Extinction of Radiations in Sterically Interacting Systems of Monodisperse Spheres Part 1: Theory

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Abstract

So far, the evaluation of extinction measurements has mostly relied on Bouguer-Lambert-Beer's law (BLBL), even though BLBL is known to be valid in the limit of low concentrations only. With higher particle concentrations, particle-particle interactions such as multiple scattering, dependent scattering and steric interactions can lead to important deviations from BLBL. In a discussion of the various interaction mechanisms, steric interactions are shown to be dominating in a wide and practically important range of parameters. For the theoretical description of steric interactions, different complementary models are introduced, including a statistical model, a layer model and a numerical simulation model. The various approaches coincide to yield a simple extinction equation in two versions, applying to the regimes of Fraunhofer diffraction and straight ray propagation, respectively. In any case, BLBL is found as the low concentration limit of the extinction equation. All considerations are restricted, so far, to the case of monodisperse spherical particles.

1 Introduction

The extinction of radiations – light, X-rays, ultrasonics – is the working principle of various methods of particle size analysis and concentration monitoring, including photosedimentation techniques, multiple wavelength extinction measurements with light, radiometric concentration monitoring, ultrasonic spectrometry and many others. Compared with other optical methods of on-line particle size and concentration monitoring, extinction methods are generally operated in the range of higher particle concentrations. Especially radiometric concentration monitoring and ultrasonic spectrometry may be applied with extremely high particle concentrations [1, 2], as they are common in processes such as wet milling, suspension crystallization, suspension polymerization and hydraulic conveying.

So far, the evaluation of extinction measurements has mostly relied on Bouguer-Lambert-Beer's law (BLBL), even tough BLBL is known to be valid in the limit of low concentrations only. With higher particle concentrations, the interaction of particles and radiation is modified by particle-particle interactions such as multiple scattering, dependent scattering and steric interactions, which can lead to important deviations from BLBL.

There are a number of elaborate theories on radiative propagation in disperse media incorporating particle-particle interactions and also dealing with higher concentrations [3-6]. However, the results of these theoretical approaches are not so readily adaptable to practical applications. Experimental results are mostly related to multiple scattering and dependent scattering [5, 7-10], whereas the phenomenon of steric interactions has attracted very little attention so far.

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This contribution is not intended to give a general approach to radiative propagation in random media. Instead, the scope of this paper is limited to the problem of steric interactions. An introductory discussion will show that steric interactions are the dominating mechanism of particle-particle interactions in a wide and practically relevant range of parameters. A theoretical understanding of steric interactions is developed on the basis of several complementary, but very simple models, and a simple extinction equation including steric interactions is derived. The solution given here may be referred to as a partial one, since it does not include multiple scattering and dependent scattering in the strict sense. All results are limited, in the first step presented here, to suspensions of monodisperse, spherical particles.

Experimental evidence for the importance of steric interactions will be presented in a second part of this paper.

2 BLBL and Inherent Assumptions

The extinction of radiations in disperse systems such as suspensions and aerosols is generally described by Bouguer-Lambert-Beer's law (BLBL). In the following, a short discussion of BLBL will be given with special attention to some assumptions inherently included in BLBL and limiting its application to low particle concentrations.

For a suspension of monodisperse spherical particles, BLBL is written as

$$E = -\ln\left(\frac{I}{I_0}\right) = C_{PA} K_{ext} \Delta z \tag{1}$$

where E signifies the extinction, I_0 and I are the intensities of radiation transmitted in the absence and presence of particles, respectively, Δz is the path length through the suspension, K_{ext}

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the extinction efficiency of a single particle of diameter x and C_{PA} the particle concentration in terms of particle projected area per suspension volume. With monodisperse spherical particles, C_{PA} is related to the particle volume concentrations C_V by

$$C_{PA} = \frac{1.5}{x} C_V . \tag{2}$$

BLBL is derived by integration from an intensity balance for a thin slab of suspension:

$$dI = -I \, K_{ext} \, C_{PA} \, dz . \tag{3}$$

This derivation introduces a number of implicit assumptions. First, radiation energy is assumed to propagate unidirectionally only; that is, the effect of multiple scattering is neglected. Second, the particles are assumed to scatter radiation independently from neighbouring particles; that is, K_{ext} is assumed to be independent of concentration and effects from dependent scattering are neglected.

Further, to allow integration, the intensity change in the suspension layer must be infinitesimally small or at least much smaller than the intensity itself:

$$dI \ll I \quad \text{(integrability condition)} \tag{4}$$

while, at the same time, the thickness of the layer in question must be superior to the particle dimension:

$$dz \geq x \quad \text{(particle integrity condition)} . \tag{5}$$

The second condition is due to the fact that particles must be treated as entities of a certain spatial extension; it does not have any physical meaning to treat particles as points with an extinction efficiency attached to them or to attribute extinction effects to an infinitesimally thin slab cut from a particle.

Only in very dilute suspensions (see Figure 1), where the intensity change within a suspension layer thick compared with the particles dimension is still small compared with the intensity itself, can integrability condition and particle integrity condition be satisfied at the same time. In a concentrated suspension, however, the intensity change will approach the order of the intensity itself for a suspension layer as thin as one particle diameter, and the integrability condition is no longer fulfilled for the minimum layer thickness.

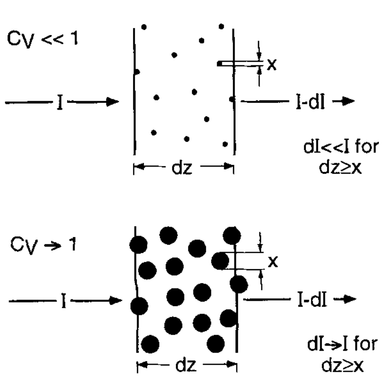

Fig. 1: Only in the limit of low concentrations can the particle integrity condition ($dz \geq x$) and integrability condition ($dI \ll I$) be satisfied simultaneously (above). With higher concentrations, either the particle integrity condition or the integrability condition have to be violated.

