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Cross section calculations of randomly oriented bispheres in the small particle regime

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Abstract

The T-matrix is used to calculate the extinction cross section of bispherical particle systems in random orientation for a monospherical size parameter $x = 0.01$. Differences between bispherical and monospherical (Mie) results are shown for a range of values of the refractive index. It is found that the size of the T-matrix that needs to be calculated can be large, thus preventing simple dipole approximations from being used. Once the T-matrix is computed, however, only a small number of terms is needed to obtain cross section values.

Keywords: Rayleigh scattering; T-matrix; Bispheres

1. Introduction

The T-matrix (or EBCM) method [1] has in recent years been used to compute light-scattering (LS) properties on bispherical clusters [2,3]. A proposed approach—merging two spheres together as a single scatterer—has proved infeasible due to convergence problems [4]. Now the superposition formalism for radiative interactions among spheres is being used to solve the problem of scattering by bi- and multi-spherical particle clusters. Several papers assess its feasibility, yielding benchmark data [5,6]. It has also been used to set up a criterion for estimating multiple-scattering dependence on concentration in colloidal suspensions [7].

The T-matrix method, combined with the superposition principle, has been oriented towards wavelength-size particles, up to the domain of geometrical optics. On the other end of the particle size range, data for small particles is scarce. This should not be interpreted as an acknowledgement that light scattering by small particle holds few secrets. Radiative-transfer methods applied to small

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particles can be in error if the Rayleigh approximation (RA) is used as a starting point, even if the particles cluster together in ensembles that never depart from the Rayleigh limit [8].

In this paper, the variation of the extinction and scattering cross sections with refractive index (both real and imaginary parts) is shown. It is found that the size of the matrices required for accurate calculations sometimes approach those needed for large particles. Once the system T-matrix has been calculated, however, only a few number of elements are needed to obtain accurate cross section values.

2. Theory

In the T-matrix method [1], both incident $\mathbf{E}_\mathrm{i}$ and scattered $\mathbf{E}_\mathrm{s}$ electric fields are expanded in a series of vector spherical harmonics $\mathbf{M}_{mn}(k\mathbf{r}), \mathbf{N}_{mn}(k\mathbf{r})$ as

$$\begin{aligned} \mathbf{E}_\mathrm{i}(\mathbf{r}) &= \sum_{n=1}^{\infty} \sum_{m=-n}^{n} [a_{mn} Rg\mathbf{M}_{mn}(k\mathbf{r}) + b_{mn} Rg\mathbf{N}_{mn}(k\mathbf{r})], \\ \mathbf{E}_\mathrm{s}(\mathbf{r}) &= \sum_{n=1}^{\infty} \sum_{m=-n}^{n} [p_{mn}\mathbf{M}_{mn}(k\mathbf{r}) + q_{mn}\mathbf{N}_{mn}(k\mathbf{r})]. \end{aligned} \tag{1}$$

Due to the linearity of Maxwell's equations, the scattered field coefficients $\mathbf{p}=[p_{mn}, q_{mn}]$ are related to the incident field coefficients $\mathbf{a}=[a_{mn}, b_{mn}]$ by means of a transition ($\mathbf{T}$) matrix, written as $\mathbf{p}=\mathbf{T}\bullet\mathbf{a}$ in compact notation. The T-matrix, which depends on the particle (size, shape, composition and orientation) but not on the incident field, can then be used to calculate light scattering properties of nonspherical particles in random orientation. In the particular case of spherical particles, the T-matrix is diagonal, and its elements are simply the a_n and b_n coefficients from Mie scattering.

Let us assume a system of N scatterers close enough that the independent scattering approximation cannot be assumed, though not so close that their circumscribing spheres interpenetrate at any point. The total scattered electric field can then be written as the sum of the fields scattered by all spheres: $\mathbf{E}_\mathrm{s} = \sum \mathbf{E}_\mathrm{s}^\mathrm{i}$. In order to apply the boundary conditions that will ultimately lead to a relationship between the field coefficients $\mathbf{a}^i = [a^i_{mn}, b^i_{mn}]$ and $\mathbf{p}^i = [p^i_{mn}, q^i_{mn}]$ for sphere i, it is necessary to write the spherical harmonics about sphere j into spherical harmonics about sphere i by means of addition theorems:

