Effect of the particle shape on the optical properties of black carbon aggregates

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ABSTRACT

Small particles tend to connect to each other and create large geometries, namely aggregates. To simplify the light scattering simulation process, they are usually modelled as assemblies of spheres positioned in point contact. This is a rough approximation because connections between them always exist. In this work we present answers to the three following questions: which optical properties of fractal-like aggregates are strongly dependent on the particle shape, what is the magnitude of the relative extinction error δC_{ext} when non-spherical particles are modelled as spheres and whether the relative extinction error δC_{ext} is dependent on the aggregate size N_p. The paper was aimed at tropospheric black carbon particles and their complex refractive index m was based on the work by Chang and Charalampopoulos. The incident wavelength λ varied from $\lambda = 300nm$ to $\lambda = 900nm$. For the light scattering simulations the ADDA algorithm was used. The polarizability expression was IGT_SO (approximate Integration of Greens Tensor over the dipole) and each particle, regardless of its shape, was composed of ca. $N_d \approx 1000$ volume elements (dipoles). In the study, fractal-like aggregates consisted of up to $N_p = 300$ primary particles with the volume equivalent to the volume of a sphere with the radius $r_p = 15nm$. The fractal dimension was $D_f = 1.8$ and the fractal prefactor was $k_f = 1.3$. Geometries were generated with the tunable CC (Cluster-Cluster) algorithm proposed by Filippov et al. The results show that when the extinction cross section C_{ext} is considered, the changes caused by the particle shape, which are especially visible for longer wavelengths λ, cannot be neglected. The most significant difference can be observed for the regular tetrahedron. The relative extinction error δC_{ext} diminishes slightly along with the number of primary particles N_p. However, even when large fractal-like aggregates are studied, it should not be considered as non-existent. On the contrary, when light scattering diagrams or the asymmetry parameter g are needed, spherical models can be used, even with relatively small fractal-like aggregates.

Keywords: light scattering, discrete dipole approximation, black carbon, soot, fractal-like aggregates

1. INTRODUCTION

Soon after emission small particles connect to each other and create more complex geometries, namely aggregates. In spite of the fact that their morphological parameters vary, they reveal fractal-like properties, and therefore, can be described by the following equation:[1,2]

$$N_p = k_f \left(\frac{R_g}{r_p} \right)^{D_f}, \tag{1}$$

in which N_p stands for the number of primary particles with the radius r_p. The fractal dimension D_f, which varies from $D_f \approx 1$ (e.g. primary particles form a straight line) to $D_f \approx 3$ (e.g. primary particles form a compact ball), reflects the overall shape of the geometry. The fractal prefactor k_f is a proportionality constant and R_g is the radius of gyration. The last parameter can be calculated with the following equation:[3]

$$R_g^2 = \frac{1}{N_p} \sum_{i=1}^{N_p} (\vec{r}_i - \vec{r}_c)^2, \tag{2}$$

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in which $\vec{r}$ is the position of the i-th primary particle and $\vec{r}_c$ is the mass centre of the aggregate. Both equations accurately describe the shape of fractal-like aggregates providing that they are composed of spherical particles positioned in point contact $C_p = 0$ (i.e. there are no intersections between them).[4] It is not hard to realize that such models are only rough approximations which are commonly used for speeding up the light scattering simulation process.[5] In reality, primary particles are not spherical and advanced connections between them are not rare.[6] The goal of this work was to approximate the optical properties of aggregates composed of much more complex particle models and decide whether they can be used interchangeably with the simplified, spherical one. In this paper black carbon nanoparticles were investigated. They are a product of incomplete combustion of carbon-based fuels, can be hazardous to health and are believed to have an impact on the global warming effect.[7,8] Their complex refractive index m, which is also in agreement with the criterion proposed by Bond et al.,[9] was adapted from the work by Chang and Charalampopoulos.[10]

