100 Years of Mie Scattering Theory: Expanded Size Range by Extreme Precision Calculations

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ABSTRACT

Exactly 100 years after the publication of the fundamental light scattering theory by Gustav Mie in 1908, this theory has significant interest in the field of particle characterisation, especially in particle size analysis.

Mie scattering calculations were limited in the past by calculation accuracy, instability problems and calculation time for large particles by former computer systems. Today, more powerful computers allow for extreme precision calculation tools, and enable expansion of the particle size range covered by Mie scattering calculations from submicron sized materials up to particles in the millimetre range.

In this paper we describe an extended precision analysis of Mie scattering theory for use in particle size analysis which extends the particle size range and increases accuracy of calculation. Based on this precision analysis a Mie validation data set has been created for different Mie parameter sets, which could be used for internal optimisation and accuracy checks of Mie light scattering calculations. This enables the evaluation of particle size distributions from submicron to millimetre particles, for transparent spherical or reflecting materials, expanding the existing particle portfolio and size range.

Keywords Mie Scattering, Precision Analysis, Particle Size Analysis, Laser Diffraction

1 INTRODUCTION

The fundamental theory of light scattering by homogeneous and isotropic spherical particles was described in 1908 by the German physicist Gustav Mie (1868 - 1957) (Mie 1908). In order to describe the colour effects of suspensions of colloidal gold nano-particles, Mie formulated the basic theory using fundamental Maxwell equations, boundary conditions and mathematical methods expanding planar incoming and scattered electromagnetic waves in spherical coordinates. Now, exactly 100 years after the publication, fundamental Mie scattering theory becomes more relevant and of adequate usability in the field of particle characterisation, especially in particle size analysis.

Mie scattering theory is necessary for analyses in which optical effects resulting from reflecting or transparent spherical particles and from polarisation effects appear. Thus, proper application of the theory requires knowledge of various optical parameters. This is in contrast to Fraunhofer diffraction theory, which requires no previous knowledge of optical parameters and is useful for analysis of non-spherical particles but which is also limited in application to opaque materials. Thus, the two theories complement one another, expanding the measurable size range to smaller particles and enhancing the overall material portfolio. Depending on particle size, significant differences in results obtained through the Mie and Fraunhofer theories can be attributed to different optical parameters, including the relative refractive index of the particles and of their surrounding medium. Especially calculations of the extinction efficiency or the volumetric concentration of a sample of particles can lead to significant differences in the results compared to Fraunhofer diffraction significantly influencing other values, e.g. the optical concentration or the total material consumption.

In this paper we first describe an extended precision analysis of Mie scattering theory leading to a Mie validation data set and expanded particle size ranges for Mie calculations and show one specific example regarding the calculation of the volumetric concentration.

2 PRECISION ANALYSIS

2.1 Main focus and preconditions

The most important parameter of Mie scattering is the Mie parameter $\alpha = \pi \cdot x/\lambda$ which is directly related to the particle size x and to the wavelength of light in the surrounding medium $\lambda = \lambda_o/n_{med}$ (given by the wavelength of light in vacuum λ_o together with the refractive index of the surrounding medium n_{med}). Another important parameter is the relative refractive index m, the ratio of the complex refractive index of the particle n_p and the refractive index of the medium n_{med} with $m = n_p/n_{med}$. Besides the main formulas of Mie scattering theory resulting from Maxwell equations using boundary conditions at spherical homogeneous and isotropic particles and expansion of planar waves in spherical coordinates (as described in literature (van de Hulst 1957; Bohren-Huffman 1983; Wiscombe 1996)), only a few papers consider problems of precision and stability in calculations and challenges to improve algorithms (Wiscombe 1996; Du 2004). Wiscombe's report (Wiscombe 1996) was the starting point for the development of our precision analysis, with the goals of increasing accuracy from single precision (6-7 digits of precision for the expansion coefficients) to at least double precision through the use of more advanced computer architectures, of expanding the limitations of particle size ($\alpha < 20000$ for Wiscombe) to larger particles, and of extending the range of allowed refractive indices of the particles. Du (Du 2004) expanded these limitations to larger particles and higher refractive indices, but computation speed has been reduced compared to Wiscombe's MIEV0 algorithm. Our precision analysis was therefore focused on recurrence and series terms and instabilities.