$$\begin{aligned} \mathbf{M}_{mn}(k\mathbf{r}^j) &= \sum_{l=1}^{\infty} \sum_{k=-l}^{l} [A^{mn}_{kl}(k\mathbf{r}^{ji}) Rg\mathbf{M}_{kl}(k\mathbf{r}^i) + B^{mn}_{kl}(k\mathbf{r}^{ji}) Rg\mathbf{N}_{kl}(k\mathbf{r}^i)], \\ \mathbf{N}_{mn}(k\mathbf{r}^j) &= \sum_{l=1}^{\infty} \sum_{k=-l}^{l} [A^{mn}_{kl}(k\mathbf{r}^{ji}) Rg\mathbf{N}_{kl}(k\mathbf{r}^i) + B^{mn}_{kl}(k\mathbf{r}^{ji}) Rg\mathbf{M}_{kl}(k\mathbf{r}^i)], \end{aligned} \tag{2}$$

where $\mathbf{r}^{ji} = \mathbf{r}^j - \mathbf{r}^i$. Then one must relate the scattered field coefficients on particle j to the incident field coefficients on particle i and scattered field coefficients of all other particles:

$$\mathbf{p}^j = \mathbf{T}^j \left(\mathbf{a}^j + \sum_{i \neq j} \mathbf{A}^{ji}\mathbf{p}^i \right), \tag{3}$$

where $\mathbf{T}^j$ represent the T-matrix for the particle j, when isolated, ($\mathbf{p}^j = \mathbf{T}^j\mathbf{a}^j$). The $\mathbf{A}^{ji}$ matrices account for the electromagnetic interaction between particles i and j. Inverting Eq. (3) yields sphere-centered transition matrices that transform the expansion coefficients of the incident field into expansion coefficients of the individual scattered fields.

$$\mathbf{p}^j = \sum_i \mathbf{T}^{ji}\mathbf{p}^i. \tag{4}$$

Finally, the scattered field expansions from the individual spheres will be transformed into a single expansion based on a single origin of the particle system. The incident and scattered coefficients $\mathbf{a}, \mathbf{p}$ for the particle system are then related via a T-matrix as [9]:

$$\mathbf{p} = \sum_j \mathbf{p}^j = \sum_{j,i} \mathbf{B}^j\mathbf{T}^{ji}\mathbf{a}^i = \sum_{j,i} \mathbf{B}^j\mathbf{T}^{ji}\mathbf{B}^i\mathbf{a} = \mathbf{Ta}, \tag{5}$$

where the $\mathbf{B}$ matrices are similar to the $\mathbf{A}$ matrices of Eq. (3). The matrix $\mathbf{T}$ so defined is the one that we seek to obtain in order to make calculations of light-scattering properties of the particle system. For the case of two-particle clusters, $N = 2$. Furthermore, spherical particles are considered. This overcomes an important limitation, that is, that the circumscribing spheres to both particles cannot overlap. In our case, spheres are just forbidden from interpenetrating each other.

In theory, the number of terms in the electric field expansion is infinite. In practical terms, only a number of terms $n_{\max}$ need to be considered. In the case of axisymmetrical particles (as for a bispherical cluster), this calls for a total of $n_{\max} + 1$ independent $[2n_{\max} \times 2n_{\max}]$ submatrices. The choice of $n_{\max}$ must be carefully chosen. If it is too low, the T matrix will be incorrectly calculated. On the other hand, values too large of $n_{\max}$ will result in numerical error due to instabilities in the calculation process of the T-matrix, as well as in unnecessarily large computer requirements (in terms of CPU usage, memory and time).

