PART I

INTRODUCTION AND REVIEW
CHAPTER I
INTRODUCTION

In the course of the last hundred years, the amassing of data and their crystallization into formulas for characterizing the radiation field in absorbing-scattering media 'under the name of Radiative Transfer' provide an excellent example of the process of the development of scientific knowledge. Astrophysicists have investigated the transmission of foggy atmospheres (Schuster, 1905), meteorologists have studied the visibility of air (Middleton, 1952), and manufacturers have tested materials like opal glass (Gurevic, 1930; Dreosti, 1930; Ryde, 1931; Ryde et al., 1931), plastics (Dunlop, 1942; Sanderson, 1942) and paper (Steel, 1935; Judd et al., 1937; Van der Akker, 1949; Stenius, 1951; Stenius, 1953). Similar approach has been used for investigating the transmitting qualities of cathode-ray tube (Logini, 1949), and to describe the luminescence of fluorescent screens excited by X-rays (Coltman, 1947; Hamaker, 1947). Biologists have used the same method for studying the chlorophyl in living leaves (Rabinowitch, 1961), leaf reflectance (Allen et al., 1973), living tissues (Logini, 1968). The diffusion of blood (Johnson, 1970), corneas (Feuk, 1970, 1971), transmission and reflection of blood (Zdrojekowski et al., 1970) and the transparency of eye lens (Dische, 1968; Benedek, 1971) have been investigated.
by use of the same technique. In the textile industry the same ideas are used for controlling dyeing processes (Stearns, 1951). The hiding power of paints and printing inks (Bruce, 1926; Kubelka-Munk, 1931; Neugebauer, 1937; Duncan, 1940; Sawyer, 1941; Munk, 1948; Callahan, 1952) and the diffuse reflection of light from crystalline powders (Johnson, 1952; Muhlschlegel, 1951; Kortum et al, 1953) have likewise been studied. Yet the development of the theory has never been complete. For example, light transmission and reflection of diffusing materials are influenced by many factors such as the nature of surface (s) of the specimen, its homogeneity, its absorbing and scattering qualities etc., and these factors simultaneously determine the physical nature of the problems and introduce complications into the development of the theory. The original equations either become too complicated or the integrals become too cumbersome for practical purposes. We, therefore, feel that further use of the theory in industry and research will be facilitated if some of the existing difficulties can be removed. Moreover, such improvement can provide better incentive for applying the theory to other problems. The present work aims at such a contribution to the theory and study of diffusing layers.

The earliest theoretical attempt to explain scattering was that made by the great physicist, Lord Rayleigh (1871), to whom we are indebted for some of the most fundamental contributions in this field. He used geometrical optics in attempting to establish a general law for interpreting scattering phenomena and later the wave
nature of light. The wave theory of light made it necessary to re-examine the existing ideas. He argued that when wavelength is gradually increased so that it becomes comparable to or greater than the dimensions of the scatterer the angular distribution of intensity of the diffracted radiation becomes comparable to that of the reflected (or refracted) part, and it would no longer be possible to separate the two. Thus, the phenomenon of reflection (or refraction) and diffraction are no longer separately definable under these conditions, and the total effect can be dealt with as a "scattering phenomenon".

The general rigorous theory of single scattering of plane waves from spherical particles, both dielectric and absorbing of any given size has been developed by Mie (1908). While in the case of Rayleigh scattering the only scattered radiation considered is that due to the electric dipoles, the theory of Mie permits the evaluation of angular distribution of intensity and of the polarization of the scattered radiation in terms of the additive contributions of a series of electric and magnetic multipoles located at the centre of the sphere. For detailed presentation of these theories the comprehensive surveys of Oster (1947), Edsall and Dundiker (1951), Van-de-Hulst (1957), Stuart (1967) and also the papers of Blumer (1925), Lowan (1949), Gumprecht and Sliepcevich (1952) and Heller et al (1946, 1957, 1961) may be referred to.

