MATHEMATICAL MODELLING OF DIFFUSE LIGHT SCATTERING. STEPNUMBER AND PATHLENGTH DISTRIBUTION

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Summary

Modelling offers a good opportunity to study the mathematical relationships of the spectroscopy of diffuse light-scattering media. The modelling of stepnumber and pathlength distributions reveals the basic relations between remission and transmission spectroscopy. The results show that the particle shape and size have a great influence on the pathlength distribution of light in diffuse media.

The mathematical formulation of the spectroscopy of diffuse light-scattering systems essentially differs from that of non-scattering media. The Bouguer–Lambert–Beer law (BLB law) (1) is not applicable directly in this case because its primary conditions: a non-scattering system, i.e. light passing strictly in straight lines, and a sample with two flat plane-parallel boundary surfaces, are not fulfilled.

$$I = I_0 e^{-\varepsilon c 1} \tag{1}$$

The basic feature of diffuse scattering media is that they contain inside scattering surfaces or centers and these surfaces are not plane-parallel. Thus, owing to multiple scattering, the route of light is neither parallel nor straight.

To study the mathematical relationships of diffuse scattering systems computer modelling was carried out using the Monte-Carlo method [1, 2]. The starting points of modelling were: the route of light inside the sample is zigzagged and photons may emerge after having travelled different pathlengths u. In the calculation of light loss due to absorption, however, the BLB law (2) can already be applied to calculate the attenuation dI for very small light beams dI_0 covering a given identical pathlength even if the routes are different. The total remittance or transmittance can be obtained by means of summing (integrating) the intensities pertaining to different pathlengths.

$$dI = dI_0 e^{-\varepsilon c u} \tag{2}$$

For the exact mathematical solution it is necessary to know the different pathlengths u covered by light and the proportion of light covering the different pathlengths. In other words, we have to find the distribution of light according to pathlength—or rather its density function $f(u)$.

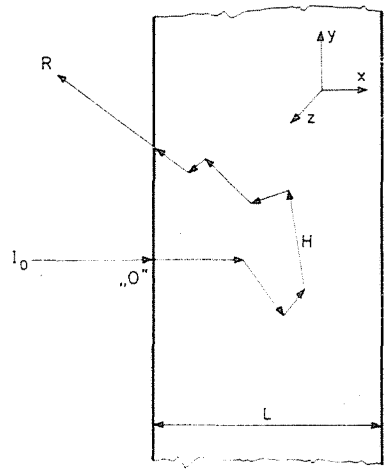

Fig. 1. Diagram of the model

The computation was made on the basis of the following model:

The "photons" fall onto a layer of thickness L at the point 0 (Fig. 1). Along the y, z axes the layer is infinite. The photons may make steps H. The steps are represented by a space diagonal calculated from three real random numbers uniformly distributed between -1 and $+1$. The computer program watched and stored the position of photon inside the layer and the sum of steplengths made by it.

If in the course of wandering the photon emerges from the layer on the illuminated side (the side of incidence) it means remission, on the opposite side it means transmission. The summation of the pathlengths of a great number of photons gives the possibility to obtain (approach) the requested density function.

The remittance or transmittance can already be calculated for samples of different absorptivity Z according to (3) by substituting the density function into (2).

$$R, T = I_0 \int_0^\infty f_{R,T}(u) e^{-Zcu}\, du \tag{3}$$

Tabulated data obtained from modelling gave the possibility to establish graphical relations for the variation of layer thickness, particle size and absorptivity. These relations cannot be directly compared with measured data, but the curves correspond to them fully in character.

Most of the theories describing diffuse light scattering (Continuum theories: Kubelka–Munk, Gurevitsch, Rozenberg [3, 4, 5, 6]; Discontinuum theories: Bodó, Johnson, Melamed, Fassler–Stodolski [7, 8, 9, 10, 11, 12]) do not consider the pathlength covered by light inside the sample or pathlength distribution. But the mathematical apparatus contains such considerations.

The situation is the simplest with the discontinuum theory which assumes the sample to consist of thin layers. The mathematical deduction is based on the summation of geometric series. This corresponds to the one-dimensional binomial distribution describing the wandering of discrete (unit) steplengths over a one-dimensional route (Fig. 2).

A more detailed examination points out that all the other theories practically contain the same distribution as they actually calculate with one dimension only and a discontinuous (possibly very small) layer thickness. Theories dealing with spherical or cube-shaped particles ultimately take an average steplength into account (Melamed).

In reality light rays move in a three-dimensional space. If the wandering of the discontinuous steplength is not considered freely in space but along the three axes a different pathlength distribution with a maximum of the density function is obtained (Fig. 3). Reality can be approached better if we suppose that the steps are made in any direction of space and the steplength is continuous in a given interval.