Hence in concentrated suspensions, even if multiple scattering and dependent scattering are not important, deviations from BLBL are to be expected. These deviations are related to the extension of the particles and their spatial arrangement. Accordingly, the corresponding mechanism of particle-particle interaction is named "steric interactions".

3 Particle-Particle Interactions in Concentrated Dispersions

Whereas extinction in dilute dispersions of particles can be described on the basis of a linear superposition of single particle interactions with the radiation, this is not the case in concentrated dispersions. In concentrated dispersions, particles can interact among each other in various ways.

In the formalistic discussion of BLBL and the assumptions inherent to it, the three major types of particle-particle interactions have been mentioned already: multiple scattering, dependent scattering and steric interactons. All of these interactions have their common origin in the exchange of momentum and energy between particles, but they do not necessarily appear simultaneously. Hence it appears useful to have a closer look at the physics of the different interactions. This will allow us to establish more precisely the conditions where the various types of interaction are expected to occur. In this paper, special attention will be given to identifying the parameter combinations where steric interactions are dominant and can be observed without interference from dependent scattering and multiple scattering.

3.1 Steric Interactions

Steric interactions have their origin in the exchange of momentum or transmission of forces between particles, which leads to a non-random, concentration-dependent arrangement of particles.

The most basic, ever-present type of force transmitted between particles is the contact forces arising upon direct contact between particles. Since contact forces prohibit an interpenetration of particles, particles have to arrange within the given space, and hence an increase in particle concentration is accompanied by a gradual transition from a disordered state (which may in general, as a good approximation, be described as a random point process) to ordered states.

The structure of the particle system is sufficiently characterized by means of the one-dimensional pair correlation function $g\langle r\rangle$ [11-14], provided the arrangement of particles is isotropic and macroscopically homogeneous. $g\langle r\rangle$ is defined as

$$g\langle r\rangle = \frac{dN\langle r\rangle}{C_N \, 4\pi r^2 dr} \tag{6}$$

that is, the number of particles found in a spherical shell of width dr at a distance r from a central particle, $dN\langle r\rangle$, is normalized to the number expected from the average particle number concentration.

In a system of non-interacting particles, one would expect $g\langle r\rangle = 1$ for all values of r and for any particle concentration. The effect of contact interactions is shown in Figure 2: for the limit of low particle volume concentration, $C_V \to 0$, contact interactions prohibit an interpenetration of particles, hence $g\langle r\rangle = 0$ for $r = 0 \ldots x$, but for $r > x$, $g\langle r\rangle = 1$ and hence the

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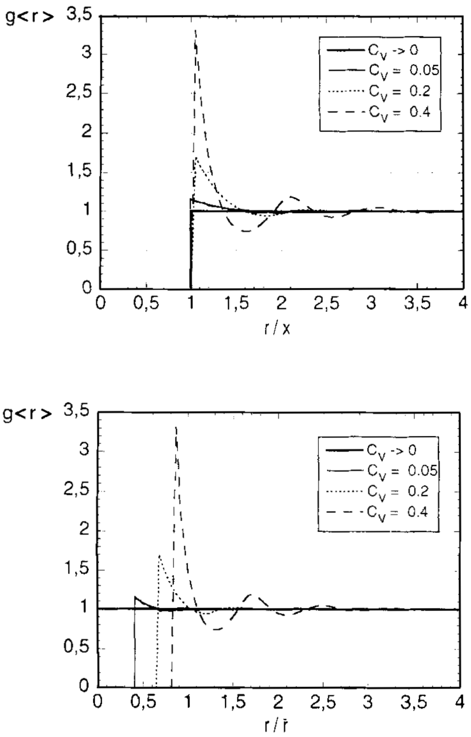

Fig. 2: Particle pair correlation function $g\langle r\rangle$ for different volume concentrations of monodisperse spherical particles, plotted as a function of r normalized to the particle diameter x (above) or r normalized to the average particle distance $\bar{r}$ (below). r is the distance between particle centres. The results were obtained from numerical simulation (see Section 4.4) assuming hard-sphere interactions.

spatial arrangement may be approximated as a random one for larger values of r. With increasing concentration, an oscillatory deviation from $g\langle r\rangle = 1$ occurs in proximity to $r = x$, which becomes clearly visible at a particle volume concentration of 5 % ($C_V = 0.05$). Both the amplitude and the reach of the oscillation grow with increasing concentration, indicating the gradual transition from disorder to low-range order and further to far-range order. With monodisperse systems, as they are considered here, highly ordered, quasi-crystalline structures are reached in the limit of highest particle concentration [12, 14–17].

So far, it was assumed that forces are transmitted upon particle contact only. In the literature, this simplifying approach is known as the hard-sphere model [14]. More elaborate models [14, 15] additionally include various field forces of different reach (atomic forces, van der Waals attraction, electrostatic and magnetic forces) as well as forces of other origin, especially hydrodynamic forces. The hard-sphere model is a good approximation as long as the reach of the significant forces remains small compared with the particle dimension. If this is not the case, the formation of ordered states may be shifted to far lower concentrations. Hence, for example, in electrostatically stabilized suspensions of submicrometre particles, strongly ordered, quasi-crystalline states are observed with concentrations as low as $C_V = 0.01$ [15, 16].

All interactions originating from forces between the particles lead to the formation of non-random spatial particle arrangements, and may therefore be named as steric interactions. Steric effects can be expected to occur at least from $C_V = 0.05$ on (due to hard-sphere interactions, compare Figure 2), but may appear earlier when long-range interaction forces are present. The effect of steric interactions on extinction and scattering is a complex problem but, simplifying again, two principal mechanisms can be identified, as follows.

Shielding effects can be traced back to near-field phenomena. In the near field of a first particle, the intensity of radiation incident upon a second particle is strongly dependent on the position. If, now, the probability of a particle occupying a certain position relative to another particle is varied as an effect of steric interactions, the average contribution of this particle to extinction and scattering of radiation is influenced. Hence the shielding effect will affect the amount of radiation transmitted and, probably, also the angular distribution of scattered radiation as well.