Single scattering theory may be used to study those scattering media in which the scatterers are isolated and have large central
distances between them. But, for media having considerably larger density of scatters, separate physical considerations are needed. This question is not merely of theoretical interest, but of great practical importance for characterization and standardization of many industrial products, such as pigments, synthetic-plastics, textiles, papers, paints etc. Also, there are many situations where knowledge of absorption and scattering provide important information about the specimen. For example, absorption data are necessary for interpretation of space probe and astronomical observations. Interpretation of remote sensing data acquired from aircraft and space craft, requires an understanding of the reflectance of the features on the surface of the earth. One specific problems in agriculture is interpretation of reflectance produced by vegetation. Further, in the development of synthetic insulating materials for space vehicles, it is desirable to maximize the absorption and minimize scattering in order to achieve a high emissivity and thereby reduce the equilibrium temperature. Hence, for these insulating materials, it is advantageous to determine the absorption and scattering components separately for the suitable candidate materials.

The development of a suitable theory to account for the optical properties of diffusing material was not done at a time or by any one investigator. The first theoretical approach towards this type of problems was made by the astronomer Arthur Schuster, when he formulated in 1905 a problem of radiative transfer through a diffuse media in an attempt to explain the appearance of absorption and
emission lines in stellar-spectra, any by Karl Schwarzschild when he introduced in 1906 the concept of radiative equilibrium in Stellar atmosphere.

Since the formulation of Schuster a good number of other workers become interested in the theory of diffuse reflection and transmission. Their aims were mostly to modify the radiative transfer equations for treating more realistic physical situations involved in an absorbing-scattering medium. The available methods appear to fall into two categories.

In the first category, simple models are available relating reflectance and transmittance to the absorption and scattering coefficients. A few attempts have been made to achieve the desired results with single constant theories. But the complexity of the process in multiple-scattering demands the use of more than one constant. Moreover, the practical usefulness of such theories depends on the number of experimentally determined constants that are necessary to have a reasonably satisfactory model for the properties of interest in such a system. The reflection and transmission of diffusing layers have therefore been treated in terms of the eight constant or the six constant theories of Ryde (1931) and Duntley (1942) and the two constant theory developed by Kubelka and Munk (1931). Similar theories have also been developed by Bruce (1926), Gurevic (1930), Smith (1931), Judd (1934), Amy (1937), Neugebaur (1937), Broser (1950), Muhlschlegel (1951), Bodo (1951), Bauer (1962), Melamed (1963), ter Vrugt (1965) etc. The majority of the workers
have used two constants theories, where the constants are intended to characterize the absorption and scattering per centimeter of layer thickness of the medium. These constants are, however, determined from transmission and reflection measurements. They made use of differential equations similar to those of Schuster and thus arrived at similar expressions. The most general are the theories of Gurevic and Kubelka and Munk. In the works of Wendtlandt and Hetch (1966) and Kortüm (1969), papers of Ingle (1942), Kubelka (1948), Akker (1949), Judd and Wyszechi (1963) and an excellent review of Kottler (1964), all the diffusion theories of this type have been worked out.

In the second category fall the more accurate methods of solving multiple scattering problems numerically for obtaining reflectance and transmittance as functions of absorption and scattering coefficients. These attempts have consisted of dividing the radiation fluxes into components going in different directions. In this manner, one can obtain rigorous solutions of the radiative transfer equation, particularly for the cases of non-isotropic scattering \( \text{Lowan et al (1948), Giovanelli (1955, 1956), Jefferies (1955), J.Reichman (1973)} \). The intrinsic mathematical difficulties of the problem called for the application of various ingenious approximation-methods such as 'variational method of Kourganoff' (1947); 'Invariance Principle' of Ambartsumian (1944); 'method of successive approximations' of Fresenkov (1916) and Schoenberg (1929); etc. The rigorous theory of radiative transfer have been discussed, among others, by Chandrasekhar...
in his book on 'Radiative Transfer'. There he gives the basic integro-differential transport equation of radiative transfer. This theory is, in fact, a generalization of the previous Schuster-Schwarzschild formulation. Unfortunately as this equation has no analytical solution, and hence all useful equations have been developed as simplifications of the actual case. There are, in fact, several of these equations. A comparison between the results based on the approximate Kubelka-Munk equations and those based on the rigorous theory is of special interest, the details of which are available in literatures by Giovanelli (1950), Jefferies (1955), Blevin and Brown (1961, 1962) and Hatch (1968).