The criterion used for determining the value of $n_{\max}$ goes along the lines of the so-called physical procedure (or P-procedure) of Ding and Xu [10]. The values of extinction and scattering cross sections $C_{\text{ext}}(n_{\max}), C_{\text{sca}}(n_{\max})$ are calculated for increasing values of $n_{\max}$ until the following inequality is satisfied:

$$\max\left[\left|\frac{C_{\text{ext}}(n_{\max}) - C_{\text{ext}}(n_{\max}-1)}{C_{\text{ext}}(n_{\max})}\right|, \left|\frac{C_{\text{sca}}(n_{\max}) - C_{\text{sca}}(n_{\max}-1)}{C_{\text{sca}}(n_{\max})}\right|\right] < \Delta, \tag{6}$$

where Δ is the desired accuracy. This is a variation of the so-called mathematical procedure (or M-procedure), in which only the elements of the T-matrix with azimuthal mode $m = 0$ need to be calculated, thereby reducing calculation demands at this stage. In our calculations, values of $n_{\max}$ obtained from the P-procedure criterion are found to be lower than those calculated from the M-procedure. That allows us both to calculate cross sections faster and for a wider range of refractive indices than by using the M-procedure.

3. Results

Following the methods of the preceding section, a computer code has been written to calculate LS properties of randomly-oriented bispherical particle systems. The extinction cross section has been

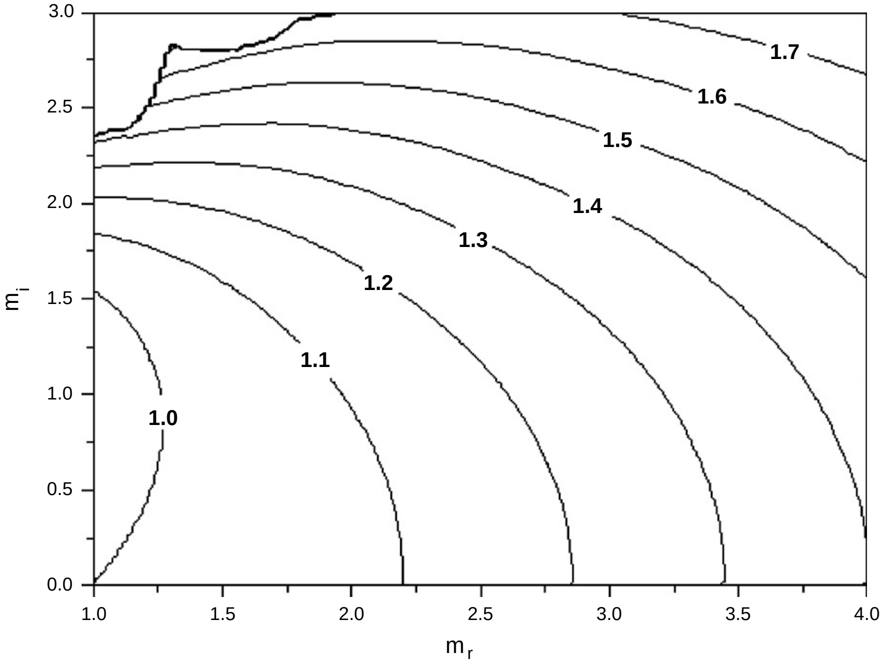

Fig. 1. Curves of constant values (as labelled) of the extinction cross section ratio as a function of the complex refractive index $m = m_r + i\ m_i$, for an accuracy parameter $\Delta = 10^{-3}$.

calculated for a set of values of the full index of refraction $m = m_r + i\ m_i$. In order to better represent the effect of interparticle interaction, the R_{ext} and R_{sca} ratio given as

$$R_{ext} = \frac{C_{ext,b}}{2C_{ext,m}}, \qquad R_{sca} = \frac{C_{sca,b}}{2C_{sca,m}} \tag{7}$$

have been plotted, where $C_{ext[sca],b}$ and $C_{ext[sca],m}$ are the bisphere and monosphere extinction [scattering] cross section for a monospherical size parameter kr. Should both particles not interact at all, R_{ext} would be equal to 2 (real refractive index) or 1 (complex refractive index) in the RA. Likewise, in the absence of interactions, $R_{sca} = 2$.

Figs. 1 and 2 shows the dependence of the normalized extinction and scattering cross section ratios R_{ext} and R_{sca} on m_r and m_i for a system of randomly oriented bispherical particles with single-particle size parameter $x = 0.01$. For the purpose of clarity, data in the horizontal coordinate axis represent weakly absorbing particles ($m_i = 10^{-3}$). The net effect of interparticle interaction is to increase cross sections in most of the $m_i - m_r$ space.

