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Forward-scattering ratios and average pathlength parameter in radiative transfer models

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Abstract. Optical properties of films containing spherical particles in a non-absorbing matrix have been modelled by a four-flux radiative transfer theory. In this paper we demonstrate methods to calculate all parameters in this model. Scattering and absorption coefficients can easily be computed from Lorenz–Mie theory if the particle concentration is not too high. Forward-scattering ratios for collimated and diffuse radiation, σ_c and σ_d, respectively, are in general not equal. We establish a method to evaluate the forward-scattering ratios from Lorenz–Mie theory and an improved version of Hartel theory, both for perfectly diffuse isotropic radiation as well as for anisotropic conditions. We also give an explicit way to calculate the average pathlength parameter in terms of particle refractive index, particle concentration, size parameter and distance from the illuminated film interface. The characterization of forward-scattering ratios and the average pathlength parameter leads to an improved understanding of the applicability of the standard four-flux model.

1. Introduction

This paper is concerned with the optical properties of inhomogeneous materials consisting of spherical particles in a non-absorbing matrix. Multiple scattering of light in these materials can be described by radiative transfer models. In the general case one has to resort to numerical solutions [1], but important simplifications are possible if the angular dependence of scattered radiation is not needed. Under diffuse illumination of opaque pigmented films, the Kubelka–Munk theory [2] can be applied, and the effect of boundary reflections at film and backing (or substrate) interfaces can easily be taken into account. For collimated illumination of opaque films, an extended Kubelka–Munk theory is often suitable [3]. Four-flux models are required when collimated components exist in the radiation field [4]. The most versatile four-flux model seems to be the one developed by Maheu and co-workers [5], which will be denoted 'MLG model' throughout this paper. This theory can be applied to the case of collimated as well as diffuse illumination. From the theory one can obtain explicit relations for specular and diffuse components of reflectance and transmittance, in terms of particle concentration, volumetric scattering and absorption cross sections of the particles, thickness of the coating, and forward-scattering ratios.

The four-flux model is useful in the following experimental situation. We consider a light scattering inhomogeneous material present as a slab or as a coating on a substrate. Measurements of total and diffuse reflectance and transmittance are carried out, for example by an integrating sphere instrument. The importance of the four-flux model comes from

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the fact that it provides a description of this situation of standard optical analysis. It can be used to predict the conditions for obtaining optical properties desirable for a specific application or to establish a model for an optical material. Thick particulate coatings or slabs of the kind envisaged here are important technological materials [6], for example we mention paints, paper, pigmented polymer foils, and fibrous insulation. More detailed optical characterization of inhomogeneous materials can be carried out by, for example, angular dependent scattering, backscattering, and photon diffusion measurements using laser techniques. These situations fall outside the scope of the theory studied in this paper.

A crucial assumption in radiative transfer models is that the interaction of electromagnetic radiation with a particle is not influenced by the presence of neighbouring particles. This means that the volume fraction of particles must not be too high. However, a study by Brewster and Tien [7] indicates that the parameter determining the onset of dependent scattering is rather the ratio of the distance between the surfaces of neighbouring particles to the wavelength. More rigorous limits for the independent scattering approximation in the simpler two-dimensional case should be possible to obtain by the formalism of Haarmans [8].

In order to confidently use the four-flux theory, the various parameters appearing in it must be known. The effective scattering and absorption coefficients of the non homogeneous film can be *a priori* defined in terms of Lorenz–Mie parameters. However, the assumption that the forward-scattering ratio of a particle, when illuminated with collimated radiation, is equal to the forward-scattering ratio under diffuse illumination, has been widely used [9–11]. Another implicit approximation involves the assignment of a specific value for the average pathlength parameter, which until now is known only in special cases.

In this paper we apply the Lorenz–Mie theory [12] to describe the interaction between single spherical particles and electromagnetic radiation, and an extended version of Hartel theory [13] to take into account multiple-scattering effects on the forward-scattering ratio, as well as on the average pathlength parameter, for any angular dependent radiation field inside the film. We remove the implicit assumptions of the MLG model (section 2), and we study the effect of the proposed generalizations by evaluating forward-scattering ratios and average pathlength parameters for different kinds of material (section 3). Hence, we have established methods to evaluate all parameters appearing in the four-flux model.

2. Theory

When a particle is illuminated with electromagnetic radiation, the amount of energy which is absorbed or scattered by the particle is related to the corresponding cross sections. The incident, scattered, and internal fields can be expanded in terms of partial wave contributions, and the involved coefficients are obtained from boundary conditions. For a spherical particle, from the knowledge of the coefficients related to the scattered field (the so-called scattering coefficients, a_n and b_n), normalized scattering and extinction cross sections of the particle can be evaluated [14]:

$$Q_{sca} = (2/x^2) \sum_{n=1}^{\infty} (2n+1)[|a_n|^2 + |b_n|^2] \tag{1}$$

$$Q_{ext} = (2/x^2) \sum_{n=1}^{\infty} (2n+1)\,\mathrm{Re}[a_n + b_n] \tag{2}$$

where $x = 2\pi r/\lambda$ is the size parameter, r is the particle radius, and λ is the wavelength of the incident radiation in the surrounding medium. The normalized absorption cross section is calculated from $Q_{abs} = Q_{ext} - Q_{sca}$. The corresponding cross sections are given by $C_{abs/sca/ext} = \pi r^2 Q_{abs/sca/ext}$. Besides the explicit dependence on the size parameter, the cross sections implicitly depend on size parameter and relative refractive index of the particle through the scattering coefficients.