For a more detailed study of the mathematical relations the pathlength distribution can be divided into stepnumber and steplength distributions. First we investigated the stepnumber (n) distribution for varying layer thicknesses for remitted and transmitted light assuming continuous steplength. The modelling was performed on a CBM 3032 microcomputer using a machine language program. The number of incident photons was 100 000. The

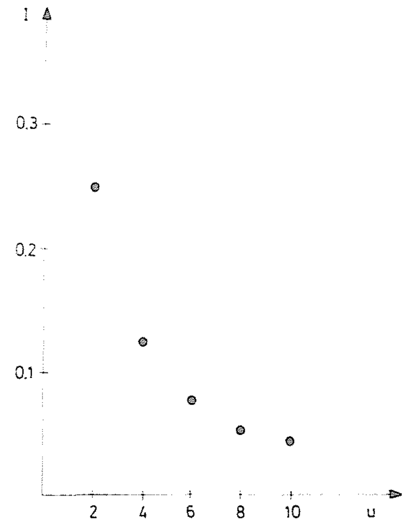

Fig. 2. Density function of the pathlength distribution of one dimensional discrete wandering (u = pathlength, I = intensity)

steplength was taken from a random number generator giving uniformly distributed real numbers between -1 and $+1$. In this modelling one step represents the projection of a step in the space to the x axis. As can be seen in the stepnumber distribution of remission increasing the layer thickness results in the increase of the intensity at greater stepnumbers and the plot approaches a limit value (Fig. 4).

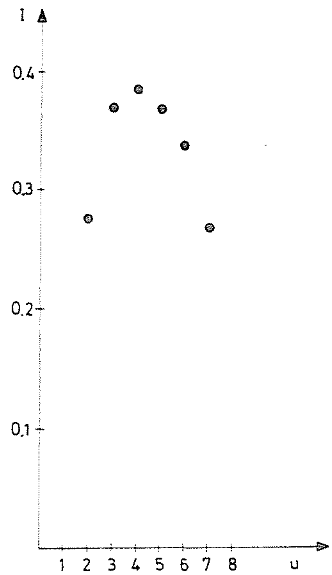

Fig. 3. Density function of the pathlength distribution of three dimensional discrete wandering (u = pathlength, I = intensity)

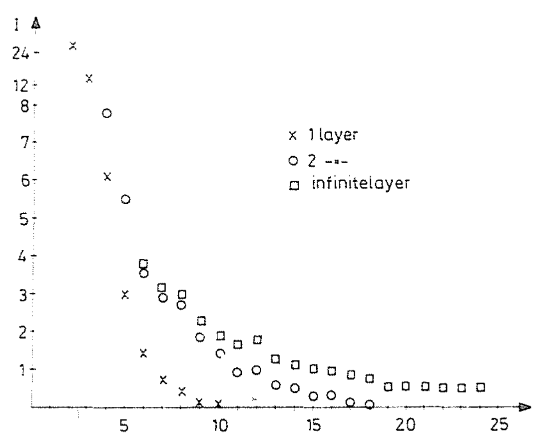

Fig. 4. Density function of the stepnumber distribution of reflected light for several layer thicknesses (n = stepnumber, I = intensity)

The stepnumber distribution of transmitted light (Fig. 5) gives plots with maxima. The increase of layer thickness shifts the maximum toward the longer stepnumber and significantly decreases the intensity.

The pathlength distribution for emitted light is given by the sum (composition) of the stepnumber distribution and the pathlength distribution for one, two, etc. steps. This composition is permissible if we may suppose that the sample is symmetrical to the x axis and every step has the same distribution in every opposite direction. Taking steplength into account in such a way gives at the same time the total pathlength for the movement in three-dimensional space.

For this purpose the one and two step pathlength distribution was calculated for steps represented by a space-diagonal calculated from three real numbers uniformly distributed between 0 and $+1$ and modelled the $1:1$ ratio composition of one and two steps. Figure 6 shows the density function of pathlength distribution for one and two steps. The maximum is near to the unit 1 and 2 and the maximum steplength approaches 1.73 for one step and 3.46 for two steps ($\sqrt{3}$ and $2 \times \sqrt{3}$).

Figure 7 shows that the composition of 1 and 2 steps definitely includes the two maxima. From this it follows obviously that the composition of more steps will also contain maxima. This means, further, that the density function of pathlength distribution for a one step function of other shape will certainly contain maxima and inflections.