If the condition $R_{ext} = 1$ is met, then bisphere clustering has no net effect in extinction-dependent LS properties, since extinction cross sections are proportional to the particle volume in the RA.

The (m_r, m_i) values for which the condition $R_{ext} = 1$ holds can be fitted as

$$m_r = 0.9975 + 0.6255m_i - 0.4119m_i^2 + 0.128m_i^3 - 0.0791m_i^4. \tag{8}$$

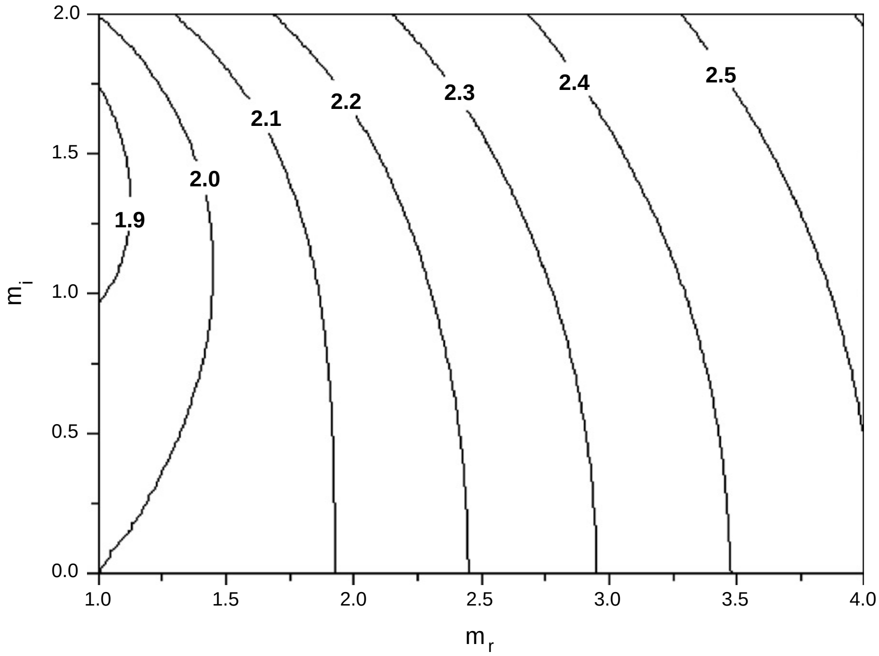

Fig. 2. Same as Fig. 1, but for the scattering cross section, and $\Delta = 10^{-4}$.

Similarly, the condition $R_{sca} = 2$ gives the set of (m_r, m_i) for which interparticle interaction does not change the value of the scattering cross section. This can be fitted as

$$m_r = 0.9953 + 0.8781 m_i - 0.5396 m_i^2 + 0.1727 m_i^3 - 0.0611 m_i^4. \tag{9}$$

A point of controversy might lie on the choice of particle size. One safe bet is to use a very small value of x. However, very small values of x will cause numerical overflow during the calculation of the T-matrix, as Bessel functions of appreciable order must be calculated for small arguments. A balance must then be established between computational needs and small-particle requirements. The value of Δ must be carefully chosen for the same reason.

A comparison of several data sets for different size parameter values showed that the largest relative difference between R_{ext} for $x = 0.01$ and 0.001 was found to be lower than 0.08%. When the particle size increases to 0.1, relative differences can be as high as 18%. The largest variation was detected for weakly-absorbing particles (large values of m_r and small values of m_i). The value $x = 0.01$, therefore, can be considered as a small particle. For that size, numerical overflows due to Bessel function calculations have limited our calculations to T-matrices with a maximum size of $n_{max} = 40$. An accuracy parameter of $\Delta = 10^{-3}$ has been found to be an adequate accuracy parameter for the calculation of extinction cross sections. On the other hand, scattering cross sections call for more restrictive accuracy requirements ($\Delta = 10^{-4}$). For that reason Figs. 1 and 2 have been calculated for different values of the imaginary part of the refractive index m_i.