2.2 Challenges in recurrence and series terms

There exists different modifications describing routines of upward and downward recurrences of the corresponding logarithmic derivatives of the Riccati-Bessel functions ($A_n(z)$ as defined in equation (2)), which are necessary for building the expansion coefficients $a_n(\alpha,m)$ and $b_n(\alpha,m)$ in equations (1) ($\psi_n(\alpha)$, $\chi_n(\alpha)$ and $\zeta_n(\alpha)$ are the corresponding Riccati-Bessel functions (Wiscombe 1996)).

$$a_n(\alpha,m) = \frac{\left(\frac{A_n(m\cdot\alpha)}{m} + \frac{n}{\alpha}\right)\cdot\psi_n(\alpha) - \psi_{n-1}(\alpha)}{\left(\frac{A_n(m\cdot\alpha)}{m} + \frac{n}{\alpha}\right)\cdot\zeta_n(\alpha) - \zeta_{n-1}(\alpha)} \qquad b_n(\alpha,m) = \frac{\left(m\cdot A_n(m\cdot\alpha) + \frac{n}{\alpha}\right)\cdot\psi_n(\alpha) - \psi_{n-1}(\alpha)}{\left(m\cdot A_n(m\cdot\alpha) + \frac{n}{\alpha}\right)\cdot\zeta_n(\alpha) - \zeta_{n-1}(\alpha)} \quad \textbf{(1)}$$

$$\zeta_n(\alpha) = \psi_n(\alpha) + i\cdot\chi_n(\alpha) \qquad A_n(z) = \frac{\psi_n'(z)}{\psi_n(z)} = \frac{d}{dz}(\ln(\psi_n(z))) \quad \textbf{(2)}$$

Our investigations concentrated especially on the stability of these different routines. Upward recurrence, which is more easily used, has been found to be unstable in the limit of small relative refractive indices and small particles. Downward recurrence however, which is stable for all parameters, can be very time consuming if the maximum index has been chosen too high, which has to be used as a starting point for downward recurrence. With the alternative Lentz method of downward recurrence (Wiscombe 1996) problems and instable results also occur for relative refractive indices in the proximity of $m \approx 1.0$ (i.e. almost no scattering) with significantly increased calculation time.

$$Q_{ext}(\alpha) = \frac{2}{\alpha^2}\cdot\sum_{n=1}^{N_{max}}(2\cdot n+1)\cdot\Re\left(a_n(\alpha)+b_n(\alpha)\right) \quad \textbf{(3)}$$

Another important consideration involves expressing planar waves using spherical coordinates, which Gustav Mie solved in 1908 using the summation of the so-called expansion coefficients (equations (1) and (3)). These equations combine the electric field inside the particle and the scattered field outside of it with the incoming electric field. In contrast to theory, an infinite number of series terms is not possible in daily calculations, so an optimal maximum summation index N_{max} has to be found (as for the extinction efficiency Q_{ext} in equation (3)), which ensures a good accuracy of the calculation on the one hand but also reduces calculation time and instabilities during calculation on the other hand. Each additional series term increases calculation time linearly, especially for large particles in the millimetre range because the number of terms necessary is at least linear dependent on the particle size. With the help of the precision analysis using the arbitrary precision calculator CALC (Bell 2003) the dependence of particle size and optical parameters on this maximum summation index was investigated. This calculator calculates series exactly on demand without truncation. The Mie algorithm