The angular dependence of the scattered radiation can be related to the so-called single-particle phase function [15]:

$$p(\cos\theta) = \frac{2}{x^2 Q_{ext}} \{|S_1(\cos\theta)|^2 + |S_2(\cos\theta)|^2\} \tag{3}$$

where θ is the polar angle (relative to the incident direction), with $S_1(\cos\theta)$ and $S_2(\cos\theta)$ the scattering amplitudes.

In the MLG model, the forward-scattering ratio ($\sigma =$ the energy scattered by the particle in the forward hemisphere divided by the total scattered energy), enters in the coupled system of differential equations, from which collimated and diffuse components of the radiation field (I_c, J_c, I_d, and J_d) are obtained [5]:

$$\frac{\mathrm{d}I_c}{\mathrm{d}z} = -(\alpha + \beta) I_c \tag{4a}$$

$$\frac{\mathrm{d}J_c}{\mathrm{d}z} = (\alpha + \beta) J_c \tag{4b}$$

$$\frac{\mathrm{d}I_d}{\mathrm{d}z} = -\xi\beta I_d - \xi(1-\sigma_d)\alpha I_d + \xi(1-\sigma_d)\alpha J_d + \sigma_c\alpha I_c + (1-\sigma_c)\alpha J_c \tag{4c}$$

$$\frac{\mathrm{d}J_d}{\mathrm{d}z} = \xi\beta J_d + \xi(1-\sigma_d)\alpha J_d - \xi(1-\sigma_d)\alpha I_d - \sigma_c\alpha J_c - (1-\sigma_c)\alpha I_c. \tag{4d}$$

Here z is a linear coordinate, measured from the illuminated side and perpendicular to the interface, $\alpha(\beta)$ is the scattering (absorption) coefficient per unit length which, within the independent scattering approximation, is evaluated as the particle volume fraction (f) times the volumetric scattering (absorption) cross section of the particle ($C_{sca}/V(C_{abs}/V)$ where V is the particle volume). Differences between pathlengths for collimated and diffuse radiation are taken into account by means of the parameter ξ, the so-called average pathlength parameter. The forward-scattering ratios, for collimated and diffuse incident radiation, are denoted by σ_c and σ_d respectively.

The solutions for the collimated components can be easily obtained. Then, following the MLG derivation, second-order differential equations for the diffuse components can be written in a concise notation, in terms of the following constants:

$$A_1 = \xi^2\beta[\beta + 2(1-\sigma_d)\alpha] \tag{5a}$$

$$A_2 = \alpha[\xi\sigma_c\beta + \xi(1-\sigma_d)\alpha + \sigma_c(\beta+\alpha)] \tag{5b}$$

$$A_3 = \alpha\{\xi[(1-\sigma_d)\alpha + (1-\sigma_c)\beta] - (1-\sigma_c)(\beta+\alpha)\} \tag{5c}$$

$$A_4 = \xi[\beta + (1-\sigma_d)\alpha] \tag{5d}$$

$$A_5 = \xi(1-\sigma_d)\alpha. \tag{5e}$$

These equations correspond to the ones given by Maheu *et al* when $\sigma_d \equiv \sigma_c$. The forward-scattering ratio for collimated incident radiation on a spherical particle can be evaluated within the framework of Lorenz–Mie theory. It is given by

$$\sigma_c = \left(\int_0^1 p(\mu)\,\mathrm{d}\mu\right)\left(\int_{-1}^1 p(\mu)\,\mathrm{d}\mu\right)^{-1} \tag{6a}$$

where $\mu = \cos\theta$. The explicit integration of the previous equation was done by Chylek [16]. He obtained

$$\sigma_c = \frac{1}{2} - (2/\delta) \sum_{m=2}^{\infty}{}'' \sum_{n=1}^{\infty}{}' p_{nm} \, \mathrm{Re}(a_m a_n^* + b_m b_n^*) - (2/\delta) \sum_{m=1}^{\infty}{}' \sum_{n=1}^{\infty}{}' q_{nm} \, \mathrm{Re}(a_m b_n^*). \tag{6b}$$

Here $\delta = x^2 Q_{sca}$, and

$$p_{nm} = (-1)^{(m+n-1)/2} \frac{(2m+1)(2n+1)(m-1)!!n!!}{(m-n)(m+n+1)m!!(n-1)!!} \tag{6c}$$

$$q_{nm} = (-1)^{(m+n)/2} \frac{(2m+1)(2n+1)m!!n!!}{m(m+1)n(n+1)(m-1)!!(n-1)!!} \tag{6d}$$

Σ' states a summation over odd integral numbers, and Σ'' means another summation which is evaluated over even integral numbers. Another way to calculate the forward-scattering ratio under collimated incident radiation is by expanding the single-particle phase function in terms of Legendre polynomials [1]. Given an incident direction along the z-axis, for unpolarized light the phase function can be evaluated from

$$p(\mu) = \sum_{i=0}^{\infty} \omega_i P_i(\mu). \tag{7}$$

By integrating (6a), only the terms corresponding to $i = 0$ and i odd contribute, and the forward-scattering ratio becomes

$$\sigma_c = \frac{1}{2\omega_0} \left[\omega_0 + \sum_{i=1}^{\infty}{}' \omega_i g_i \right] \tag{8a}$$

where $\omega_0 = Q_{sca}/Q_{ext}$ is the particle albedo, and

$$g_i = \int_0^1 P_i(\mu)\, \mathrm{d}\mu = (-1)^{(i-1)/2} \frac{(i!!)^2}{i(i+1)i!} \qquad \text{when } i \text{ is odd, otherwise } g_i = 0. \tag{8b}$$

(6b) and (8a) give always the same numerical results, provided the set of ω_i coefficients are evaluated as indicated below.