The pioneering researches of Steel (1935) and Judd (1937), both of whom used the Kubelka-Munk (K-M) theory, resulted in special solutions and various mathematical aids that have been responsible, at least in part, for the widespread use of that theory. Moreover, a number of laboratories having a long-term interest in the optics of turbid media have developed their own specialized graphical aids to the use of the theory. This form of graphical solution has obvious commercial importance and, because of its convenience, may be used in industry. Successful application of these aids have also been made possible to paint films (Komodromos, 1961; Stennius, 1955; Gardner and Sward, 1950). Thus the popularity of the K-M theory shows that it is useful in the study of many samples. Yet, over the years, significant discrepancies of the theory have been noted. And Foote (1939), Akker (1949, 1963, 1966), Duncan (1949), Giovanelli...
(1955, 1956, 1957, 1959), Wilson (1960, 1961, 1962a,b), Blevin and Brown (1961), Pike and Komodromos (1961), Judd and Wyszechi (1963), Nordman (1966), Lathrop (1966) to name only a few workers did their best to remove the drawbacks of the K-M theory, and, indeed, succeeded to some extent. Consequently, many of the bulk properties of homogeneous diffusing media have been fairly well established. These include the diffuse reflection characteristics of semi-infinite media, the reflection and transmission properties of parallel layers, and the radiant intensities within media of a wide range of shapes when irradiated externally or from sources distributed through the medium.

Although these advances have resulted in new findings and useful applications, yet, surprisingly very little attention has hitherto been paid to the consideration of inhomogeneous diffuse media. The existing theories that have been found suitable in interpreting the reflectance spectrum assume that the absorption and scattering coefficients of the diffusers are constants, though a vast majority of diffusers do not fall under this class. Today measurements of transmittance and reflectance of scattering (turbid) media are becoming increasingly important in many fields of quantitative analysis. The determination of the amount of separated substance contained in a stained zone in thin-layer chromatography or electrophoresis, the determination of exact composition of powdered media, various measurements in textiles and paper industry etc., are only a few examples in which the study of the optical characteristics in
terms of inhomogeneous media are so much desired that it calls for a fresh appraisal of the old theories. For example, Stenius (1951) observed that for a given wavelength, the specific scattering and absorption coefficient in the case of hand made paper are not constants, but increase with increasing area weight of the paper in grams per m². When interpreting these results, we must assume that the papers do not represent homogeneous layers, but that the inner parts of the layers are more densely packed and, therefore, scatter more strongly than its outer parts. In fact, it is now widely recognised that there are many practical situations where it is more appropriate to consider the absorption and scattering co-efficients as variables or the media as inhomogeneous. To the best of our knowledge, except a recent restricted study (Lin and Kan, 1970), no comprehensive treatment of the inhomogeneous media in the context of the K-M theory is available.

Even the K-M theory for homogeneous media is valid under a few physical conditions that are not always easy to fulfil; and the theory correctly predicting the results for one case may fail when applied to another. But the Schwarzschild approximation may be assumed to be valid when the intensity at any point inside the medium varies slowly with the polar angle measured from the direction of thickness of the medium. This approximation no longer remains an approximation but yields correct result when the intensity is independent of the polar angle. Judging from the reported success of the K-M equations in conforming with various experimental results, as
noted earlier, for the type of diffusing media we are concerned with our present discussion, it is obvious that such media satisfy, for all practical purposes, the aforesaid conditions. It is precisely in this context that the K-M theory is assumed to be based on the more rigorous theory of radiative transfer (Chandrasekhar, 1950). The above remarks are also valid for inhomogeneous media in which the scattering and absorption co-efficients are functions of the co-ordinate along the thickness of the media, provided that the variations of these functions are not large over a distance of the order of the wavelength of light. In diffusing media, in contrast with thin films, this last condition is usually satisfied.