All aggregate models used in this study were generated with the FLAGE (Fractal-Like Aggregate Generation Environment) software and the implementation of the CC (Cluster-Cluster) algorithm proposed by Filippov et al. was used.[11–14] The fractal dimension was $D_f = 1.8$ and the fractal prefactor was assumed to be $k_f = 1.3$. The maximum number of primary particles, with the volume $V = 4/3 \cdot \pi \cdot (15nm)^3$, was $N_p = 300$. They were modelled as: spheres, cubes, tetrahedrons and octahedrons (note, that V was constant regardless of the particle shape).[8,15,16] Although these are approximate value of investigated morphological parameters of black carbon aggregates, note, that different techniques for measuring them exist.[17–24] Therefore, they may vary across publications. All interactions of generated black carbon aggregates with organic (e.g. acid) and inorganic (e.g. sulphate) matter were neglected.[25] Examples of investigated particle models and generated aggregates are presented in Fig. 1 and Fig. 2 respectively.

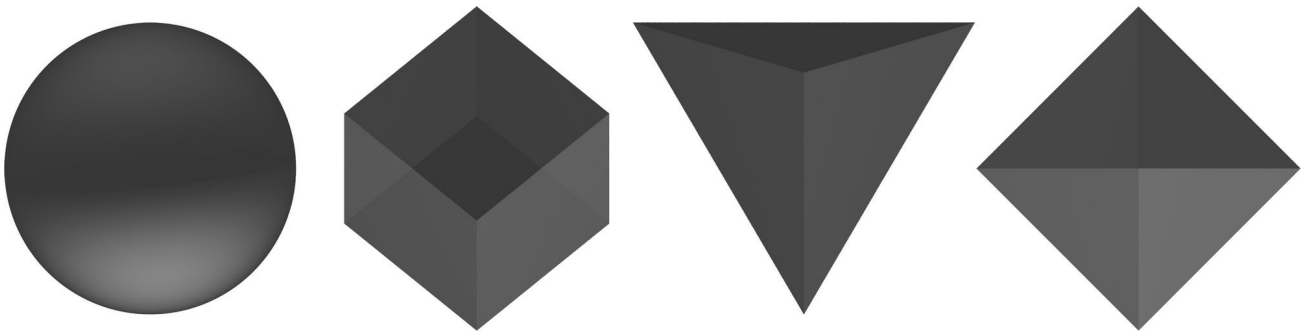

Figure 1: Different primary particle models used in this study. From left to right: sphere, cube, tetrahedron, octahedron.

Light scattering techniques have been commonly used for identifying and measuring various objects, including black carbon aggregates, erythrocytes and fibers.[26–35] In this study the incident wavelength varied from $\lambda = 300nm$ to $\lambda = 900nm$ with the step $\Delta\lambda = 20nm$. For the light scattering calculations the ADDA algorithm was used.[36,37] The polarizability expression was IGT_SO (approximate Integration of Greens Tensor over the dipole) and the results for primary particles were averaged orientationally. To reduce the computation time, when large aggregates were studied, only one polarization state was investigated. However, centers of primary particles were always kept in fixed positions, regardless of the particle model used. To guarantee accurate results, every primary particle was decomposed into ca. $N_d \approx 1000$ volume elements (dipoles) to precisely describe its shape.

2. SIMULATION RESULTS - PARTICLES

The absorption cross section C_{ext} and the scattering cross section C_{sca} for investigated primary particle models are presented in Fig. 3. Additionally, in Fig. 4 the relative error is shown, i.e. δC_{abs}, δC_{sca}. The results prove that the particle shape has a significant impact on the absorption cross section C_{abs}, what is especially visible for long wavelengths λ. The most significant absorption error C_{abs} was observed for the tetrahedronal geometry. This proves that even when the volume of the primary particle V is conserved, its diameter d should not be

