VERIFICATION OF MIE SCATTERING ALGORITHMS BY EXTREME PRECISION CALCULATIONS

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ABSTRACT

The fundamental theory of light scattering by homogeneous and isotropic spherical particles was introduced and invented in 1908 by the German physicist Gustav Mie (1868 - 1957). More than 100 years later the Mie scattering theory has still growing interest in the field of particle size analysis.

For transparent homogeneous and spherical materials, especially in the submicron range, Mie Scattering theory is the appropriate model for evaluation including optical effects resulting from reflecting or transparent spherical particles and from different polarisation effects in the submicron particle size range. Due to different optical parameters, including the relative refractive index of particles and the surrounding medium, significant changes in physical values can be explained dependent on the particle size. Especially calculations of the Extinction Efficiency or of the Volume Concentration of particles can lead to interesting results, e.g. related to material consumption. Furthermore, discrimination parameters and decision criterions can be found for the validation area of Fraunhofer Diffraction in the border range of the corresponding approximations, depending on size and optical parameters of the related particles.

Mie Scattering calculations, however, were limited in the past by the calculation accuracy. In the range of coarse particles instability problems are significant, resulting from large numbers of series terms in the calculation. Furthermore, calculation time and accuracy were limited by former computer systems. Today, more powerful computers allow for extreme precision calculation tools, and enable to expand the particle size range covered by Mie scattering calculations from submicron materials up to particles in the millimetre range. Precision calculations are also used to create a Mie validation data set. This data set is necessary and indispensable for accuracy checks of Mie light scattering calculations performed on the instruments' computer, requiring speed and precision optimised Mie calculation algorithms.

The presented Mie scattering calculations are based and verified on this precision analysis. They offer the evaluation of particle size distributions from submicron to millimetre particles, for transparent spherical or reflecting materials, expanding the existing particle portfolio.

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, more than 100 years after the publication, fundamental Mie scattering theory becomes more relevant and of adequate usability in the field of particle characterization, 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 polarization 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 the analysis of non-spherical particles but 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 by the Mie and Fraunhofer theories can be attributed to different optical parameters, including the relative refractive index of the particles related to 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, thus significantly influencing other values, e.g. the optical concentration or the total material consumption.

Here we describe an extended precision analysis of the Mie scattering theory leading to a Mie validation data set and expanded particle size ranges for Mie calculations.

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 $\lambda=\lambda_0/n_{med}$ (given by the wavelength of light in vacuum λ_0 divided by the refractive index of the surrounding medium n_{med}). Another important parameter is the relative refractive index $m = n_p/n_{med}$, the ratio of the complex refractive index of the particle n_p and the refractive index of the medium n_{med}. Besides the main formulas of the Mie scattering theory resulting from Maxwell's equations using boundary conditions at spherical homogeneous and isotropic particles and expansion of planar waves in spherical coordinates as described in literature by van de Hulst (1957), Bohren-Huffman (1983), and 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 was the starting point for the development of our extreme 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 by the use of more advanced computer architectures,
- expanding the limitations of particle size ($\alpha < 20\,000$ for Wiscombe) to larger particles, and
- extending the range of allowed refractive indices of the particles. 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 exist 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 eq. 2), which are necessary to build the expansion coefficients $a_n(\alpha,m)$ and $b_n(\alpha,m)$ in eq. 1. $\psi_n(\alpha)$, $\chi_n(\alpha)$ and $\varsigma_n(\alpha)$ are the corresponding Riccati-Bessel functions (Wiscombe, 1996). 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.

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

$$b_n(\alpha,m)=\frac{\left(mrA_n(m\alpha)+\frac{n}{\alpha}\right)\cdot\psi_n(\alpha)-\psi_{n-1}(\alpha)}{\left(mrA_n(m\alpha)+\frac{n}{\alpha}\right)\cdot\zeta_n(\alpha)-\zeta_{n-1}(\alpha)}$$

$$\zeta_n(\alpha)=\psi_n(\alpha)+i\cdot\chi_n(\alpha) \qquad (2)$$

$$A_n(z)=\frac{\psi_n'(z)}{\psi_n(z)}=\frac{d}{dz}(\ln(\psi_n(z)))$$

Downward recurrence however, which is stable for all parameters, can be very time consuming if the maximum index used as the starting point has been chosen too high. 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.

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

Another important consideration involves expressing planar waves in spherical coordinates, which Gustav Mie solved in 1908 using the summation of the so-called expansion coefficients (eq. 1 and eq. 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 eq. 3), which ensures a good accuracy of the calculation on one hand but also reduces calculation time and instabilities on the other hand.

Each additional series term increases calculation time linearly, especially for large particles in the millimeter range because the number of terms necessary is at least linearly 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 computes 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 of $\alpha \geq 20\,000$.

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 and b_n of the Mie series (eq. 1) which leads to a float-precision of 6-7 significant digits only.

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 Dave criterion used by Wiscombe. This is due to 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, 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 $\varsigma_n(\alpha)$ (eq. 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, all calculated values are erroneous, especially the expansion coefficients and all physical values (extinction efficiency, intensities, etc.) derived 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.

2.4 Mie validation data set

To ensure a high precision of the Mie series calculation a validation data set has been established with the help of the precision calculator CALC with more than 44 000 entries of different Mie parameters, optical parameters and scattering angles.

The pure calculation time to create the validation data set was approximately three months using the precision calculator. The data set is extendable, if additional parameter sets need to be added for validation.

With this Mie validation data set the corresponding Mie algorithm has been optimized to fulfill proper precision conditions on standard computers at minimum calculation time.

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…	

Tab. 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 polarization perpendicular (i_s) and parallel (i_p)).

The validation data set especially covers the Mie parameters from 0.0001 up to 50 000, corresponding to particle sizes of $x < 1$ nm up to 10 mm, in several steps.

The real and imaginary part of the particle property 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 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 which also applies to the extinction efficiency Q_{ext} (eq. 3). In tab. 1 the Mie scattering results obtained by extended precision calculation are shown for a given Mie parameter set.

3 CONCLUSIONS

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

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