In order to evaluate the set of coefficients ω_i, we need to obtain them from equations (3) and (7). By applying the orthonormal condition for Legendre polynomials, one can invert these equations to obtain

$$\omega_i = \frac{2i+1}{x^2 Q_{ext}} \left\{ \sum_{n=1}^{\infty} \gamma_n \sum_{m=1}^{n} \gamma_m \left[\frac{W_{nm} \eta_{nmi} I_{nmi} + V_{nm} \nu_{nmi} J_{nmi}}{1 + \delta_{nm}} \right] \right\} \tag{9a}$$

where

$$\gamma_n = \frac{2n+1}{n(n+1)} \tag{9b}$$

$$W_{nm} = \mathrm{Re}[a_n a_m^* + b_n b_m^*] \tag{9c}$$

$$V_{nm} = \mathrm{Re}[a_n b_m^* + b_n a_m^*] \tag{9d}$$

$$I_{nmi} = \int_{-1}^{1} [\pi_n \pi_m + \tau_n \tau_m] P_i(\mu)\, \mathrm{d}\mu \tag{9e}$$

$$J_{nmi} = \int_{-1}^{1} [\pi_n \tau_m + \pi_m \tau_n] P_i(\mu)\, \mathrm{d}\mu \tag{9f}$$

with

$$\pi_n = \frac{\mathrm{d}P_n}{\mathrm{d}\mu} \qquad \tau_n = \mu \frac{\mathrm{d}P_n}{\mathrm{d}\mu} - (1-\mu^2) \frac{\mathrm{d}^2 P_n}{\mathrm{d}\mu^2}. \tag{9g}$$

The integrals I_{nmi} and J_{nmi} have been evaluated by Chu and Churchill [17] and applied by Clark *et al* to calculate the coefficients ω_i in terms of size parameter, and refractive index [18]. A misprint should be noted in their equation (7). I_{nmi} must be symmetric under n and m permutation. The integrals I_{nmi} and J_{nmi} are given by

$$I_{nmi} = [n(n+1) + m(m+1) - i(i+1)]^2 \frac{(n+i-m)!(m+i-n)!(n+m-i)!}{(n+m+i+1)!} \times \left\{ \frac{[(n+m+i)/2]!}{[(n+i-m)/2]![(m+i-n)/2]![(n+m-i)/2]!} \right\}^2 \tag{9h}$$

when $j = n+m-i$ is an even number; zero if j is an odd number, and

$$J_{nmi} = [(n+m-i)(n+i-m+1)(m+i-n+1)] \times \frac{(n+i-m+1)!(m+i-n+1)!(n+m-i-1)!}{(n+m+i+1)!} \times \left\{ \frac{[(n+m+i+1)/2]!}{[(n+i-m+1)/2]![(m+i-n+1)/2]![(n+m-i-1)/2]!} \right\}^2 \tag{9i}$$

if j is an odd number; zero if j is an even number. Furthermore, $\eta_{nmi} = 1$ if $0 \leqslant n+m-i \leqslant 2m$ and otherwise it will be zero; $\nu_{nmi} = 1$ if $1 \leqslant n+m-i \leqslant 2m+1$ and otherwise it will be zero. We have used equations (3) and (7) to test consistency of equations (9) when calculating the set of coefficients ω_i.

In order to obtain the forward-scattering ratio under perfectly diffuse (isotropic) radiation, incident on a particle, one must generalize the phase function for any incidence and scattering directions (specified by the angles θ' and θ, respectively). This can be done by applying the addition theorem for Legendre polynomials [19]. By assuming azimuthal symmetry,

$$p(\mu, \mu') = \sum_{n=0}^{\infty} \omega_n P_n(\mu) P_n(\mu'). \tag{10a}$$

The corresponding forward-scattering ratio is given by

$$\sigma_d(z) = \left(\int_0^1 \mathrm{d}\mu' \int_0^1 I(z, \mu') p(\mu, \mu') \, \mathrm{d}\mu \right) \left(\int_0^1 \mathrm{d}\mu' \int_{-1}^1 I(z, \mu') p(\mu, \mu') \, \mathrm{d}\mu \right)^{-1} \tag{10b}$$

where z is the smallest distance between the particle position and the illuminated film interface; $I(z, \mu')$ specifies the angular dependence of the radiation field at the film depth z. For isotropic radiation, the intensity does not depend on the polar angle, θ', and in this case one obtains

$$\sigma_d \equiv \sigma_d^{(i)} = \frac{1}{2\omega_0} \left[\omega_0 + \sum_{n=1}^{\infty}{}' \omega_n g_n^2 \right]. \tag{11}$$

For a collimated radiation field perpendicular to the film interfaces, $I(z, \mu') \to I(z, \mu')\delta(\mu' - 1)$, and $\sigma_d \to \sigma_c$. This behaviour is also obtained for highly anisotropic radiation fields with maximum intensity in some specific direction: $I(z, \mu') \to I(z, \mu')\delta(\mu' - \mu'_0)$. Both (8$a$) and (11) are in agreement with the formulations of Reichman and Ishimaru [3, 4].

A more general radiation field which depends on the polar angle, and at a specific depth or distance from the illuminated film interface, can be expanded in terms of Legendre polynomials [20],

$$I(z, \mu') = \sum_{n=0}^{\infty} c_n(z) P_n(\mu'). \tag{12}$$

The angular dependence of the diffuse radiation intensity comes from multiple scattering events. After each scattering event, the radiation scattered into the forward hemisphere, as well as into the backward hemisphere, both depend on angle. In addition some of the radiation might be absorbed by the spherical particles. This leads to an angular dependence and a depth dependence of the total diffuse radiation. The decomposition of the diffuse intensity in terms of Legendre polynomials weighted by coefficients which depend on the geometrical depth from the illuminated side, has been extensively used in connection to numerical schemes to solve the radiative transfer equation for semi-infinite or plane-parallel geometries [21].