Interference effects arise from the far-field interference of radiation scattered by individual particles. With randomly distributed scatterers, interferences will cancel out statistically, leaving only a granular structure superimposed on the scattering signature of the single particle [18]. In contrast, with scattering from a collective of particles having some degree of order, the signature of scattering is influenced by an angular dependence of preferred constructive and destructive interference, respectively. Other than the shading effect, the interference effect does not change the total amount of scattered radiation.

In some cases, interference effects appear isolated (that is, without the simultaneous presence of shading effects, multiple scattering and dependent scattering) and can be used to determine the pair correlation function in two- and three-dimensional particulate systems. Important applications include small-angle X-ray scattering in dense suspensions and in packings [11–13] and light scattering from highly ordered dilute suspensions.

3.2 Steric Interactions versus Dependent Scattering

Dependent scattering denotes scattering processes where the mechanism of particle-wave interaction itself is modified by the presence of neighbouring particles. Two or more particles form a complex with scattering properties differing from those of an arrangement of single, independent scatters.

The physical conditions for dependent scattering are given when the interparticle clearance a is inferior to the wavelength of the radiation (see Figure 3), thus allowing an intense, mutual coupling of wave fields within and in the vicinity of neighbouring particles. The condition $a/\lambda \leq 0.3$ for the onset of dependent scattering [10, 19] is, from the physical point of view, closely related to the criterion for the onset of frustrated total reflection or optical tunnel effect, respectively, [20, 21] and has approximately the same value.

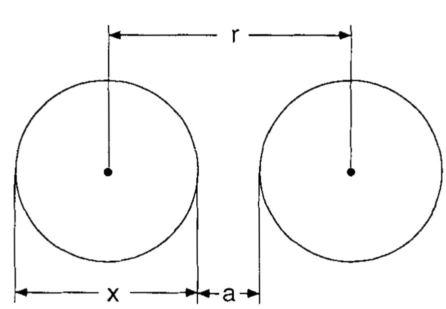

Fig. 3: Geometric configuration in the case of dependent scattering.

Assuming a regular cubic lattice of spherical particles, the $a/\lambda \leq 0.3$ criterion may be used to estimate the particle volume concentration which is critical for the onset of dependent scattering:

$$C_{V,crit} = \frac{\frac{\pi}{6} x^3}{(x + a_{crit})^3} = \frac{\pi}{6} \left(\frac{\frac{\pi x}{\lambda}}{0.3\pi + \frac{\pi x}{\lambda}} \right)^3 . \qquad (7)$$

As Eq. (7) shows, the critical concentration depends on the particle size parameter $\pi x/\lambda$.

Going more into detail, two limiting cases of dependent scattering may be distinguished:

i) If the criterion $a/\lambda \le 0.3$ is used with particles smaller than the wavelength, $x \ll \lambda$, this implies that the average distances between particle centres are small compared with the wavelength even for low concentrations. Characteristically, the wave propagation velocity in such media depends on the particle concentrations, and scattering is less intense than would be expected when assuming independent scatterers [5, 10]. In the literature, this case is treated by so-called "effective medium" theories [6], alluding to the circumstance that radiative propagation in such media shows a strong resemblance to wave propagation in continua.

ii) If the particles are much larger than the wavelength, $x \gg \lambda$, it is evident that, even when particles are in direct contact, the criterion for radiative tunnelling, $a/\lambda \le 0.3$, can be fulfilled only locally in the point of contact and its surroundings (Figure 4). As the particle size increases, the fraction of particle surface fulfilling the criterion for radiative coupling will decrease. This leads to an important conclusion: with $x \gg \lambda$, dependent scattering phenomena as predicted by Eq. (7) do exist, but they are not relevant in practice, since radiative coupling can take place only through a negligible fraction of the particle surface. For an estimate of the critical particle size, one may assume that dependent scattering is negligible as long as the radiative coupling area associated with a single particle contact, S_{rc}, does not exceed 1% of the particle surface S. Using

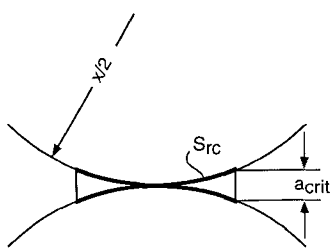

Fig. 4: Geometry of the radiative coupling area S_{rc} in the case of direct particle-particle contact.

$$S = \pi x^2, \; S_{rc} = \pi x \frac{a_{crit}}{2}$$

and

$$a_{crit} = 0.3\,\lambda \qquad (8)$$

the critical particle size parameter for dependent scattering with particles in direct contact is estimated as

$$\pi x/\lambda \le 47\,. \qquad (9)$$

With particle size parameters higher than $\pi x/\lambda = 47$, dependent scattering effects will be negligible even in the case of a consolidated packing of particles.

In order to define a region in the $\pi x/\lambda - C_V$ plane where steric interactions can be observed without additional dependent scattering, Figure 5 combines the critical curve for dependent scattering, Eq. (7), with the criterion of negligible radiative tunneling in a consolidated packing, Eq. (9), and the criterion for steric interactions, $C_V \ge 0.05$. Indeed, steric interactions are found to be prevalent within a wide range of concentration and particle size parameters, which is of interest with respect to radiometric, optical and ultrasonic extinction measurements in production processes such as crystallization, wet milling, emulsion polymerization and many others.

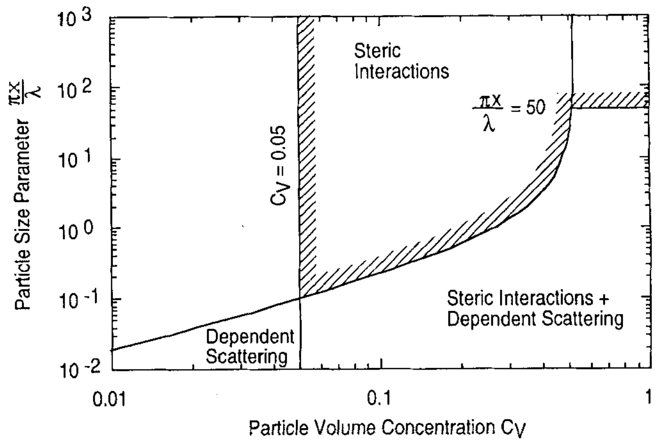

Fig. 5: Steric interactions versus dependent scattering in the $\pi x/\lambda - C_V$ plane.