It is interesting to point out that in the usual applications of the K-M theory, individual layers are treated separately and the expressions for the reflectance and transmittance are obtained separately. This approach is most lucidly illustrated in the literature of Kortüm (1969). But it is not convenient, particularly for treating multilayered media. Also, expressions for the net forward and the net backward intensities inside the medium are not usually considered. In many cases, where the medium is not a solid one, for example, a plant canopy or a gaseous envelope, explicit expressions for the forward and the backward intensities are useful in studying the evolution of light distribution inside the medium. We, therefore, feel that the studies of the properties of inhomogeneous diffusing media may bring a significant advancement in understanding the properties of the diffusing media and may be helpful in relating
correctly the measured reflectance or the transmittance to the absorption and scattering parameters. This incentive is, however, the basis of the present work.

Recently Som (1978) has given an excellent treatment on the extension of two-constant theory by use of matrix formulation. The matrix theory unifies the study of the properties and characteristics of the homogeneous as well as the inhomogeneous media under a single representation. The salient feature of this theory is that the optical properties of the diffusing layers may be specified entirely in terms of the characteristic matrix of the layer. Characteristic matrices are well known in the theory of multilayered thin films (Jackson, 1966). In the case of thin films, the use of characteristic matrices makes it possible to deduce certain general theorems that deal with useful properties of multilayer films in a general way. Similar theorems also hold for diffusing layers. It may be remarked that the theorems that are valid for layered media consisting of homogeneous layers, hold as well for layered media consisting of layers some or all of which may be inhomogeneous. This is because an inhomogeneous layer may be thought of as consisting of many suitably chosen homogeneous layers. Further it has been found that a layered medium is equivalent to a combination of two homogeneous layers, but is not, in general, equivalent to a single layer; and that if the scattering and the absorption co-efficients are proportional to each other and vary together periodically with the same period, and if the thickness of the diffusing layer is equal to
an integral multiple of the period of variation, then the layer behaves like a homogeneous layer of the same thickness. Besides, it is possible to appreciate more fully the significance of the earlier observation (Kubelka, 1954) regarding assymmetric behaviour of the total reflectance and transmittance of a diffusing media with the direction of incidence of light. Of course, the validity of the matrix representation is subject to certain conditions.

The simple relations that exist between the reflectance and transmittance and the elements of the characteristic matrix suggest that, in many applications where the scattering and absorption co-efficients are not directly required, the matrix elements themselves, instead of the absorption and the scattering co-efficients, may be used as a physical parameters characterizing the medium. This proposal is very attractive for unsupported layers in which case only two matrix elements of first column are needed. The advantage of the proposal is all the more evident for inhomogeneous layers. The design of multilayer diffusers (Fragstein, 1973) for modifying the spectral content of diffused radiation can be conveniently handled in the present theory. But because such modifications can be effected only by use of wavelength dependent absorption in the layers, such designs are not expected to utilize too many layers. Nevertheless, even a few layers can be better handled in this approach. In experimental studies it may sometimes be convenient, or even necessary, to sandwich the sample between the diffusing supports of known properties. The analysis of the experimental results under such situations becomes simple in terms of matrices. Even the characteristic matrix for the combination is determined directly in terms of the measured reflectance and transmittance.
SUMMARY OF THE WORK
The present work consists of three parts. Part I is mainly devoted to a review of the theoretical basis of the present work. It consists of three chapters including this introductory discussion.

Chapter II describes the development of the usual Schuster-Kubelka-Munk (S-K-M) theory, its related assumptions and implications.

Chapter III is entirely devoted to a review of the new and very useful matrix formulation (Som, 1977) of the S-K-M theory. This formulation may be used in the study and analysis of both homogeneous and inhomogeneous diffusing media. A brief mention of the theory has already been made earlier in this chapter. But in Chapter III of Part I a thorough discussion of the matrix formulation has been given to form a basis of much of the present work.

Part II is devoted to the new contributions to the theory of inhomogeneous diffusing media in the context of the matrix formulation. It consists of seven chapters.

As already pointed out, the merit of the matrix theory is that diffusing layers, under the usual assumption of the S-K-M theory, may be represented by 2 by 2 matrices. In this sense, a single layer may be characterized by a 'characteristic matrix' whose elements are directly related to the reflectance and the transmittance of the layer. The explicit evaluation of the characteristic matrix for a medium requires the prior knowledge of the solutions of the pertinent
differential equations for the medium. Unfortunately, in most cases, these equations cannot be solved exactly but only by approximations.