The composition of steplength for low stepnumbers will typically show the shape of the one step distribution function. For more steps this will be deformed. According to the Ljapunov theorem of mathematical statistics [13] the composition of any kind of distribution approaches the normal distribution for a high stepnumber. This is well demonstrated by the following example:

Figure 8 shows the density functions of pathlength distribution of one-dimensional wandering with continuous steplength uniformly distributed between 0 and $+1$ for stepnumbers $1, 2, 3, \ldots$ etc. To visualize the situation the curves for the various stepnumbers are normalized to equal maximum pathlength values. The distribution of one step on the basis of the starting point is uniform. For the stepnumbers 2, 3, etc. the curves already show maxima and the value of half band width gradually decreases. The intensity of maximum density increases while the area under the curves, which means the number of photons, will of course stay constant. For one-step pathlength distribution of other shapes the multistep distribution varies similarly and a curve similar in marginal case (of Gaussian character) is obtained.

Considering that for remission the probability of one step is the greatest, the shape of its distribution function is of decisive importance. This distribution depends on the structure of the sample, the particle size, the particle shape, the position of particles and on the refractive indices. In view of the fact that the

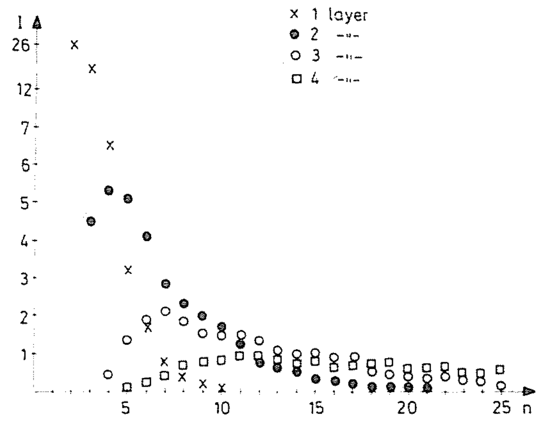

Fig. 5. Density function of the stepnumber distribution of transmitted light for several layer thicknesses (n = stepnumber, I = intensity)

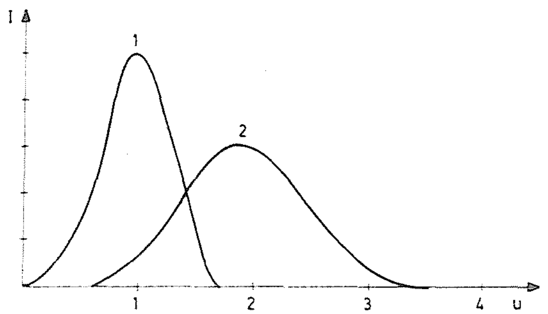

Fig. 6. Density function of pathlength distribution for 1 and 2 steps for continuous steplength (u = pathlength, I = intensity)

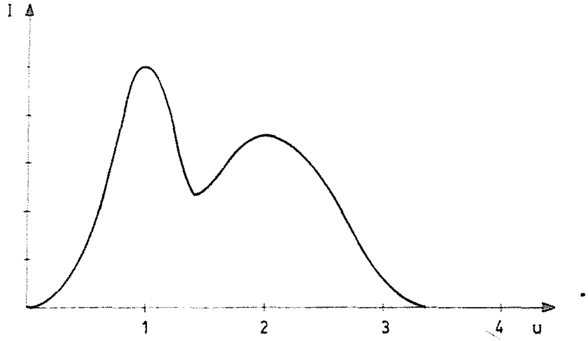

Fig. 7. Density function of pathlength distribution for 1 : 1 ratio composition of 1 and 2 steps for continuous steplength

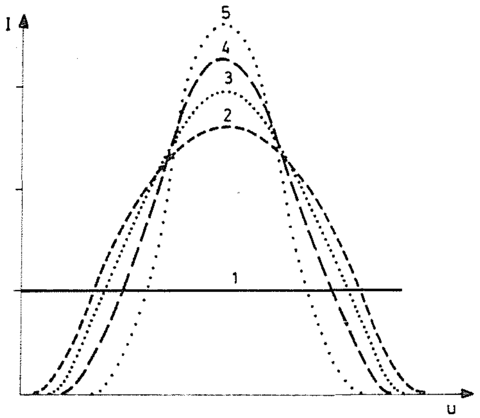

Fig. 8. Density functions of pathlength distribution for 1–5 steps for the uniform distribution of one steplength

shape of particles and the buildup of samples is, in general, irregular, the pathlength distribution of one step cannot be determined by mathematical deduction.

Nevertheless, modelling points out the main problems of mathematically formulating the spectroscopy of diffuse light-scattering media.

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