3.3 Steric Interactions versus Multiple Scattering

The mechanism of multiple scattering implies that radiation undergoes interaction with different particles consecutively, i.e. radiation scattered by a first particle is scattered by a second particle and so forth. Multiple scattering also includes multiple retroreflections of radiation between neighbouring particles. Multiple scattering does not imply that the mechanism of interaction between particle and wave is modified in any way.

Since multiple scattering is a statistical process (at least in random media), multiply scattered radiation is characterized by a distribution of optical path lengths. Compared with radiation passing directly from the emitter to the receiver, there is a loss of coherence (if there has been any before) and a broadening of the angular distribution of radiation.

In general [4, 7-9, 22], extinction measurements suffer from disturbances due to multiple scattering at concentrations which are far too low to produce dependent scattering or steric interactions. Even when they exist, steric interactions or dependent scattering may be masked and rendered unobservable by a dominance of multiple scattering. It has to be discussed, therefore, which criteria are relevant to evaluate a possible dominance of multiple scattering.

A simplified approach given by *Ishimaru* [4] is well suited to discuss this question, and is presented here in a slightly modified version. Assume a beam of collimated radiation with intensity I_{coll} passing through a disperse system. The decrease in I_{coll} will be proportional to the extinction efficiency of the particles, K_{ext} (BLBL is assumed to be valid):

$$-\ln \frac{I_{coll}\langle \Delta z, C_{PA} \rangle}{I_{coll}\langle z = 0 \rangle} = K_{ext}\, C_{PA}\, \Delta z \qquad (10)$$

while the decrease in the total intensity, I_{tot}, is approximately proportional to the particle absorption efficiency K_{abs}:

$$-\ln \frac{I_{tot}\langle \Delta z, C_{PA}\rangle}{I_{tot}\langle z=0\rangle} = K_{abs}\, C_{PA}\, \Delta z \; . \tag{11}$$

Now, the absorption efficiency is always smaller than the extinction efficiency:

$$K_{abs} \le K_{ext} \, , \tag{12}$$

so that I_{coll} will decrease faster than I_{tot}, leaving as the difference a certain amount of diffuse intensity, I_{diff}, that has been scattered once or multiply without being absorbed:

$$I_{diff} = I_{tot} - I_{coll} \; . \tag{13}$$

Figure 6a gives a qualitative plot of I_{coll}, I_{tot} and I_{diff} as a function of $C_{PA}\, \Delta z$. It is seen that for large values of $(K_{ext} - K_{abs})\, C_{PA}\, \Delta z$, the total intensity is dominated by diffuse intensity, thus allowing the approximation

$$I_{diff} \cong I_{tot} \quad \text{for} \quad (K_{ext} - K_{abs})\, C_{PA}\, \Delta z \gg 1 \; . \tag{14}$$

In a final step, regarding the disturbance of extinction measurements by multiply scattered radiation, the different sensitivity of radiation sensors to diffuse and collimated radiation has to be taken into account. As a general rule, the relative sensitivity of a sensor to multiply scattered radiation, η_{ms},

$$\eta_{ms} = \frac{\text{sensitivity to diffuse radiation}}{\text{sensitivity to coherent or collimated radiation}} \tag{15}$$

is smaller than unity, which is due to the incoherence and wide angular spread of multiply scattered radiation, compared with the small aperture angles of typical receivers.

Assuming the additivity of collimated and diffuse contributions to the receiver signal I_{rec}:

$$I_{rec} = I_{coll} + \eta_{ms}\, I_{diff} \tag{16}$$

gives an estimate of the influence of multiple scattering on extinction measurements with intensity receivers (any type of receiver based on quantum effects, such as photodiodes, photomultipliers and scintillation counters, including an optical system). A modified argument can be used with antenna-type receivers (electric antennas, piezoelectric transducers and similar devices). With antenna-type receivers, it is more appropriate to distinguish between coherent intensity I_c and incoherent intensity I_i (instead of I_{coll} and I_{diff}), and the additivity of wave amplitudes instead of intensities is expressed by

$$I_{rec} = \left(\sqrt{I_c} + \sqrt{\eta_{ms}}\, \sqrt{I_i}\right)^2 \; . \tag{17}$$

Figure 6b shows the superposition of coherent and incoherent contributions to the received signal for an intensity receiver.

Taking equal contributions from collimated and diffuse radiation to the received signal or $I_{coll} = \eta_{ms}\, I_{diff}$ as a criterion for disturbances from multiple scattering, the critical value of $(K_{ext} - K_{abs})\, C_{PA}\, \Delta z$ is derived as

$$((K_{ext} - K_{abs})\, C_{PA}\, \Delta z)_{crit} = -\ln(\eta_{ms}) \tag{18}$$

and the critical concentration limit is expressed as

$$(C_{PA}\, \Delta z)_{crit} = \frac{-\ln(\eta_{ms})}{(K_{ext} - K_{abs})} \; . \tag{19}$$

To avoid disturbances from multiple scattering in practice, the parameter $C_{PA}\, \Delta z$ has to remain well below this critical limit. Typical values of η_{ms} range from $\eta_{ms} = 10^{-1} - 10^{-3}$ for intensity receivers down to $\eta_{ms} = 10^{-4} - 10^{-6}$ for antenna-type receivers. Hence the effective impact of multiple scattering on extinction measurements is a question of receiver type and design. Examples of this can be found in a large number of publications, only few of which are cited here [2, 7, 9, 22].