We now focus on a method for estimating the coefficients $c_n(z)$. We make use of an order of scattering expansion: a method originally introduced by Hartel. This theory is applicable for describing the angular and optical depth dependences of forward scattering by a collection of monosized and randomly distributed scatterers illuminated with unpolarized electromagnetic radiation. The particle concentration is assumed to be sufficiently small so that dependent scattering can be neglected. The angular distribution of each scattering order is specified by a generalized phase function $f_k(\mu)$ [13]. As pointed out by Orchard [22] the basic form of Hartel theory [13, 23, 24] is characterized by an anomalous behaviour in the case of optically thick films containing non-absorbing particles: a saturation value of the total forward intensity at large optical depth values is predicted. This is a consequence of implicitly assuming that the average pathlength parameters of the scattering orders are equal to unity. A plausible and phenomenological way to remove the bad behaviour of Hartel's theory is by taking into account the average pathlength parameters, ξ_k, corresponding to the different scattering orders: $k = 1, 2, 3, \ldots$. Given the angular distribution of the diffuse radiation emerging from k scattering events, by means of the average pathlength parameters we take into account the pathlength of the diffuse radiation relative to the pathlength of a beam of collimated radiation. For the forward diffuse radiation corresponding to the kth scattering order the average pathlength is given by

$$\xi_k = \left(\int_0^1 f_k(\mu)\,\mathrm{d}\mu\right)\left(\int_0^1 \mu f_k(\mu)\,\mathrm{d}\mu\right)^{-1}$$
$$= 2\left\{\left(1 + {\sum_{n=1}^{\infty}}' (2n+1) g_n [\Psi_n]^k\right)\left[1 + 2\left(\frac{\omega_1}{3\omega_0}\right)^k + 2 {\sum_{n=2}^{\infty}}'' (2n+1) h_n [\Psi_n]^k\right]^{-1}\right\} \quad (13a)$$

with

$$\Psi_n = \frac{\omega_n/\omega_0}{2n+1} \qquad h_n = \int_0^1 \mu P_n(\mu)\,\mathrm{d}\mu \quad (13b)$$

and [13]

$$f_k(\mu) = \frac{1}{4\pi}\sum_{n=0}^{\infty}(2n+1)\left[\frac{\omega_n/\omega_0}{2n+1}\right]^k P_n(\mu). \quad (13c)$$

In terms of the scattering order index, the asymptotic value of the average pathlength parameter is $\xi_k \to 2$ as $k \to \infty$. The differential equations coupling the amount of radiation in the successive scattering orders, Q_k, can be written as

$$\frac{\mathrm{d}Q_1}{\mathrm{d}z} = \alpha Q_0 - \xi_1(\alpha + \beta) Q_1 \quad (14a)$$

$$\frac{\mathrm{d}Q_k}{\mathrm{d}z} = \xi_{k-1}\alpha Q_{k-1} - \xi_k(\alpha + \beta) Q_k \qquad k = 2, 3, \ldots. \quad (14b)$$

In the original Hartel theory for $\xi_k \equiv 1$ for $k = 1, 2, \ldots$ and the solutions of the previous system are $Q_k(z) = [(\alpha z)^k/k!]\,\mathrm{e}^{-(\alpha+\beta)z}$ with the boundary conditions $Q_k(z = 0) = 0$. In the general case $\xi_k \neq 1$. In order to devise an extended version of Hartel theory we define $Q_k(z) \equiv p_k(z)\,\mathrm{e}^{-(\alpha+\beta)z}$. By using an induction procedure based on the integrating factor method one can see that the general solutions of (14), for the successive scattering orders, are of the form

$$p_k(\tau) = F_k[1 - \mathrm{e}^{-(\xi_k-1)\tau}] + \sum_{i=1}^{k-1} G_{i,k}[\mathrm{e}^{-(\xi_k-1)\tau} - \mathrm{e}^{-(\xi_i-1)\tau}] \tag{14c}$$

where $\tau = (\alpha + \beta)z$ is the optical depth, and with the boundary conditions $p_k(z = 0) = 0$. A set of recurrence relations is obtained by inserting the solutions (14*c*) into the differential equation (14*b*). Namely,

$$F_k = \omega_0 \frac{\xi_{k-1}}{\xi_k - 1} F_{k-1} \tag{15a}$$

$$G_{k-1,k} = \omega_0 \frac{\xi_{k-1}}{\xi_k - \xi_{k-1}} \left[F_{k-1} - \sum_{i=1}^{k-2} G_{i,k-1} \right] \tag{15b}$$

$$G_{i,k} = \omega_0 \frac{\xi_{k-1}}{\xi_k - \xi_i} G_{i,k-1} \tag{15c}$$

with the following initial values:

$$F_1 = \frac{\omega_0}{\xi_1 - 1} \qquad G_{1,2} = \frac{\omega_0}{\xi_2 - \xi_1} F_1 \tag{15d}$$

which are obtained by solving explicitly for the first and second scattering orders. As the scattering order index reaches large values $\xi_k \to \xi_{k-1} \to 2$, and the previous solutions do not apply due to the diverging coefficients $G_{i,k}$. In these cases the solutions can be approximated by

