COMMENTS ON THE THEORIES OF DIFFUSE LIGHT SCATTERING

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Summary

The aim of the paper is to give a general evaluation of the remission data measured in the investigation of diffuse light scattering and of the relevant theories and to justify the necessity of further developments.

Illuminating a diffuse scattering system, *reflected radiation is observed to be composed of two components.* One of them is the regular radiation reflected from the surface of the investigated system.

The relative refractive index n and the absorption index κ of the sample are calculated from the value of measured *regular reflection*, by using the Fresnel equations, as a function of wavelength λ.

The other component of reflected radiation is due to *diffuse reflection (remission)*, which takes place when part of the beam of light enters the sample, where it is scattered on the individual particles. Passing through them it is partly absorbed and the rest of it emerges through the surface of incidence on the illuminated side of the sample.

The two types of reflection appear at the same time in such a form that the reflection spectrum is less structured when both components are present. The difference can be observed very well in scattering systems having a glossy surface (e.g. printing ink), that is the proportion of mirror reflection is definitely higher than on layers of dull surfaces. If the surface of the sample is glossy, the amount of light entering it will be smaller, i.e. a smaller portion takes part in the absorption process, and for this reason, even in the case of medium of high absorbance, the specifically characteristic absorption region does not appear to such a degree as when the proportion of remission would dominate.

Thus, it is feasible *to eliminate the regular component* from experimental work.

The diffuse nature of scattering and the proportion of regular reflection are functions of the surface of the sample.

Before passing over to some leading theories, some statements of general importance are introduced.

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The theories of scattering systems postulate either that *illumination* should be *diffuse* or that the rays of light should fall on the sample in a parallel beam (eventually at right angles). According to the Kubelka–Munk theory diffuse illumination can be substituted by parallel beam illumination at 60°.

The angle of *observation* is 0°, 45° or diffuse.

Thus, the optical arrangement is:

$$_0R_{45},\quad _0R_\mathrm{D},\quad _{45}R_0,\quad _{60}R_\mathrm{D},\quad _\mathrm{D}R_\mathrm{D}$$

In remission measurement the proportion of radiation that penetrates through the sample decreases with increasing layer thickness and the measured value of remission for a given sample always attains the same limit R_∞ *independently of the background*. This value is one of the most important data characterizing scattering systems. It can be defined in several ways.

Campbell and Benny assigned the value R_∞ to a layer thickness which does not transmit any considerable amount of light. This formulation is not exact, although practitioners may surely interpret it correctly. According to investigations by Huszár the value R_∞ appears at the critical layer thickness where transmission is approximately 2%. Considering also the background R_∞ is the value which, in measurements against a white background, does not decrease any more despite increasing the layer thickness, but stays constant (e.g. in the printing industry). Applying a black background, the remission value increases with increasing layer thickness up to reaching R_∞, then it remains constant.

According to Kortüm, the two main questions to be answered by remission measurement are the following:

1) To what extent can the proportion of regular reflection be eliminated during a measuring process?
2) Can a diffuse reflection spectrum supply measured data from which the absorption spectrum can be quantitatively deduced?

These two questions show clearly that Kortüm and his followers were interested in the problems outlined in these points, since the word "quantitative" also refers to the possibility of determining concentrations. Indeed, their investigations are almost totally of chemical character and pertain to the field of structural and analytical research, respectively.

Kortüm and his coworkers were the first to investigate *the first problem* in detail. They observed that the proportion of regular reflection can be eliminated from the results of measurement with polarized light in crossed polarized sheets.

To analyse powder they worked out another special method. The sample should be mixed with the non-absorbing standard in such a dilution that the regular reflections of the sample and the reference medium become nearly identical, i.e. they should not have any effect within the measuring accuracy.

This is actually the first appearance of the relative remission measurement worked out later.

The *second problem* raised by Kortüm may be answered by a theory that relates the absorption coefficient of the sample to the measured remission data.

The reflection properties of scattering systems were studied by many researchers. The theories published in the literature can be divided into two groups:

1) theories based on *continuum models*, and

2) theories developed on the basis of the *statistical model.*

Continuum models describe the scattering and absorption properties by *two* (or more) phenomenological *constants*. These theories can be regarded as the various levels of the approximate solution of the general transport equation of radiation.

The statistical models (in another grouping: discontinuum theories) are based on the *summation of the transmittances and reflectances of individual layers or particles*. Some assumptions should be made for the nature of basic units. The validity of final results depends on the extent to which the assumptions approach reality.

The Kubelka–Munk theory was published in 1931. Its purpose was to perform theoretical investigation into the opacity of dye layers, and it established a relation between the optical properties of a transparent layer, on the one hand, and the absorption and scattering coefficients, on the other.

Kubelka and Munk formulated the basic assumptions of the theory for a very well defined, ideal hypothetic sample as follows:

A dull, homogeneous, isotropic plane-parallel layer of thickness "d" illuminated with diffuse and monochromatic light. The sample should be of a size to eliminate edge effects, and of a sufficient thickness to be taken as opaque.