In a plot of particle concentration versus path length Δz (Figure 7), the domain of disturbances from multiple scattering is delimited by a hyperbola. Steric interactions or dependent scattering without the simultaneous presence of multiple scat-

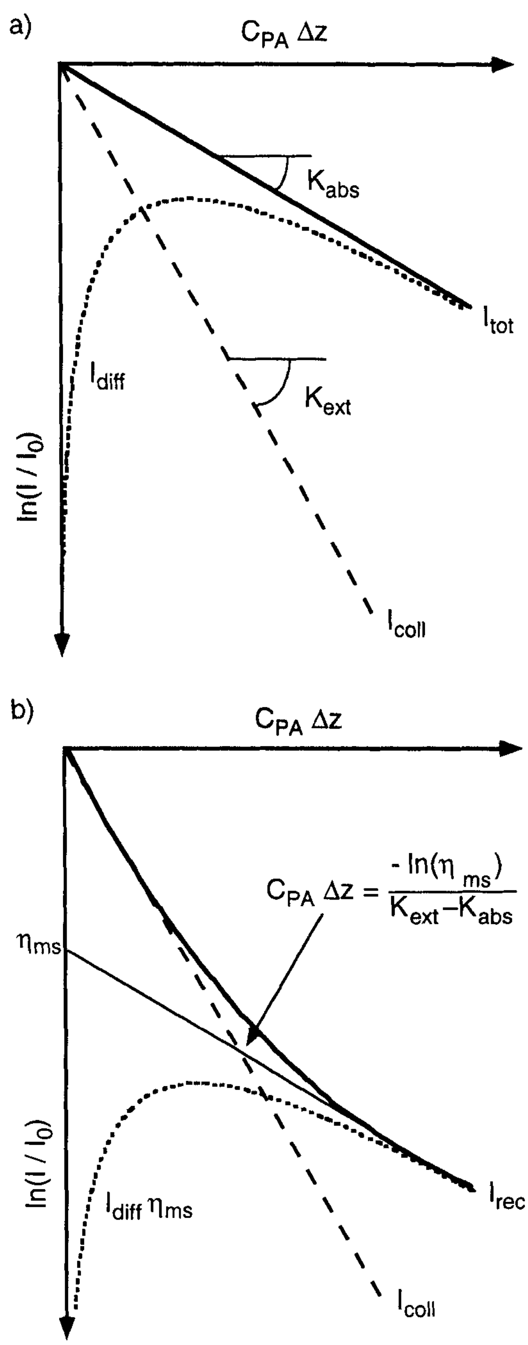

Fig. 6: Components of radiation intensity in a multiply scattering disperse system.

tering can always be found with sufficiently short path lengths. In total, the supression of disturbances from multiple scattering is mainly a technical problem. Either by an appropriate choice of receivers that show an extremely low sensitivity to multiply scattered radiation or by a sufficiently short path length, effects from multiple scattering are securely avoided.

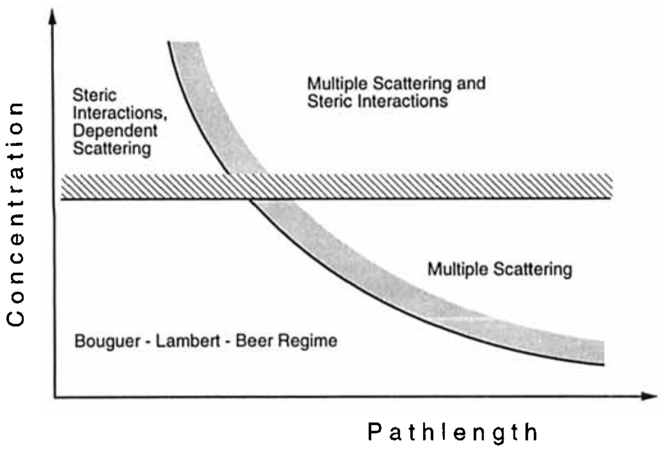

Fig. 7: Regimes of multiple scattering and steric interactions in the $C_V - \Delta z$ plane.

4 Modelling of Steric Interactions

In the modelling of steric interactions, it appears difficult to conceive a simple model that incorporates both an adequate representation of the disperse system including its gradual change with increasing concentrations and a physically correct treatment of particle-radiation interaction. As a consequence, a number of complementary models had to be developed in order to cover both aspects of the problem and to overcome the specific shortcomings of the single models.

4.1 Lattice Models

The lattice model, published by *Javanaud* and *Franklin* in 1985 [23], describes the suspension as an alignment of particles to the sites of an imaginary cubic lattice (Figure 8). The lattice constant b is identified with the particle diameter, whereas the proportion of occupied lattice sites varies with the particle concentration. The model is based on the assumption of ray propagation and restricted to the case of non-scattering (i.e. purely absorbent) particles, since refraction and reflection of the radiation are excluded.

Using the Poisson distribution and binomial distribution for the ranges of low and high concentrations, respectively, *Javanaud* and *Franklin* derived a variety of equations for cubic and spherical particles. With the limit of low particle concentration, BLBL is obtained. For high concentrations of cubic particles of edge length b, the extinction is given as

$$E_{CL} = \frac{\Delta z}{b} C_V^{1/3} \ln(1 - K_{ext} C_V^{2/3}) \,, \tag{20}$$

whereby $C_{PA} = C_V/b$ is used instead of Eq. (2).

A slightly modified theory, describing phase and amplitude modification on the wave on passing through a single particle with a complex transmission coefficient, was presented more recently by *Perdigão* et al. [24, 25]. Even though the refraction of the radiation is neglected, the authors claimed to have obtained the full information on the wave amplitude and coherent by combining the transmission coefficient with the probability distributions of the number of particles on a line of sight through the lattice.

Criticism on lattice models will mainly focus on the assumption concerning the suspension structure, which seems rather artificial. Further, the handling of these models is impractical, since the calculus involves the binomial coefficients.

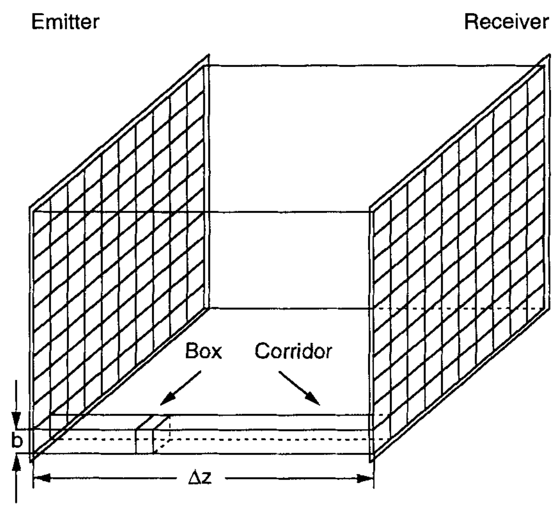

Fig. 8: Geometric configuration of the lattice model (from *Perdigão* et al. [24]).