The relation between the index of refraction and the T-matrix dimension ($=2n_{max}$) needed to achieve $\Delta = 10^{-3}$ accuracy is shown in Fig. 3. The values of n_{max} have been found to be only slightly dependent on x (in the range 0.00l–0.1) and Δ (0.001–0.01). When any of both parameters

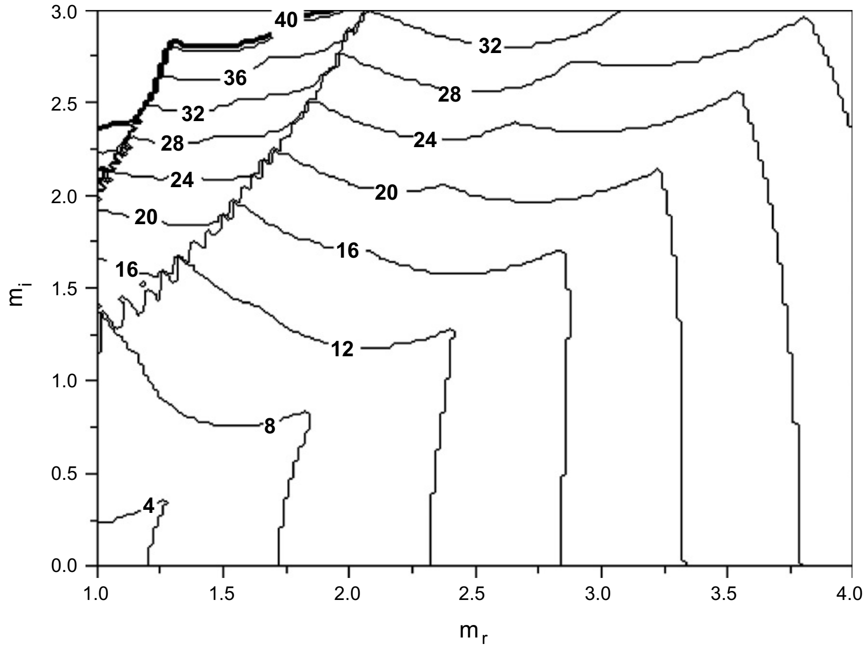

Fig. 3. Plot of constant values (as labelled) of the T-matrix dimension n_{max} needed to calculate the extinction cross section ratios of Fig. 1, as a function of the complex refractive index $m = m_r + i\ m_i$.

fall below 10^{-3}, however, the dimension of the T-matrix increases significantly. Regardless of the precise value of x and Δ, the fact remains that even bispherical systems within the Rayleigh regime can demand large matrices for small values of the real and/or imaginary part of the refractive index. It was also found that only the $n = 1$ matrix elements of the T-matrix are needed for accurate calculations of cross sections. This falls in line with the usual suggestion that two n_{max} values be used for T-matrix calculations [11]: one to accurately compute the T-matrix (n^1_{max}) and another to calculate light scattering properties (n^2_{max}).

An n^2_{max} value of 1 has been obtained for all calculated values of R_{ext} and R_{sca}, which according to Eq. (4) describes a dipolar behavior. But the bisphere radiative properties cannot just be calculated as two monosphere dipoles plus some low-order multipole interactions. With the exception of low values of m_i and $m_r - 1$, simple dipole approximations like those given in the literature [12,13] just fail to describe interparticle interactions in a two-sphere particle system.

Figs. 4 and 5 show the effect of bisphere clustering for nonabsorbing ($m_i = 0$) and transparent ($m_r = 1$) particles. In the absence of absorption, larger values of the refractive index have the effect of enlarging the differences between bisphere and monosphere extinction (scattering) cross sections, at least as far as we are able to calculate ($m_r = 10$). This not the case for transparent particles, as Fig. 5 shows. Starting from initial values $R_{ext} = 1$ and $R_{sca} = 2$, both curves reach a minimum ($R_{ext} = 0.966$ when $m_i = 1.16, R_{sca} = 1.848$ when $m_i = 1.4$), returning to the initial values $R_{ext} = 1 (m_i = 1.54)$ and $R_{sca} = 2 (m_i = 1.99)$. It is unclear from Fig. 5 whether cross section ratios increase monotonically with growing m_i, but data computed for lower accuracy values ($\Delta = 10^{-2}$) suggest this to be the case.