A layer dx inside the sample, parallel with the surface, be illuminated with light of intensity I in direction x. Part of the light, $kI\,dx$, is absorbed in the layer dx and the amount $sI\,dx$ gets lost due to scattering. k and s denote the absorption and scattering coefficients, respectively.

On the other side of the layer dx reflected light of intensity J enters from the subsequent layers, the amount of which decreases due to absorption and scattering in an analogous way.

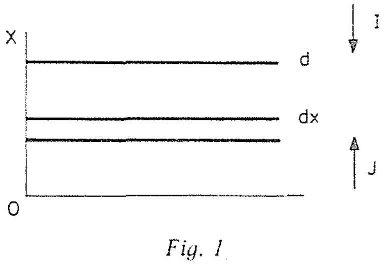

Fig. 1

The absorption and the scattering process are described by *two differential equations*

$$-\frac{dI}{dx}=-(k+s)I+sJ$$

$$\frac{dJ}{dx}=-(k+s)J+sI$$

The exponential solution of the differential equations gives complicated relations both for transmission and remission.

The relation for transmission goes over into the BLB law if it refers to a non-scattering medium ($s=0$), the relation for remission for infinite layer thickness, however, gives the equation

$$\frac{k}{s}=\frac{(1-R_{\infty})^2}{2R_{\infty}}\equiv F(R_{\infty})$$

i.e. formally a relation which is suitable for investigating insoluble materials because only the remission measurement is possible. As Kortüm wanted to solve structural research problems and analytical tasks on the basis of the relation between remission data and the absorption coefficient, in his opinion the second question was solved.

Some remarks on the Kubelka–Munk theory:

A) Two marginal cases of the basic relations can be discussed:

a) for $k=0$, i.e. when only scattering is taken into account, the original differential equations are modified as follows:

$$-\frac{dI}{dx}=-sI+sJ; \qquad \frac{dJ}{dx}=-sJ+sI$$

that is

$$\frac{dI}{dx}=\frac{dJ}{dx}$$

which has the following meaning:

If the continuous line is J, there is no re-scattered light on the surface of entry; if the dashed line is J, its magnitude is not given. Thus, a relation that gives the magnitude of J is required in any case.

b) for $s=0$ the relations goes over into the BLB law.

B) According to the mathematical formulation of the theory, only one re-scattering takes place in each layer in the direction of the x axis, consequently *the model is one-dimensional.*

The intricate relations were simplified by Kubelka himself. It is worth examining at least part of the series of formulae given by him, to see which of them are suitable to check or direct experimental work.

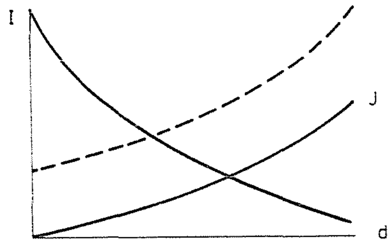

Fig. 2

Let us prepare a Table, the first column containing the quantities to be measured, of which one can be calculated as a function of the others. The second column contains the necessary relations.

In the third and the fourth columns, the simplifying assumptions and the simplified relations are shown, respectively.

We write the criteria for the approximate formulae in the fifth column and the approximate formulae in the sixth.

The following criteria are set for the approximations:

a) Bright material, its scattering power may be high

$$R_\infty \to 1, \qquad SX < \infty$$

b) Dark material, with little scattering

$$R_\infty \to 0, \qquad SX > 0$$

c) Sample of low scattering power or thin sample of low reflectivity

$$SX \to 0, \qquad R_\infty > 0$$

d) Sample of high scattering power, or a thick sample of high reflectivity

$$SX \to \infty, \qquad R_\infty < 1$$

In the Table we have included the system of formulae which seems to be simpler, that is the solutions published in Kubelka's paper. Obviously, by grouping the quantities to be measured differently, a large number of various relations can be given, which, however, contain the quantities generally hard to measure (R_∞, R_0, SK).

However, the functions shown in column 2 of the Table are still too complicated, owing to which approximate equations have been deduced with the assumptions given above. These equations are much simpler to apply but their drawback is that they cannot be used unless the assumptions are carefully observed. The quantities listed in the sixth column, however, are still the ones hard to measure, a fact that does not reduce the error limits increased owing to the approximate character of the formulae.