4.2 Statistical Model

As a counterpart to the lattice model, the statistical model [26] does not need any specific assumptions on the arrangement of particles. For spherical, perfectly absorbing particles, and with the assumption of geometric ray propagation ($K_{ext} = K_{abs} = 1$), the problem of radiative transmission is reduced to the problem of sampling from a suspension. According to the statistical model, a ray of radiation with diameter D will be transmitted whenever a cylindrical sample volume of diameter $(D + x)$ and length Δz does not contain any particle (see Figure 9). The transmission through the suspension is then identical with the

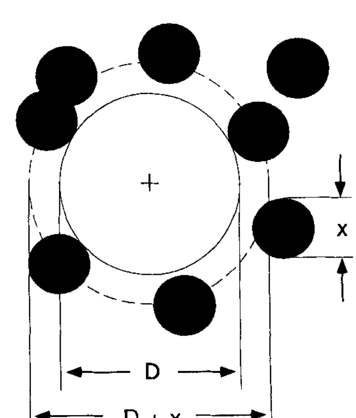

Fig. 9: Geometric configuration of the statistical model. The direction of radiative transport is perpendicular to the plane of the paper.

probability that a ray of infinitesimally small diameter can pass through the suspension. The result is given by the equation

$$E_{SM} = -\frac{1.5}{P}\frac{\Delta z}{x}\ln(1 - PC_V) \tag{21}$$

with

$$P = \frac{1}{1-\varepsilon^*}$$

and for

$$K_{ext} = 1 \ .$$

In this context, ε^* signifies the minimal porosity of a suspension sample, and hence P can be understood as a parameter related to the suspension structure. Assuming a densest pack of monodisperse spheres, the minimum value of ε^* is 0.259 ($P = 1.35$). This value is certainly too low to describe the conditions in a flowing suspension. Assuming simple cubic packing, the minimal porosity would be $\varepsilon^* = 0.474$ ($P = 1.90$), which seems to be a more reasonable estimate.

In the limit of low particle concentration, the logarithm can be developed into a series, and BLBL is obtained as the low concentration limit of Eq. (21). For $C_V = 1/P$, E_{SM} shows an asymptotic rise to infinity, which corresponds to a total blocking of directly transmitted radiation.

It is possible to express Eq. (21) as a factor of deviation from BLBL, which is a function of the particle volume fraction only:

$$F\langle C_V\rangle = \frac{E_{SM}}{E_{BLBL}} = \frac{-\ln(1-PC_V)}{PC_V} \ . \tag{22}$$

A plot of $F\langle C_V\rangle$ is given in Figure 10.

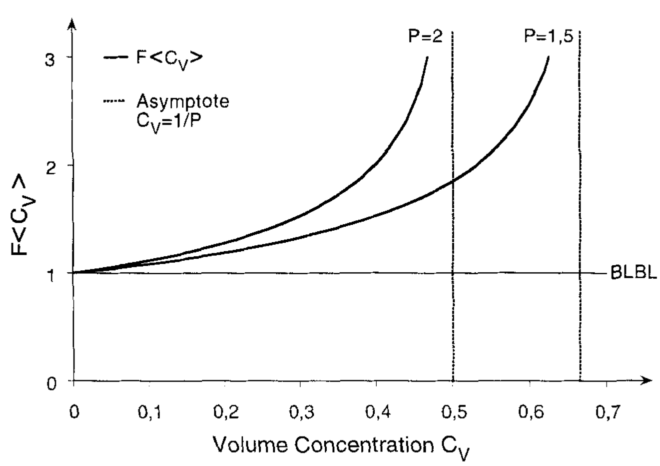

Fig. 10: A plot of $F\langle C_V\rangle$ for two values of the structure parameter P.

4.3 Layer Model

The layer model is derived in analogy to BLBL, but the conflict between the integrability condition and the condition of particle integrity is solved by avoiding integration. The suspension is taken as an empilement of N_L discrete suspension layers of finite thickness z_L extending perpendicular to the direction of radiation propagation (Figure 11):

$$N_L = \frac{\Delta z}{z_L} \ . \tag{23}$$

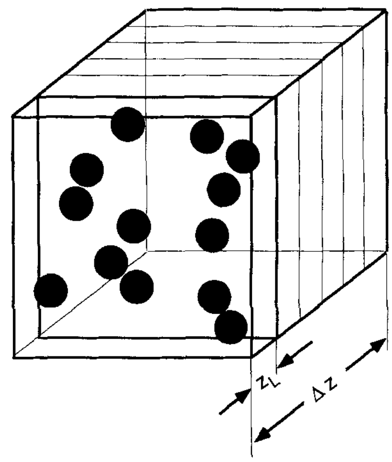

Fig. 11: Geometric configuration of the layer model. The direction of radiative transport is perpendicular to the layers.

Assuming that the layers are statistically independent with respect to the particle arrangement, the transmission T through an empilement of N_L layers is given by

$$T = (T_L)^{N_L} \tag{24}$$

where T_L is the transmission of a single layer.

Introducing the layer thickness z_L as $P/1.5$-fold the particle diameter x:

$$z_L = \frac{P}{1.5}x; \quad P \geq 1.5 \ , \tag{25}$$

the number of independent monolayers is found as

$$N_L = 1.5\frac{\Delta z}{Px} \tag{26}$$

and the monolayer density β, that is, the ratio of layer projection surface covered by particles, is given by

$$\beta = P\,C_V \ . \tag{27}$$

Now, for the interaction of particles and radiation, two different cases can be incorporated into the layer model:

i) For opaque particles and extinction by the mechanism of Fraunhofer diffraction, the transmission through a monolayer of spherical particles is to a good approximation expressed as [27]

$$T_{L,FD} = (1-\beta)^{K_{ext}}$$

for Fraunhofer diffraction with $1 \leq K_{ext} \leq 2$. (28)

In this equation, the variation of monolayer transmission resulting from variations of the receiver aperture angle is sufficiently accounted for by using K_{ext}, the single particle extinction efficiency valid for the given combination of particle size, wavelength and aperture angle. Fraunhofer diffraction may be assumed for the interaction of light or ultrasonics with many types of particles, even if some light is transmitted through the particles [27, 28].