$$p_k(\tau) = F_k[1 - \mathrm{e}^{-(\xi_k-1)\tau}] \tag{15e}$$

which in the limit of large optical depth values are solutions of (14*b*) with $\xi_k = \xi_{k-1} \cong 2$. These solutions are consistent with the recurrence relation (15*a*). Because of the isotropic distribution of high-scattering-order contributions to the total diffuse radiation intensity, the high-order scattering coefficients, $Q_k(z)$, are characterized by a very smooth dependence on z. This fact validates the use of the solutions (15*e*) for all optical depth values. Once each $p_k(z)$ has been computed the corresponding $Q_k(z)$ must be divided by $k!$ in order to have the appropriate weighting factors in the expansion of the forward diffuse radiation intensity. Given $|\xi_k - \xi_{k-1}| \leqslant \varepsilon$ in most cases numerical stability of the anisotropic solutions (14*c*) can be obtained for ε larger than 10^{-3}. For smaller ε (15*e*) has to be used instead. This extended version of Hartel theory does not display a bad behaviour in the case of media containing non-absorbing particles. The forward diffuse intensity is given by

$$I(z, \mu) = \sum_{k=1}^{\infty} Q_k(z) f_k(\mu). \tag{16a}$$

Hence using (12),

$$c_n(z) = \frac{2n+1}{4\pi} \sum_{k=1}^{\infty} Q_k(z) \left[\frac{\omega_n/\omega_0}{2n+1} \right]^k. \tag{16b}$$

By expanding each Legendre polynomial in powers of its argument, the integrations involved in (10*b*) can be explicitly evaluated to obtain

$$\sigma_d(z) = \left(\sigma_d^{(i)} + \frac{1}{2}\sum_{n=1}^{\infty}{}' \frac{c_n(z)g_n}{c_0}\left[1 + \frac{\omega_n\chi_{nn}}{\omega_0}\right] + \frac{1}{2}\sum_{n=1}^{\infty}{}' \frac{\omega_n g_n}{\omega_0}\sum_{m=2}^{\infty}{}'' \frac{c_m(z)\chi_{nm}}{c_0}\right) \times\left(1 + \sum_{n=1}^{\infty}{}' \frac{c_n(z)g_n}{c_0}\right)^{-1} \tag{17a}$$

where $\chi_{nm} = \int_0^1 P_n(\mu)P_m(\mu)\,\mathrm{d}\mu$ is equal to zero if $n \neq m$ and $n + m$ is an even number. Moreover, $\chi_{nn} = 1/(2n+1)$, and if $n + m$ is odd

$$\chi_{nm} = \frac{1}{2^{n+m}}\sum_{k=0}^{[n/2]}\sum_{j=0}^{[m/2]} \frac{(-1)^{j+k}}{[n+m+1-2(j+k)]}\frac{(2n-2k)!(2m-2j)!}{(n-k)!k!(n-2k)!(m-j)!j!(m-2j)!} \tag{17b}$$

where $[n/2]$ means the integral part of $n/2$. In the case of an isotropic radiation field, $c_n(z) = 0$ for $n = 1, 2, 3, \ldots$ and $c_0(z)$ will correspond to the intensity of the radiation field. Consequently $\sigma_d = \sigma_d^{(i)}$. Within this formalism, the forward-scattering ratio becomes a function of the particle position or film depth, z, while in the MLG model a constant value is assumed.

Now we focus on the average pathlength parameter, ξ. It has been assumed constant in the framework of MLG radiative transfer theory, and used as a fitting parameter in specific applications of this model [9, 10, 25]. It has also been assumed to be independent of physical parameters of the system: particle position, size, refractive index and concentration as well as wavelength of the incident radiation and film depth. For films containing non-absorbing particles, whose scattering pattern is described by the Henyey–Greenstein phase function [26], the average pathlength parameter has been given in terms of the particle asymmetry factor and film optical thickness [27]. This method does not however take into account the real scattering pattern of the particles, possible absorption from them and multiple-scattering effects. It does not seem to be a general method to evaluate the average pathlength parameter. This parameter is rigorously known only for specific cases: it is one for a collimated beam and two for a perfectly diffuse radiation field.

The definition of the average pathlength parameter is as follows. At a certain position z inside the film, a light beam travels a distance ΔL at an angle θ' with the z-axis. The projection of ΔL on the z-axis is denoted Δz. These distances are related by $\Delta L\cos(\theta') = \Delta z$. By weighting both sides with the intensity of the radiation field, and integrating in the forward hemisphere, one obtains

$$\int_0^1 I(z,\mu')\Delta L\mu'\,\mathrm{d}\mu' = \int_0^1 I(z,\mu')\Delta z\,\mathrm{d}\mu'. \tag{18a}$$

At this point, we introduce the average pathlength parameter, ξ, which defines the average ratio between ΔL and Δz. Then, from the previous equation, one has

$$\xi = \left(\int_0^1 I(z,\mu')\,\mathrm{d}\mu'\right)\left(\int_0^1 I(z,\mu')\mu'\,\mathrm{d}\mu'\right)^{-1} \tag{18b}$$

(18*b*) is in agreement with Ishimaru's formulation [4], as well as the MLG four-flux model [5]. By integrating this equation, we have obtained an explicit expression for the average pathlength parameter:

$$\xi(z) = 2\left[\left(1 + \sum_{n=1}^{\infty}{}' \frac{c_n(z)}{c_0(z)}g_n\right)\left(1 + \frac{2c_1(z)}{3c_0(z)} + 2\sum_{n=2}^{\infty}{}'' \frac{c_n(z)}{c_0(z)}\chi_{n1}\right)^{-1}\right]. \tag{19}$$

Through the coefficients $c_n(z)$, the average pathlength parameter becomes a function of film depth. For a collimated radiation field parallel to the z-axis, (18*b*) leads to $\xi = 1$ which is in agreement with the MLG model when diffuse components of the radiation field are neglected in comparison to collimated ones. The two-stream model of Bohren is one of these approaches [28], valid for very anisotropic scattering. For a perfectly diffuse radiation field, (19) gives $\xi = 2$, as assumed in the two-flux theory of Kubelka and Munk [2] and the three-flux model of Reichman [3], and in agreement with the MLG model. A special case corresponds to a highly anisotropic radiation field with some specific orientation relative to the z-axis: $I(z, \mu') \rightarrow I(z, \mu')\delta(\mu' - \mu_0)$. The average pathlength parameter becomes $\xi_0 \rightarrow 1/\mu_0$, and $\sigma_d \rightarrow \sigma_c$. The two-flux model of Sagan and Pollack [29] corresponds to this kind of particular situation (with $\mu_0 = 1/\sqrt{3}$ as pointed out by Lyzenga [30]), as well as a particular case considered by Kubelka [31], i.e. $\xi = 2$ for an anisotropic incident radiation field with $\theta_0 = 60^\circ$.