was implemented in this precision calculator based on the programming language C. The Mie code was also implemented under the mathematical software package Maple 10 for comparison. The maximum summation index for different particle sizes and optical parameters was determined including an expansion of the Mie parameter range to values exceeding Mie parameters of $\alpha > 20000$. By successively increasing N_{max} in steps and comparing the results with an error range given by the convergence criterion, the values were obtained for different particle sizes and optical parameters. In the report of Wiscombe (Wiscombe 1996) the convergence criterion is given by the so called Dave criterion with $|a_n(\alpha)|^2 + |b_n(\alpha)|^2 < 5 \cdot 10^{-14}$ for the expansion coefficients $a_n(\alpha)$ and $b_n(\alpha)$ of the Mie series (equations (1)) which leads to only a float-precision of 6-7 significant digits. By increasing the accuracy (with the help of the precision calculator the number of significant digits could be chosen directly) using a modified Dave criterion with $|a_n(\alpha)|^2 + |b_n(\alpha)|^2 < 5 \cdot 10^{-80}$ the number of N_{max} is only slightly increased compared to the previous Dave criterion as Wiscombe used before, because of the strongly converging Riccati-Bessel functions for $n > \alpha$. As N_{max} increases in a super-linear fashion with increasing Mie parameter, calculation time grows significantly with larger particles and with higher requirements of accuracy. Once N_{max} is obtained, additional checks ensure that the Dave criterion was fulfilled in each of the last twenty iterations (at least) before the value was reached, thus excluding the possibility of instabilities.

2.3 Instabilities

Instabilities in the Riccati-Bessel functions can occur if the given accuracy of a series term calculation is not high enough using standard computer architectures. In particular, the real part $\psi_n(\alpha)$ of the Riccati-Bessel function $\zeta_n(\alpha)$ (equation (2)) converges increasingly rapidly to zero if the number of series terms exceeds the given Mie parameter and therefore a given particle size. Due to accuracy errors however, small differences between iterative results can lead to a divergence of $\psi_n(\alpha)$ away from zero without the value ever having actually reached zero or having fulfilled a given convergence criterion at a specific summation index. Instabilities look like a kink in the graphical view of the Riccati-Bessel function and can therefore be easily detected. If the summation index of the instability occurs after the convergence criterion is reached, the accuracy is chosen as good enough. If the instability occurs at a summation index before the convergence criterion is reached, then all calculated values are erroneous, especially the expansion coefficients and all derived physical values (extinction efficiency, intensities, etc.) from these coefficients. Furthermore, the convergence criterion is not reached, so algorithm problems or infinite loops can possibly occur.

With increasing accuracy instabilities are shifted to higher summation indices and therefore shifted across given convergence limits like the Dave criterion. So the main goal is to find a maximum number of series terms $N_{done} < N_{max}$ which fulfils a given precision condition by the convergence criterion, avoids instabilities and reduces calculation time.

2.3 Mie validation data set

To ensure high precision of Mie series calculation a validation data set has been established with the help of the precision calculator CALC with more than 44000 entries of different Mie parameters, optical parameters and scattering angles. The pure calculation time for creating the validation data set was approximately three months using the precision calculator. The data set is extendable, if additional parameter sets are needed to be added for validation. With this Mie validation data set the corresponding Mie algorithm has been optimised to reduce calculation time, but fulfil proper precision conditions on standard computers.

Mie parameter: 1.0	refractive index: 1.50 – i·0.10		scattering angle: 85°
Q_{ext}	0.48237045634698685612701876216 36…	Q_{sca}	0.20874001831483718847723838557 2…
i_s	0.07815653982023038113148036344532…	i_p	0.00172975830062537505959779732895…

Table 1. Mie scattering results using extended precision calculation for a given Mie parameter set (Q_{ext},Q_{sca}: extinction and scattering efficiency, i_s, i_p : relative intensity of scattered light with polarisation perpendicular (i_s) and parallel (i_p)).