1	2	3	4	5	6
1) R, R_∞, R_g, SX	$R=\frac{1-R_g(a-b\,\mathrm{ctanh}\,bSX)}{a+b\,\mathrm{ctanh}\,bSX-R_g}$ $SX=\frac{1}{b}\left(\mathrm{Ar\,ctanh}\frac{a-R}{b}-\mathrm{Ar\,ctanh}\frac{a-R_g}{b}\right)$	$R_g=0$ $R=R_0$	$R_0=\frac{1}{a+b\,\mathrm{ctanh}\,bSX}$ $SX=\frac{1}{b}\mathrm{Ar\,ctanh}\frac{1-aR_0}{bR_0}$	a b	$R\approx 1-\frac{1-R_g}{(1-R_g)SX+1}$, $R_0\approx\frac{SX}{SX+1}$, $SX\approx\frac{R_0}{1-R_0}$ $R\approx R_\infty+(R_g-R_\infty)\exp\left(-\frac{SX}{R_\infty}\right)$; $R_0\approx R_\infty\left[1-\exp\left(-\frac{SX}{R_\infty}\right)\right]$
2) R, R_∞, R_g, R_0	$R=\frac{R_0-R_g(2aR_0-1)}{1-R_0R_g}$ $R_0=\frac{R-R_g}{1-R_g(2a-R)}$ $a=\frac{1}{2}\left(R+\frac{R_0-R+R_g}{R_0R_g}\right)$			 c d	$SX\approx R_\infty\ln\frac{R_g-R_\infty}{R-R_\infty}$; $SX\approx R_\infty\ln\frac{R_\infty}{R_\infty-R_0}$ $R\approx R_g+[(a-R_g)^2b^2]SX$; $R_0\approx SX$; $R_0\approx R_\infty-2bR_\infty^2\exp(-2bSX)$ $SX\approx\frac{1}{2b}\ln\frac{2bR_\infty^2}{R_\infty-R_0}$
3) R, R_1, R_g, R_0	$R=\frac{R_0(1-R_g)+R_1R_g(1-R_0)}{1-R_0R_g}$ $R_1=\frac{R-R_0+R_0R_g(1-R)}{R_g(1-R_0)}$			a b	$T\approx\frac{1}{SX+1}$; $SX\approx\frac{1-T}{T}$ $T\approx\exp\left(-\frac{SX}{2R_\infty}\right)$; $SX\approx-2R_\infty\ln T$
4) T, R_∞, SX	$T=\frac{b}{a\sinh bSX+b\cosh bSX}$ $SX=\frac{1}{b}\left(\mathrm{Ar\,sinh}\frac{b}{T}-\mathrm{Ar\,sinh}\,b\right)$		 $bSX=-\ln T$	c d	$T\approx 1-aSX$; $SX\approx\frac{1-T}{a}$ $T\approx 2bR_\infty\exp(-bSX)$; $SX\approx\frac{1}{b}\ln\frac{2bR_\infty}{T}$
5) T, R_∞, R_0	$T=[(a-R_0)^2-b^2]^{1/2}$ $R_0=a-(T^2+b^2)^{1/2}$ $a=\frac{1+R_0^2-T^2}{2R_0}$			b d	$T\approx\left(\frac{R_\infty-R_0}{R_\infty}\right)^{1/2}$; $R_0\approx R_\infty(1-T^2)$; $R_\infty\approx\frac{R_0}{1-T^2}$ $T\approx[2b(R_\infty-R_0)]^{1/2}$; $R_0\approx R_\infty-\frac{T^2}{2b}$; $R_\infty\approx R_0+\frac{T^2}{2b}$
6) T, R, R_0, R_g	$T=\left[(R-R_0)\left(\frac{1}{R_g}-R_0\right)\right]^{1/2}$ $R=R_0+\frac{T^2R_g}{1-R_0R_g}$				

The problems enumerated above stimulated many researchers to study, on the one hand, the constants of the Kubelka–Munk theory, and on the other, to introduce *new constants* into the theory. To facilitate the calculation of measured data new theories were worked out in parallel with the two-constant theory, *raising the number of constants to three, four and finally eight.*

Several researchers expressed view against the Kubelka–Munk-theory. They worked out modifications and graphs to enhance its applicability.

In another, very significant *theory*, the remission and transmission properties of a thick layer built up from the elementary layers of scattering particles are considered. The basic postulate of the theory is that the thickness of the elementary particles is not infinitesimal but agrees with the size of particles.

The latter theory, called *statistical method or discontinuum theory* in the literature, was studied by several researchers.

After Bodó's paper the essential features of the theory are the following.

The particle layers situated behind each other partly reflect and partly transmit illuminating light.

Assuming the intensity of illuminating light to be unit, denote the diffuse reflection of the first elementary layer by R_1 and its transmission by T_1. Be the joint reflection of the number i of layers R_i and their transmission T_i. For a number n of layers the corresponding quantities are R_n and T_n, which can be written down according to the summation rule of infinite geometrical series as

$$R_n = R_1 + \frac{T_1^2 R_{n-1}}{1 - R_1 R_{n-1}}$$

and

$$T_n = \frac{T_1 T_{n-1}}{1 - R_1 R_{n-1}}$$

An interesting novel idea was raised by Melamed, who interpreted discontinuity by fully rejecting the assumption of plane-parallel layers, carrying out instead the statistical summation for individual particles.

In a work published in 1977 Hecht investigated the theories of diffuse reflection spectra according to how they interpret the spectra. He stated that "Only the statistical models lead to expressions from which absolute absorptivities and scattering coefficients can be calculated and related to the actual particle characteristics."

It should be added that *the discontinuum theory also* applies unambignously to discrete steplengths and *one-dimensional models.*

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