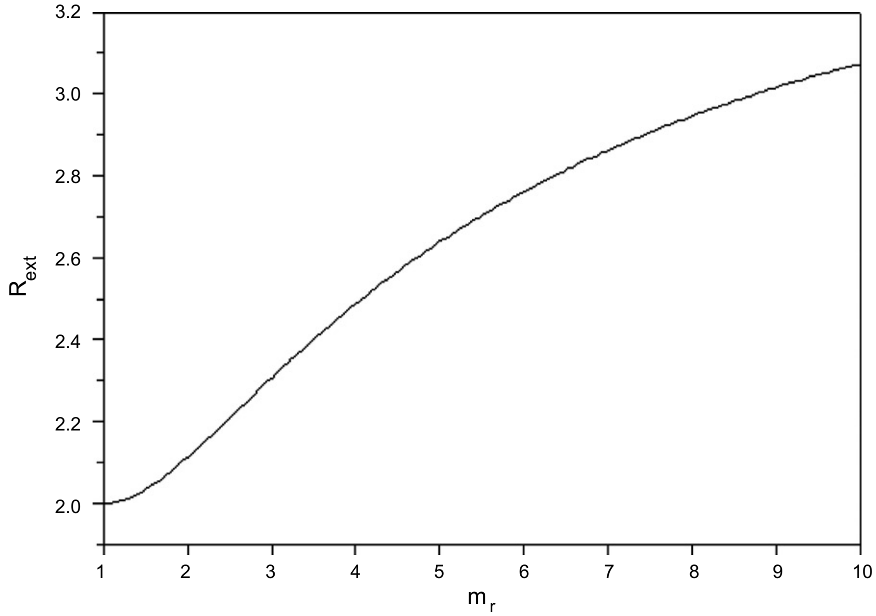

Fig. 4. Extinction cross section values for nonabsorbing particles ($m_i = 0$) as a function of the imaginary part of the refractive index.

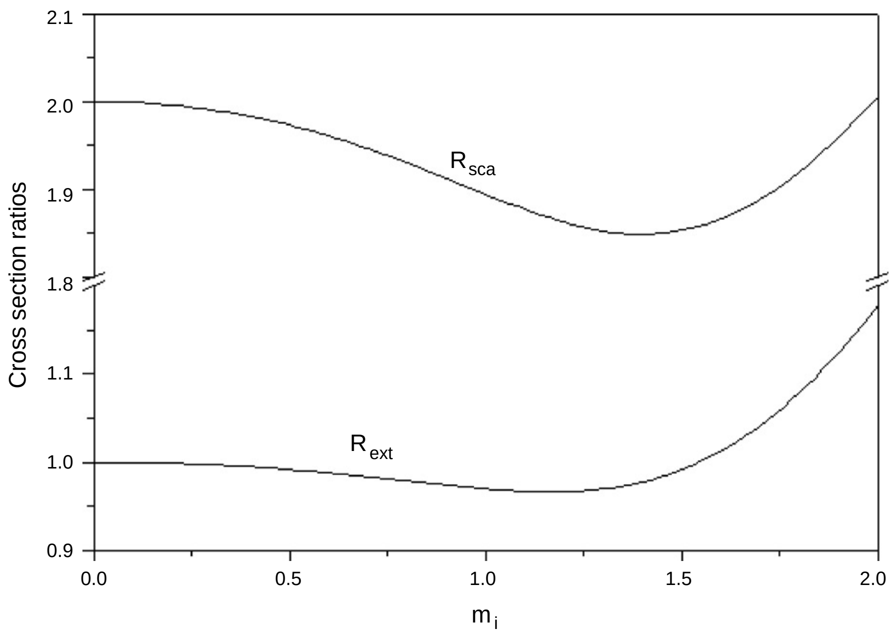

Fig. 5. Extinction and scattering cross section values for transparent particles ($m_r = 1$) as a function of the real part of the refractive index.

4. Conclusions

We have shown that the aggregation of small particles into bispherical clusters does have an appreciable effect in extinction and scattering cross sections. The deviation of these quantities from those given by the Rayleigh approximation for spheres, is an issue that has to be taken into account in practical applications, particularly when highly absorbing particles with large, but often ill-quantified, values of m_i, are present.

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