The validation data set covers especially the Mie parameters from 0.0001 up to 50000 (corresponds to particle sizes of x < 1nm up to 10mm) in several steps. The real and imaginary part of the particle is

varied in different steps from 0.2 – 3.0 for the real part and 0.0, respectively 10^{-5} up to 8.0 for the imaginary part. Different scattering angles are also included, especially at 0° and 90° in order to cover some special angles. The accuracy is given by the given Dave-criterion of $|a_n(\alpha)|^2 + |b_n(\alpha)|^2 < 5 \cdot 10^{-80}$, so that both expansion coefficients allow for almost 40 significant digits in accuracy and therefore also the extinction efficiency Q_{ext} (equation (3)). In Table 1 the Mie scattering results obtained through use of extended precision calculation are shown for a given Mie parameter set.

3 MIE SCATTERING EXAMPLE: VOLUMETRIC CONCENTRATION

As an example for efficient Mie light scattering analysis, the following example is shown for the calculation of the volumetric concentration of particles dispersed in a liquid (e.g. water) for different particle sizes at a given and fixed optical concentration OC. In equation (4) the definition of the optical concentration OC is given for transmission T, which is obtained from Lambert-Beer-Law including the total absorption index γ, which can be obtained from all single particles by summation over all absorption indices γ_i by equations (5).

$$OC = 1 - T \qquad \text{with} \qquad T = \exp(-\gamma \cdot d) \tag{4}$$

$$\gamma = \frac{1}{d} \cdot \ln\left(\frac{1}{1-OC}\right) = \sum_i \gamma_i \qquad \text{and} \qquad \gamma_i = \frac{N_0 \cdot dQ_0(x_i)}{V} \cdot \frac{\pi \cdot x_i^{\,2}}{4} \cdot Q_{ext}(x_i) \tag{5}$$

$$c_V = \frac{\sum_i V_i}{V} = \frac{N_0 \cdot \sum_i dQ_0(x_i) \cdot \frac{\pi}{6} \cdot x_i^{\,3}}{V} \qquad \text{with} \qquad N_0 = \frac{1}{d} \cdot \ln\left(\frac{1}{1-OC}\right) \cdot \frac{V}{\sum_i dQ_0(x_i) \cdot \frac{\pi \cdot x_i^{\,2}}{4} \cdot Q_{ext}(x_i)} \tag{6}$$

In equation (5) especially the extinction efficiency factor Q_{ext} plays a major role, which is directly calculated by Mie scattering theory. By combination of equations (4) + (5) the total number of particles interacting are obtained from equation (6) with the total volume V and therefore the volumetric concentration c_V as defined in equation (6) could be expressed as follows in equation (7) using some additional particle arithmetics.

$$c_V = \frac{2 \cdot \ln\left(\frac{1}{1-OC}\right)}{3 \cdot d} \cdot \frac{\sum_i dQ_0(x_i) \cdot x_i^{\,3}}{\sum_i dQ_0(x_i) \cdot x_i^{\,2} \cdot Q_{ext}(x_i)} = \frac{2 \cdot \ln\left(\frac{1}{1-OC}\right)}{3 \cdot d} \cdot \frac{1}{\sum_i dQ_3(x_i) \cdot \frac{Q_{ext}(x_i)}{x_i}} \tag{7}$$

$$c_V = \frac{2 \cdot \ln\left(\frac{1}{1-OC}\right)}{3 \cdot d} \cdot \frac{x}{Q_{ext}(x)} \tag{8}$$

In order to investigate monodisperse particles equation (7) reduces to equation (8), because summation is only done over one particle, so that the summation vanishes. In equation (8) we can see the particle size dependent factors are given by the quotient of the particle size x and the corresponding extinction efficiency factor $Q_{ext}(x)$. With the help of Mie scattering theory and the corresponding approximations in the small particle limit (x << 1µm) and the large particle limit (x >> 1µm) it is possible to formulate trends of the volumetric concentration in the given limits. These limits are given in equation (10) with the corresponding extinction efficiency factors in equation (9).

$$Q_{ext}(x) \approx 2 \quad \Big| \quad Q_{ext}(x) \sim x^4 \quad (k = 0) \quad \Big| \quad Q_{ext}(x) \sim x \quad (k > 0) \tag{9}$$

$$c_V \sim x \quad \Big| \quad c_V \sim x^{-3} \quad \Big| \quad c_V = \text{const.} \tag{10}$$

With the help of the Mie scattering routines the volumetric concentration curves as a function of the particle size for a given and fixed optical concentration are shown in Figure 1 for different absorbing particles by variation of the imaginary part of the corresponding refractive index.

