hinton, H. E.; Jarman, G. M. *J. Insect Physiol.* **1973**, *19*, 533.
(89) Hinton, H. E. In *Insect Ultrastructure*; Neville, A. C., Ed.; Blackwell Scientific Publications: Oxford, 1970.
(90) Hinton, H. E. In *Illusion in Nature and Art*; Gregory, R. L., Gombrich, E. H., Eds.; Charles Scribner's Sons: New York, 1973.
(91) Hinton, H. E. *Nature* **1969**, *221*, 953.
(92) Parker, A. R. *Proc. R. Soc. London B* **1995**, *262*, 349.
(93) Parker, A. R. *Proc. R. Soc. London B* **1998**, *265*, 861.
(94) Parker, A. R.; McKenzie, D. C.; Large, M. C. J. *J. Exp. Biol.* **1998**, *201*, 1307.
(95) Wasserthal, L. T. *J. Insect Physiol.* **1975**, *21*, 1921.
(96) Wong, P. Y.; Miaoulis, I. N. In *Adv. Heat Mass Transfer Biotechnol.* **1995**, *322*, 5.
(97) Wong, P. Y.; Hess, C. K.; Miaoulis, I. N. *Int. J. Heat Mass Transfer* **1992**, *35*, 3315.
(98) Heinrich, B. *Insect Thermoregulation*; Wiley: New York, 1981.
(99) Miaoulis, I. N.; Heilman, B. D. *Ann. Entomol. Soc. Am.* **1998**, *91*, 122.
(100) Barth, F. G. *Insects and Flowers: The Biology of a Partnership*; Princeton University Press: Princeton, 1991.
(101) Goldsmith, T. H. *Q. Rev. Biol.* **1990**, *65*, 281.
(102) Maxwell, J. C. *Proc. R. Inst. G.B.* **1872**, *6*, 260.
(103) MacAdam, D. L. *Sources of Color Science*; The MIT Press: Cambridge, MA, 1970.
(104) Bernard, G. D.; Remington, C. L. *Proc. Natl. Acad. Sci.* **1991**, *88*, 2783.
(105) Bernard, G. D. Personnel Communication.
(106) Prum, R. O.; Torres, R. H.; Williamson, S.; Dyck, J. *Nature* **1998**, *396*, 28.
(107) Dyck, J. *Biol. Skrift.* **1997**, *18*, 1.
(108) Prum, R. O.; Torres, R. H.; Williamson, S.; Dyck, J. *Proc. R. Soc. London B* **1999**, *266*, 13.
(109) Raman, C. V. *Proc. Indian Acad. Sci. A* **1935**, *1*, 1.

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