As a result, the same extinction equation as with the statistical model is obtained; only the underlying interpretation of the structure parameter P is slightly different:

$$E_{LM,FD} = \frac{\Delta z}{x} \frac{1.5}{P} K_{ext} \ \ln(1 - P\, C_V)$$
for Fraunhofer diffraction . (29)

Once again, the deviation from BLBL can be expressed by Eq. (22). It is most remarkable that $F\langle C_V \rangle$ does not depend on K_{ext}, when Fraunhofer diffraction is assumed.

ii) Another equation can be used to describe the monolayer transmission for the case that the particles are very large compared with the wavelength, partially transparent to the radiation and have a refractive index of 1. This case corresponds to the interaction of particles with penetrating radiation such as X-rays and γ-rays, but it also applies to the extinction of light by spongy agglomerates and other highly porous structures.

With straight ray propagation through the particles, the extinction efficiency K_{ext} is

$$K_{ext} = 1 - \frac{I_{PA}}{I_0} = 1 - \frac{2}{(\alpha x)^2} (1 - (\alpha x + 1)\, e^{-\alpha x}) \, , \tag{30}$$

where I_{PA} is the average of the intensity transmitted through the particle projected area, measured in a plane behind the particle, I_0 is the intensity in the same plane, but without the particle, and α is the difference between the particle and fluid absorption coefficients. If the radiation is absorbed more strongly by the fluid than by the particle, α becomes negative and a negative K_{ext} emerges.

For the above case, the transmission through a monoplayer is given by

$$T_{L,RP} = (1 - \beta\, K_{ext}) \, . \tag{31}$$

This equation is exact for the case of wide-angle receivers, where the diffracted part of intensity is still within the aperture angle and $K_{ext} \leq 1$ in any case. K_{ext} may also be negative, as is the case with particles absorbing the radiation less strongly than the suspending fluid. Eq. (31) may also be used for narrow-angle receivers with single-particle extinction efficiencies up to $K_{ext} = 0.5$, where the contribution of diffraction to extinction may still be neglected compared with the contribution from absorption. Eq. (31) leads to an extinction equation differing slightly from Eq. (29):

$$E_{LM,RP} = \frac{\Delta z}{x} \frac{1.5}{P} \ln(1 - P\, K_{ext}\, C_V)$$
for ray propagation with $K_{ext} \leq 1$. (32)

Hence, for ray propagation with partially transparent particles, the deviation from BLBL will depend not only on the particle volume concentration, but also on the particle extinction efficiency, which may be expressed by a correlation function $F\langle C_V, K_{ext} \rangle$ defined in analogy to Eq. (22). Figure 14 gives a plot of $F\langle C_V, K_{ext} \rangle$ for various positive and negative values of K_{ext} together with the corresponding results from numerical simulation. The limiting case for the application of Eq. (29) or (32) is the combination of strongly absorbent particles with a wide-angle receiver (all of the forward diffracted radiation is received), which results in $K_{ext} = 1$. In this case, both solutions coincide exactly.

4.4 Numerical Simulation of Steric Interactions

Applying the condition of straight ray propagation to partially transparent or perfectly absorbent, monodisperse spherical particles (compare Eq. (32)), the effect of steric interactions on the extinction of radiation also can be estimated from numerical simulations. Numerical simulations offer the advantage that realistic three-dimensional structures can be simulated.

The geometric arrangement upon which the numerical simulations are based is shown in Figure 12. The disperse system, consisting of monosized spherical particles, is contained in a cube with an edge length Δz. From one side, a homogeneous beam of parallel radiation is incident upon the disperse system, whereas on the opposite side, the pattern of projected particle shadows appears on a screen. The transmission of radiation is then determined from the average fraction of radiation received on the screen.

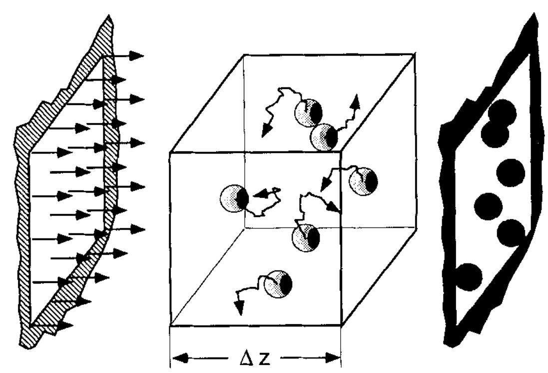

Fig. 12: Geometric arrangement for the numerical simulations.

In a first step of the simulation, the cube is filled with the number of particles required to obtain a certain volume concentration, whereby random particle coordinates are chosen and particles are allowed to intersect. In a second step, particle-particle interactions are accounted for by introducing pair interaction potentials. A diffusion process resulting in a Boltzmann distribution of particle potentials is simulated to allow a relaxation of the structure. Disturbances from wall effects are avoided by using the method of toroidal edge correction [29]. When a stationary state has been reached (which is controlled by monitoring the particle pair correlation function), the diffusion process is continued in order to obtain the average transmission for a large number of random particle configurations. Alternatively, the introduction of pair interaction potentials may be omissed in order to simulate non-interacting particles.

For the simulation results shown here, only hard-sphere interactions were used, which corresponds to an interaction potential of infinity for interpenetrating particles and an interaction potential of zero for non-contacting particles.