The calculation of the volume concentration for a fixed optical concentration clearly shows the difference of Mie scattering and Fraunhofer diffraction for small particles. For larger particles the curves overlap while reaching the diffraction limit, where volume concentration is directly proportional to particle size for a given optical concentration. In the submicron range, however, the curves strongly depend on the imaginary part of the refractive index. If the particle is transparent with a negligible imaginary part of the refractive index the scatter limit with $c_V \sim x^{-3}$ is reached. For absorbing particles the limit is a constant plateau dependent on the imaginary part and therefore on the absorption of the

particle. In effect this means that a much higher volume concentration for smaller transparent particles is needed and therefore much more material is necessary to reach the same optical concentration. However, strongly absorbing particles can be considered in the diffraction limit even in the submicron range.

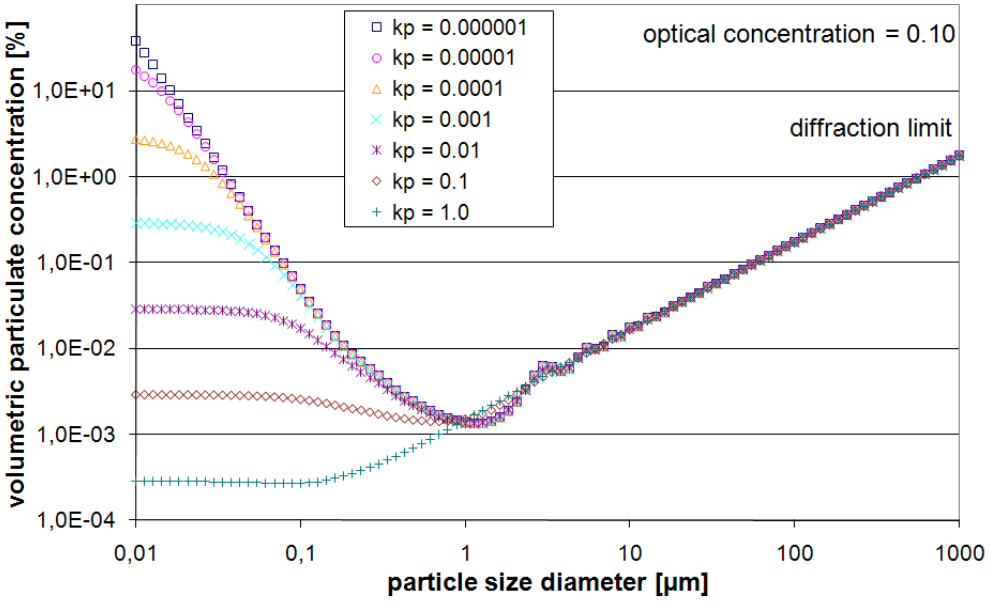

Figure 1. Volume concentration in dependence of particle size for particles with differing imaginary part (k_p) of the refractive index of the particles. The real part of the refractive index as well as the optical concentration is kept fixed. For large particles (> 10µm) the diffraction limit causes overlapping curves independent of the imaginary part. For smaller particles, however, a significant split of the curves is visible for different imaginary parts.

4 CONCLUSIONS

With the help of the precision analysis an extended Mie scattering calculation tool is available together with a validation data set for optimisation of Mie light scattering algorithms and expansion of particle size ranges. This also allows for the combination of several measuring ranges.

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