Within the formalism that we have summarized, (17*a*) and (19) provide a general framework to evaluate the forward-scattering ratio for any angular dependent radiation field, as well as the average pathlength parameter. Through the c_n coefficients, multiple-scattering effects are taken into account and σ_d and ξ become dependent on the physical parameters of the system: film depth, refractive indices of the particles and surrounding medium, wavelength of the incident radiation, particle size and particle concentration.

When computing the optical depth dependence of the total diffuse transmission, the original and extended Hartel theories give similar values in the limit of small optical depths. In this small-optical-depth limit the amount of scattered radiation increases linearly with the optical depth [32]. Beyond the small-optical-depth limit, for small or medium-sized weakly absorbing particles the original Hartel theory overestimates the total diffuse transmission. At medium or large optical depths there is a fairly good agreement between the original and extended Hartel theories in the case of large absorbing particles. This is expected because the average pathlength parameter is close to unity in such a case.

The original and extended Hartel theories neglect the backward components of the scattered radiation. A more general approach taking into account the radiation scattered in backward directions has been devised by Vargas and Niklasson by solving the radiative transfer equation for a semi-infinite medium [33]. The best agreement between this generalized multiple-scattering approach and the extended Hartel theory corresponds to large absorbing particles. It is within this multiple-scattering approach that the so called backscattering enhancement could be considered [34, 35].

3. Numerical calculations

We evaluated the forward-scattering ratio from (17*a*), in terms of the optical depth. Figure 1 displays the results. Representative materials have been considered: (a) weakly scattering and non-absorbing amorphous SiO_2 particles in a polymer binder, (b) highly scattering and non-absorbing TiO_2 (rutile) pigments in polyethylene, (c) highly scattering and weakly absorbing crystalline Si particles in an amorphous alumina matrix and (d) weakly scattering and strongly absorbing Fe particles in air. The refractive indices correspond to the middle of the visible wavelength range. In all cases, the most relevant and expected feature is that $\sigma_d \rightarrow \sigma_d^{(i)}$ at large optical depth, while in the opposite limit $\sigma_d \rightarrow \sigma_c$. In the Rayleigh limit of small size parameter values ($x \approx 0.1$), $\sigma_d^{(i)} \equiv \sigma_c \equiv 1/2$. Beyond the Rayleigh limit, small differences between $\sigma_d^{(i)}$ and σ_c arise. These differences are more pronounced at intermediate values of the size parameter ($x \approx 3$), and they decrease at large size parameter

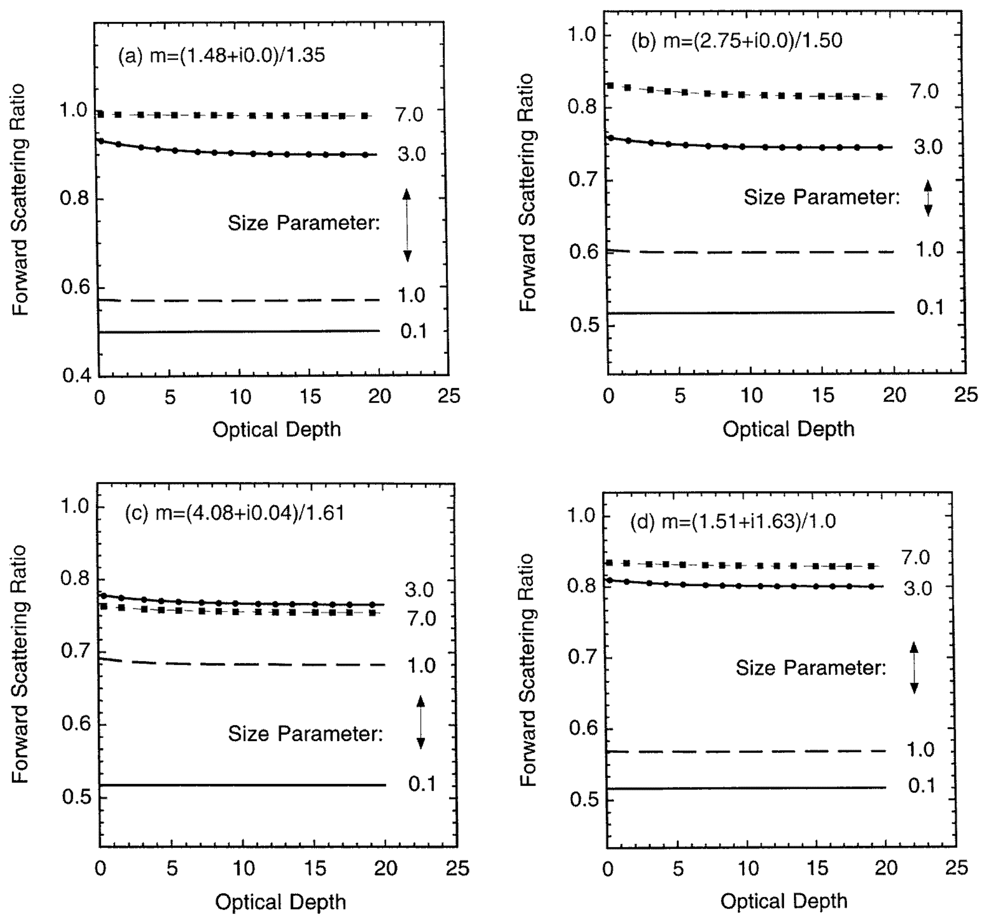

Figure 1. Forward-scattering ratio in terms of optical depth, for different materials and particle size parameters. The particle volume fraction and free space wavelength of the impinging radiation were put to 0.05, and 0.55 μm respectively. For each case, the particle refractive index divided by the matrix refractive index has been indicated in the corresponding figure.