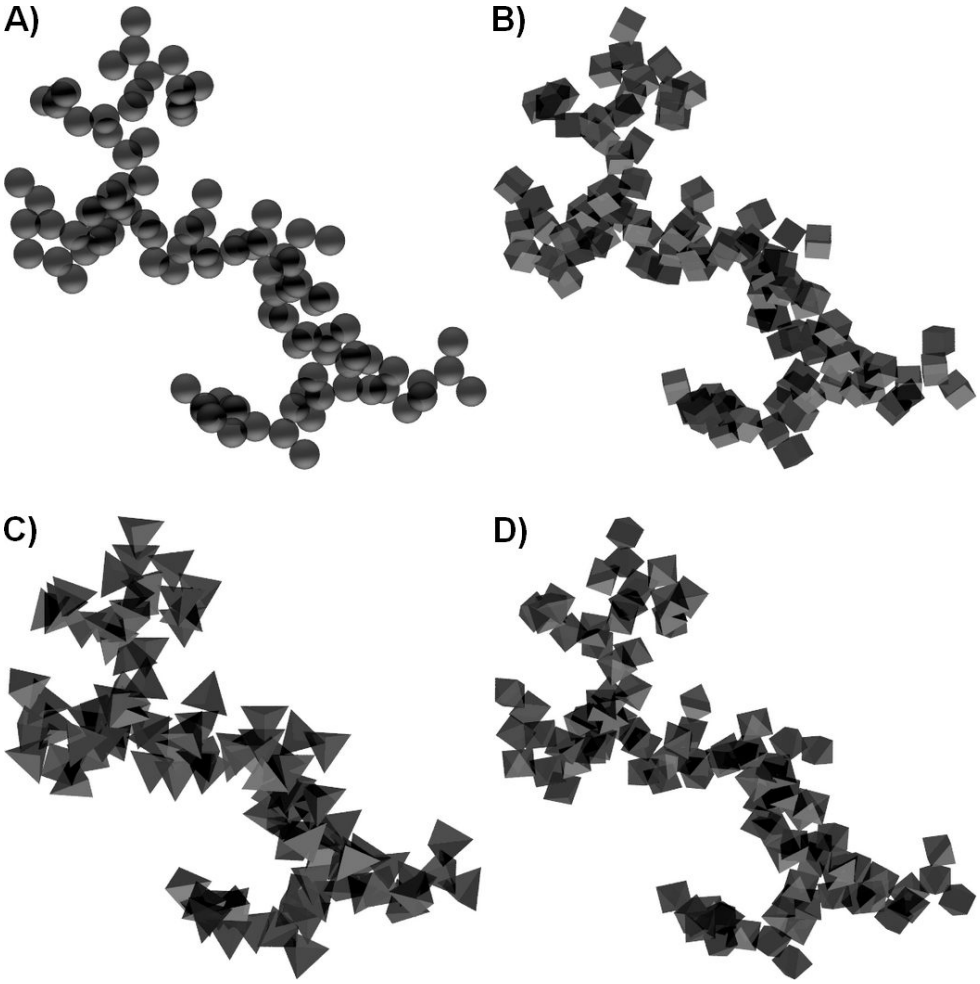

Figure 2: Sample fractal-like aggregate models composed of $N_p = 100$: A) spherical, B) cubical, C) tetrahedronal, D) octahedronal primary particles.

changed carelessly. The least significant absorption error C_{abs} was observed for the octahedronal geometry. This was expected because it resembles the classic, spherical primary particle model. The relative scattering error δC_{sca} was much lower in every case. Furthermore, the value of the scattering cross section C_{sca} is about two orders of magnitude lower than the value of the absorption cross section C_{abs}. Therefore, it does not contribute to the extinction cross section C_{ext} significantly. The scattering diagrams are presented in Fig. 3. They are barely affected by the shape of the investigated model. This proves that, providing that primary particles are small (e.g. $r_p = 15nm$), when scattering diagrams or the asymmetry parameter g are investigated, even complex particle shapes can be replaced with simple spherules.