Figure 13 resumes the results of two runs of the numerical simulation program for $K_{ext} = 1$ with and without hard-sphere interactions. Without interaction, particles are allowed to interpenetrate, and a result corresponding to BLBL actually emerges, i.e. $F\langle C_V \rangle = 1$. Further, the numerical results with hard-sphere interactions are compared with the theoretical results given by Eq. (22), (29) or (32), whereby the parameter P was chosen to be 2.0 for a best fit. It is seen that the theory and numerical simulations fit very well for low and intermediate concentrations up to about $C_V = 0.35$, but with higher concentrations, the theoretical value of $F\langle C_V \rangle$ rises faster than the values predicted from numerical simulation.

Figure 14 gives some numerically simulated results for partially transparent particles with hard-sphere interactions, including the cases of perfectly absorbent particles ($K_{ext} = 1$) and of negative extinction efficiencies. It seems remarkable that strongly negative extinction efficiencies lead to strong deviations from BLBL at low volume concentrations.

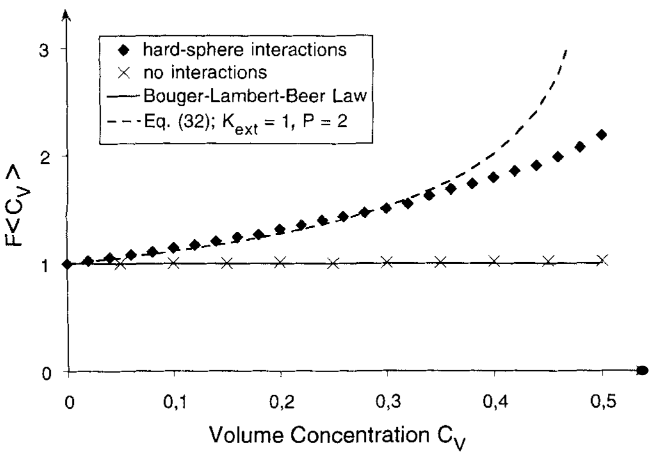

Fig. 13: Results from numerical simulations for perfectly absorbent particles ($K_{ext} = 1$) without steric (hard-sphere) interactions, expressed as $F\langle C_V \rangle$. Without steric interactions, Bouguer-Lambert-Beer's law is found, which corresponds to $F\langle C_V \rangle = 1$. A good fit of Eq. (32) to the numerical results is obtained with $P = 2$.

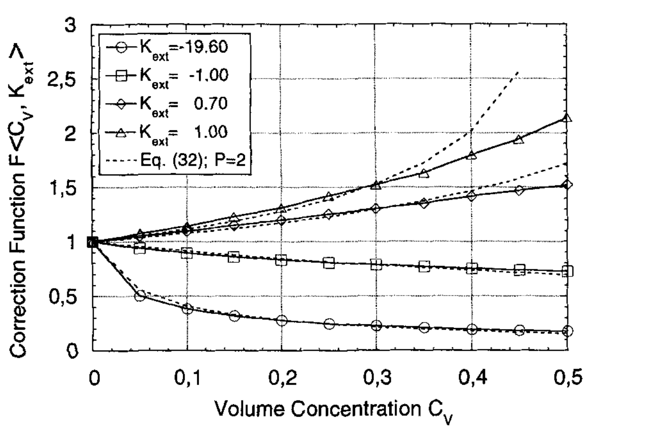

Fig. 14: $F\langle C_V, K_{ext} \rangle$ for partially transparent particles and straight ray propagation with various positive and negative values of K_{ext}. Results from numerical simulation together with the corresponding results according to the layer model, Eq. (32) with $P = 2$.

5 Conclusion

Whereas the extinction of radiation in dilute suspensions is sufficiently well described by Bouguer-Lambert-Beer's law (BLBL), the extinction in concentrated suspensions can be modified by particle-particle interactions such as multiple scattering, dependent scattering and steric interactions, which may result in significant deviations from BLBL. A discussion of particle-particle interactions shows that steric interactions are dominant over dependent scattering for a wide and practically relevant range of concentrations and particle size parameters. On the other hand, steric interactions are often masked and rendered unobservable by multiple scattering, but appropriate technical means are available (even though not commonly applied) to suppress disturbances from multiple scattering. Hence, a better knowledge of steric interactions is a key to a better understanding and a quantitative evaluation of extinction measurements at extremely high particle concentrations.

For a theoretical description of the effect of steric interactions on extinction in concentrated suspensions, various independent, complementary approaches are feasible. The cubic lattice model and the layer model are more easily adapted to different mechanisms of particle-wave interactions, but rely on some questionable assumptions concerning the suspension structure. The statistical model is free from any explicit assumption on the suspension structure, but remains restricted to opaque particles in combination with straight ray propagation. The simulation model, finally, is more versatile, allowing the suspension structure to be influenced by introducing pair interaction potentials of different types.

The various models (except for the cubic lattice model) coincide in yielding the same type of extinction equation, whereby two slightly different versions of the extinction equation are obtained for opaque particles with Fraunhofer diffraction and for straight ray transmission through absorbent particles. In any case, BLBL is found to be the low concentration limit of the extinction equation. The simulation results are in good agreement with the theoretical results, which proves that the assumptions made on the suspension structure are not too critical.

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7 Symbols and Abbreviations

a	distance between particles (surface-surface)
b	box dimension (lattice model)
BLBL	Bouguer-Lambert-Beer's law
C_N	number concentration
C_{PA}	particle projection area concentration
C_V	volume concentration
D	beam diameter (statistical model)
E	extinction
$F\langle C_V \rangle$	correction function
$g\langle r \rangle$	pair correlation function
I_{coll}	collimated part of intensity
I_{diff}	diffuse part of intensity
I_{rec}	received intensity
I_{tot}	total intensity
I_0	intensity in absence of particles
K_{abs}	absorption efficiency
K_{ext}	extinction efficiency
N	number of particles, number of monolayers
P	structure parameter
r	radial distance between particles (centre-centre)
S	surface
T	transmission

x	particle/spherical object diameter
z	coordinate of radiative propagation
Δz	pathlength
β	monolayer density
ε^*	minimal porosity of a suspension sample
η_{ms}	relative sensitivity to multiply scattered radiation
λ	wavelength

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