values ($x \approx 7$). The effect of absorption seems to be the smoothing of this difference between $\sigma_d^{(i)}$ and σ_c. Most specific applications of the MLG model, have been concerned with thick films, and the approximation $\sigma_d \equiv \sigma_c$ has been assumed. As we have shown, it is just in this thick-film range that σ_d tends to be significantly different from σ_c.

Figure 2 depicts the behaviour of ξ in terms of optical depth. The radiation field is expected to have an increasing degree of isotropy as the optical depth increases. The behaviour of ξ is in agreement with that, for the different cases considered. Saturation values of the average pathlength parameter are displayed, and they depend on particle size, concentration and refractive index. These saturation values decrease as the size parameter increases. The effect is more pronounced for weakly scattering and non-absorbing materials (figure 2(a)), and tends to be less significant when absorption increases (figure 2(c)). Also for low film depths the radiation field becomes more anisotropic when the size parameter increases. This effect is most pronounced for weakly scattering particles. In the Rayleigh limit at large film depths, absorption decreases the degree of isotropy.

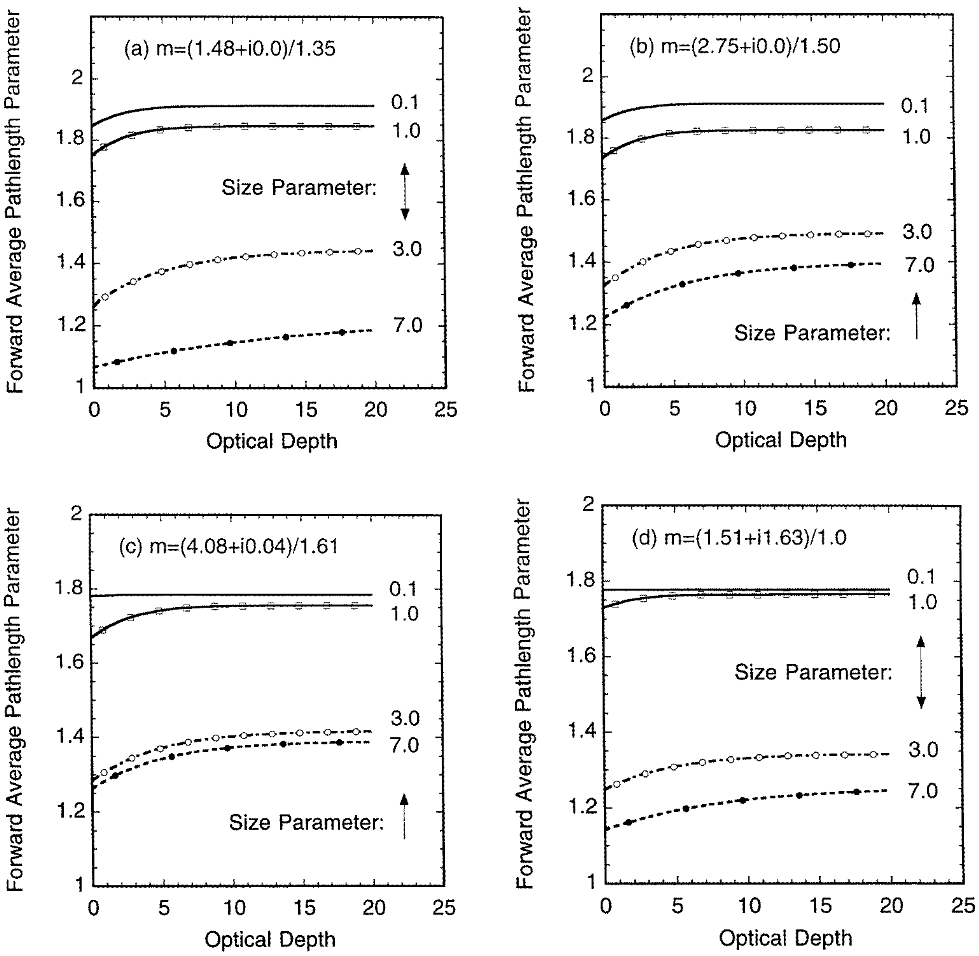

Figure 2. Average pathlength parameter as a function of optical depth and for different particle relative refractive indices and size parameters, as indicated in the corresponding figures.

The MLG model employs constant values of σ_d and ξ. It is seen from figures 1 and 2 that in most cases this is a good approximation for thick films, with optical thicknesses larger than 10. In this limit ξ tends to a constant value and σ_d can be put equal to the value for an isotropic radiation field, $\sigma_d^{(i)}$. For thinner films the MLG theory is not rigorous, since both σ_d and ξ display a marked dependence on film depth, z. The theory may still be used in an approximate way, but σ_d and ξ must then be interpreted as averages of the z-dependent quantities over the film thickness.