3. SIMULATION RESULTS - AGGREGATES

In the next part of the study, due to the fact that the absorption cross section C_{abs} is the dominant component of the extinction cross section C_{ext} (even for large aggregates), only the second parameter, i.e. C_{ext}, was investigated. The relative extinction error C_{ext} for aggregates composed of a different number of primary particles N_p are presented in Fig. 6, Fig. 7 and Fig. 8. Once again, the tetrahedronal model turns out to be most erroneous one, regardless of the aggregate size N_p. However, its value is much smaller than in the previous study and diminishes slightly along with the number of primary particles N_p. This proves that, even when the diameter of the primary particle d is relatively small compared to the diameter of the aggregate, the

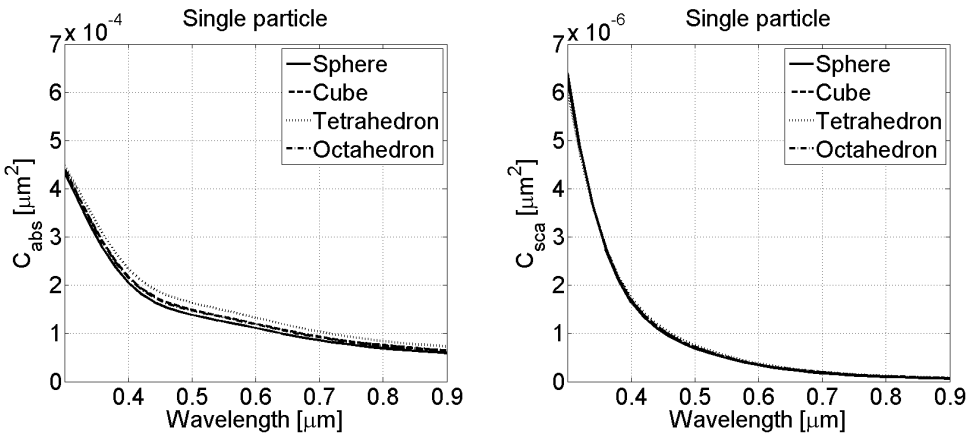

Figure 3: The comparison of the absorption cross section C_{abs} and the scattering cross section C_{sca} for different particle models.

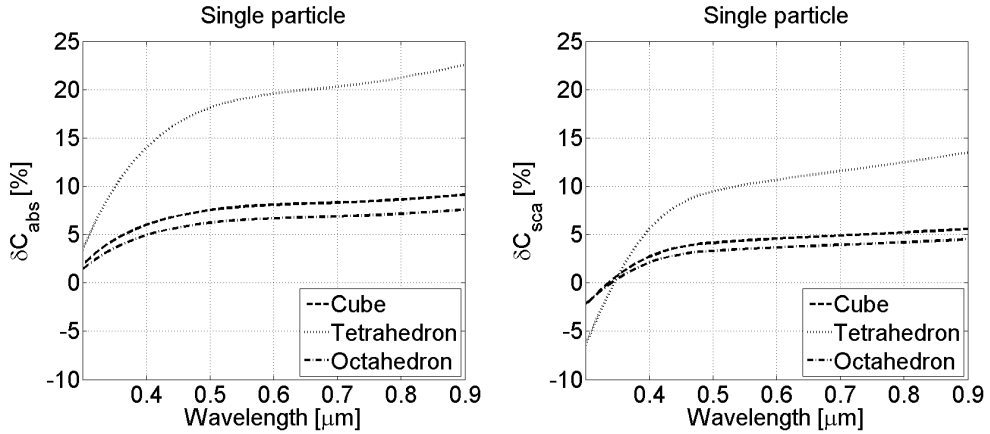

Figure 4: The comparison of the relative absorption error δC_{abs} and the relative scattering error δC_{sca} for different particle models.