In Chapter IV, the cases for which the exact determination of the characteristic matrices seemed to us possible, were presented. This analysis gave explicit expressions for a few useful quantities, such as reflectance, transmittance etc. of a few model but representative inhomogeneous media.

In Chapter V, numerical study of the exact solutions has been undertaken. The influence of varying absorption coefficient and constant scattering coefficient on the calculated reflectance and transmittance of a model inhomogeneous medium has been studied. The results point out the instances where the reflectance or the transmittance measurements are important for studying the properties of inhomogeneous media.

In Chapters VI to IX, we have discussed a few approximate solutions and their numerical illustrations.

In Chapter VI and VIII, we have developed techniques for the evaluation of the characteristic matrices in terms of a few approximate solutions of the differential equations.

These approximate methods of solutions fall into the following two categories:
1. Approximate Solutions-I:

The techniques for getting the approximate solutions-I have been discussed in Chapter VI. The results show that complicated diffuser problems may be investigated with the aid of this method. Two distinct cases were discussed. The first case (the method 1A) involves separate solutions of separate integrals for different inhomogeneous media. This inconvenience was removed in the second case (the method 1B), where it is shown that any form of $\zeta(x)$, with $\eta(x)$ as constant, can be studied in a single mathematical analysis. The numerical studies based on the approximate solutions-I have been made in Chapter VII.

2. Approximate Solutions-II:

In Chapter VIII we presented another approximate method based on the Schelkunoff's method (Schelkunoff, 1946) of solving linearly and slightly non-linear differential equations. The analysis shows that any arbitrary variations in the absorption and the scattering coefficients can be dealt with. Because of this advantage, the method seems to be very useful for investigating the properties of inhomogeneous media. In Chapter IX, a few numerical examples have been considered to illustrate the applicability of the approximate solutions-II.

In Chapter X, we have investigated the validity of the approximate methods by intercomparing the numerical results of the approximate methods with those of the exact method. For such a comparison,
one of the model media for which the exact and the approximate solutions were obtained in the foregoing chapters has been chosen as an example. Schelkunoff's method does seem to give more accurate solutions than the other two methods. Moreover, with the aid of the Schelkunoff's method (Method II) we may consider cases in which the absorption and the scattering coefficients may vary rather strongly. As the method is simpler to deal with numerically and is applicable to arbitrary forms of variation, the conclusion is that this technique may prove to be useful in the study of the absorption and the scattering coefficients of inhomogeneous media. However, the approximate solutions-I, particularly the method 1B, can be used when the variation in the absorption and the scattering coefficients are weak.

Upto this point of our study of the inhomogeneous diffusing media, in the context of the matrix theory and hence the K-M theory, we confined our attention mainly to the theoretical analysis. We have shown in Chapter III that the matrix theory leads to hitherto unlooked for relations and effects, some of which need experimental verification.

In Part III (Chapter XI), we have described the experimental investigations that was carried out for studying the validity of the matrix theory for multilayered samples. The experimental technique used has a wider applicability in the study of the multilayered samples. The results presented were obtained for a few selected three-layered samples, such as, (I) white tracing paper, (II) dyed
tissue paper and (III) dyes on glass slides. It is seen that the agreement between the theoretical and the experimental results are, on the whole, quite satisfactory. So far as the measurements were concerned, we deviated from the ideal conditions of optical geometry, dictated by the basic postulates of the usual S-K-M theory. This was necessary due to limitations of the optical geometry of the measuring instruments available in our laboratory. But the results show that even with their non-ideal optical geometry the matrix theory remains valid.

In this dissertation we have summed up the works done so far. In the future, we intend to continue further theoretical and experimental investigations. On the theory side, one of our aims is to further explore the validity of the approximate methods, particularly that based on the Schelkunoff's approximation. On the experimental side, our immediate aim is to test the validity of the matrix theory in the context of different optical geometries of measurement, and also with respect to various other combinations of diffusing samples.
Publications

1. The materials covered by Chapter IV have already been published. The reference is:


- S.C. Som and B. Chaudhuri,

2. Some of the Materials Covered by Chapter VI and VII have also been published. The reference is:

"Theory of Total Reflectance and Transmittance with Non-Homogeneous Strongly Absorbing-Scattering Media"

- B. Chaudhuri,