In figure 3 we illustrate the behaviour of the forward-scattering ratio as a function of the size parameter. We compare σ_c, $\sigma_d^{(i)}$ and the value of σ_d at a position of one mean free path from the frontside of the film. In most cases, $\sigma_d^{(i)} < \sigma_d < \sigma_c$. At very low size parameter values, the Rayleigh limit, $\sigma_d \to \sigma_d^{(i)} \to \sigma_c$. It is well known that in this case the angular distribution of the single-scattered radiation tends to be symmetric with respect to the forward and backward directions. One may think that the isotropic radiation field assumption would be valid, but the behaviour of the corresponding average pathlength parameters (see figure 2) indicates that actually this is a very anisotropic condition ($\xi \approx \sqrt{3}$). For low-scattering particles (figures 3(a) and 3(d)), a mainly collimated radiation field is present at large size parameter values ($\sigma_d \rightarrow \sigma_c$). As expected the average pathlength parameter tends to unity in these cases. As the real part of the particle refractive index tends to unity, and the imaginary part tends to zero, $\sigma_d \rightarrow \sigma_c \rightarrow 1$, and $\xi \rightarrow 1$. This is precisely the applicability conditions of the small-angle approximation [36]. For highly scattering particles, at large size parameter values, σ_d is between $\sigma_d^{(i)}$ and σ_c, with values closer to σ_c. It should be noted that somewhat beyond the Rayleigh limit ($x \approx 1$), $\sigma_d \approx \sigma_d^{(i)}$ even though ξ could be significantly less than two.

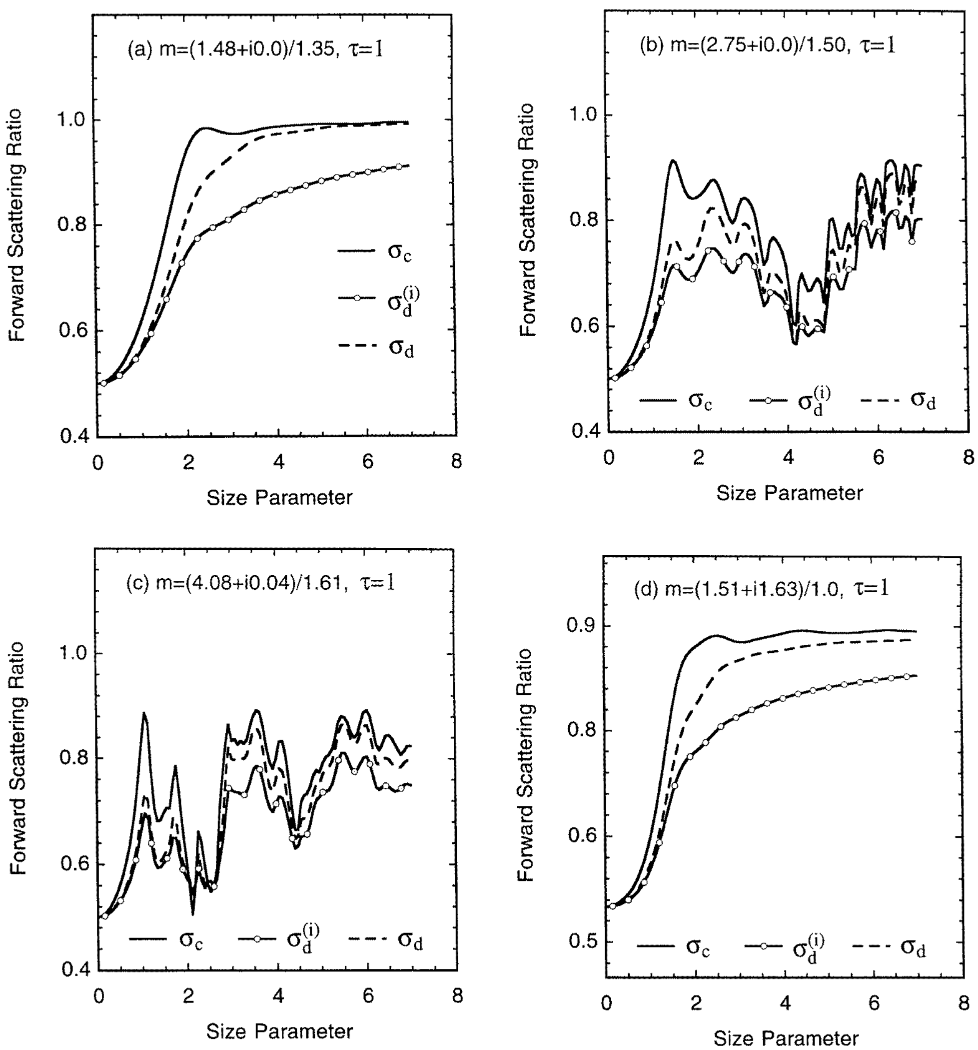

Figure 3. Forward-scattering ratios in terms of particle size parameter. The particle volume fraction, and free-space wavelength of the impinging radiation, were put to 0.05, and 0.55 μm respectively. For each case, the particle refractive index divided by the matrix refractive index has been indicated in the corresponding figure. The optical depth was put to unity.

4. Conclusions

By using the Lorenz–Mie theory to describe the interaction between a single particle and an incident radiation field, and the extended Hartel theory to incorporate multiple-scattering effects, we have established a general method to calculate the basic parameters involved in the MLG four-flux radiative transfer model. In particular we focus on the forward-scattering ratio for any angular dependent incident radiation field, σ_d, and the average pathlength parameter, ξ. We have shown that both σ_d and ξ depend on optical depth. This feature is not allowed for in the MLG model. For sufficiently thick films both σ_d and ξ tend to constant values and hence the MLG theory becomes more rigorous.

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