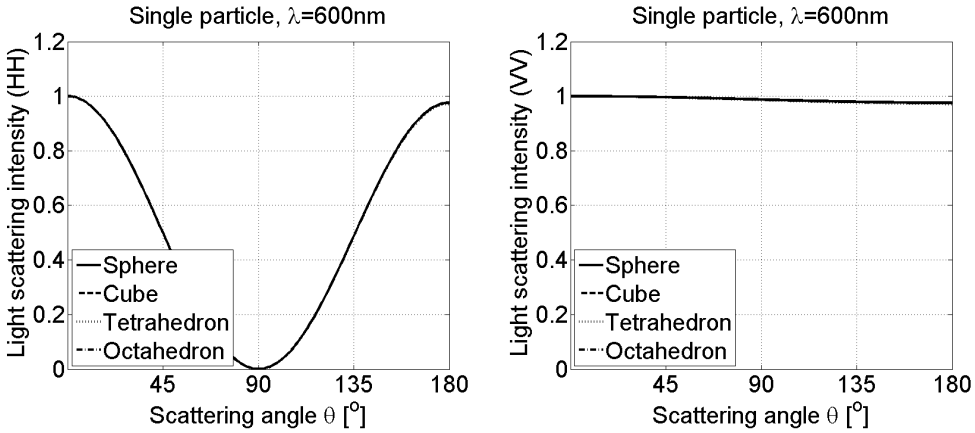

Figure 5: The comparison of the light scattering diagrams for different primary particle models. The incident wavelength was $\lambda = 600nm$.

complex particle shape should not be neglected. On the contrary, the changes in the scattering diagrams, and therefore, the asymmetry parameter g, are almost negligible, what is presented in Fig. 9.

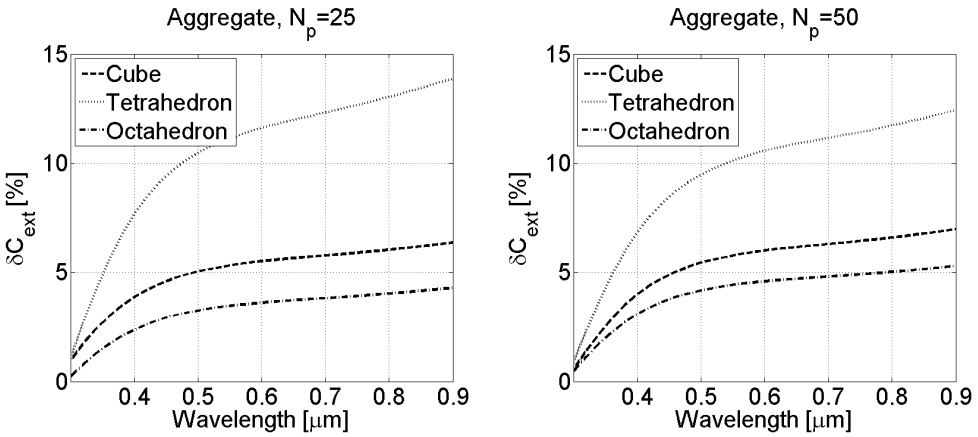

Figure 6: The comparison of the relative extinction error δC_{ext} for aggregates composed of $N_p = 25$ and $N_p = 50$ primary particles.

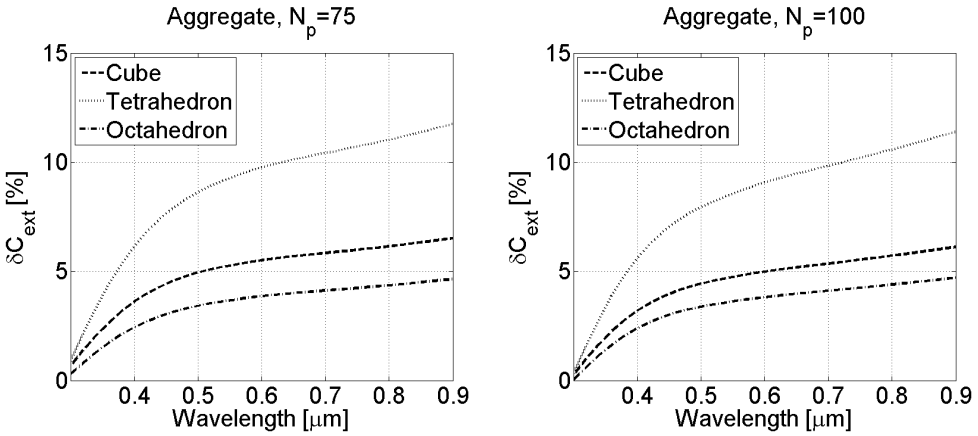

Figure 7: The comparison of the relative extinction error δC_{ext} for aggregates composed of $N_p = 75$ and $N_p = 100$ primary particles.

4. CONCLUSIONS

In the study the impact of different primary particle models on the optical properties of fractal-like aggregates was investigated. Providing that primary particles are small and only scattering diagrams (or the asymmetry parameter g) are required, even "extreme" shapes like tetrahedrons can be replaced with simple spherules. On the other hand, when the extinction cross section C_{ext} is needed, such simplifications can result in slightly erroneous data. Furthermore, even when fractal-like aggregates are large (e.g. they are composed of $N_p = 300$ primary particles) such changes cannot be considered as non-existent.

5. ACKNOWLEDGEMENT

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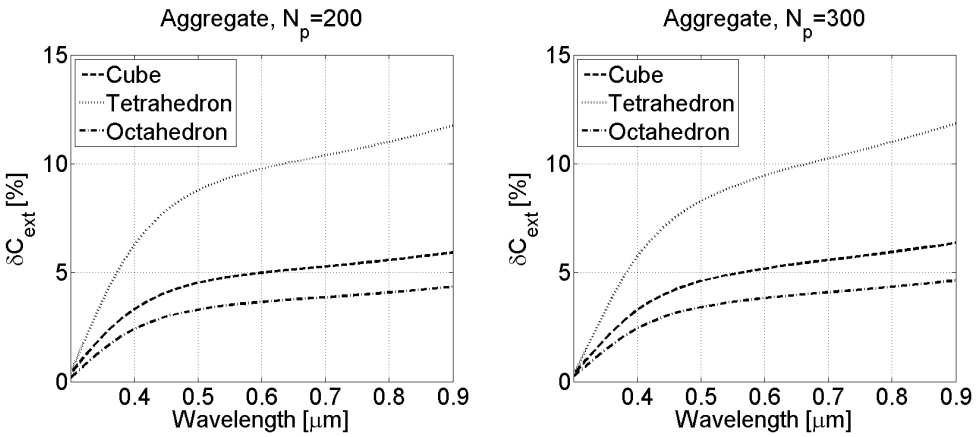

Figure 8: The comparison of the relative extinction error δC_{ext} for aggregates composed of $N_p = 200$ and $N_p = 300$ primary particles.

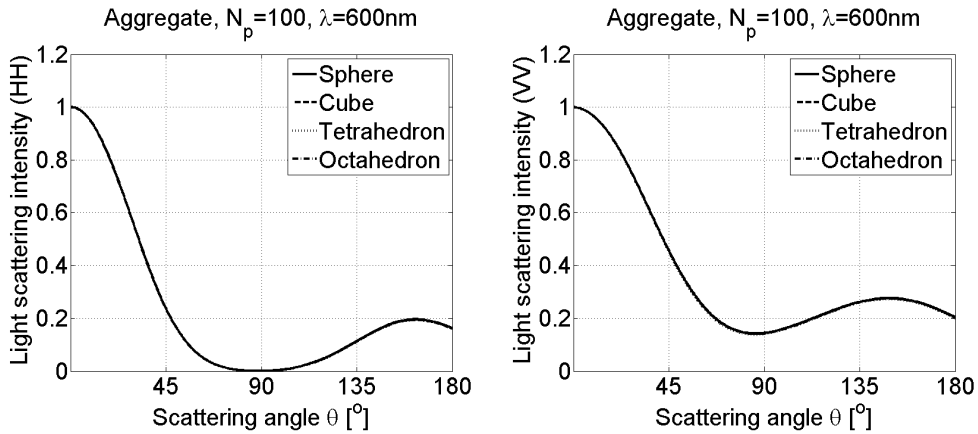

Figure 9: The comparison of the light scattering diagrams for aggregates composed of $N_p = 100$ primary particles. The incident wavelength was $\lambda = 600nm$.

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