Effect of the necking phenomenon on the optical properties of soot particles

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Abstract

Fractal-like aggregates are commonly modeled as assemblies of spheres positioned in point contact only. The necking phenomenon is usually neglected. Such an approach has some advantages, e.g. faster light scattering simulation programs can be used, however, it may result in many additional errors and inaccuracies. In our study we try to approximate them and select the most suitable connection model. In our work we focus on the impact of the necking phenomenon on the optical properties of two and five monodisperse soot particles. The results show that small connections can be neglected. Different connection types (the cylindrical, the linear and the quadratic connector) can be used interchangeably, therefore, we recommend the most basic one (i.e. the cylindrical connector). Additionally, when particles are not positioned in point contact (they tend to overlap) this phenomenon should not be omitted due to its impact on the resulting scattering cross sections.

1. Introduction

Small particles tend to aggregate and create large structures that may reveal some general fractal-like properties [1,2]. This process is considered as a universal, independent of particle material and shape, phenomenon [3]. In most studies aggregates are represented as assemblies of spheres positioned in point contact only. Common phenomena like overlapping or necking are neglected what may result in additional errors and inaccuracies [4,5]. Nevertheless, real fractal-like aggregates are much more complex and specific connections between primary particles, e.g. due to the sintering process, always exist [6]. The goal of our research was to investigate the impact of different connections on the optical properties of such structures. To highlight this effect, only aggregates composed of two \( N_p = 2 \) and five \( N_p = 5 \) soot particles were considered. In our study we were focused on the absorption cross section \( C_{\text{abs}} \) which is, in this case, the main component of the extinction cross section defined by the following equation:

\[
C_{\text{ext}} = C_{\text{abs}} + C_{\text{sca}},
\]

where \( C_{\text{sca}} \) denotes the scattering cross section. Our results can be used to approximate the relative error that persists when no connectors are implemented or to improve the modeling process, which is necessary for understanding many physical phenomena [7]. The simulations were performed with the DDScat code, which is capable of simulating the amount of the light scattered by any shape [8,9].

2. Methodology

The first step of our study was to create four different connector types, which are specified as follows.
2.1. Cylindrical connector

It can be visualized as a cylinder positioned between the particle centers, as presented in Fig. 1. To keep the same volume of the structure \( V \) the reduction of the particle radius \( r_p \) can be compensated by the growth of the neck. The dimensionless parameter \( Y_{\text{con}} \) denotes the radius of this cylinder in the following manner:

\[
Y_{\text{con}} = \frac{r_{\text{con}}}{r_p}.
\]

(2)

It varies from \( Y_{\text{con}} = 0 \) (the connection does not exist) to \( Y_{\text{con}} = 1 \) (the radius of the cylinder \( r_{\text{con}} \) is equal to the particle radius \( r_p \)).

2.2. Linear connector

The next connector type is based on the following linear function:

\[
y = |ax| + b,
\]

(3a)

\[x \in [-l/2; l/2], \quad y \in [0; r_p],
\]

(3b)
in which \( a \) and \( b \) are parameters dependent on \( Y_{\text{con}} \). The particle centers are aligned along the X-axis, i.e. \((-l/2, 0)\) and \((l/2, 0)\), and the center of the coordinate system \((0,0)\) is positioned in the same point as the geometric center of the connector. The value of \( y \) for the \( x = 0 \) condition is determined by the parameter \( Y_{\text{con}} \) in the following manner:

\[
y_{x=0} = Y_{\text{con}} \cdot r_p
\]

(4)

and the boundary points are defined as follows:

\[
y_{y=(l/2)} = r_p.
\]

(5)

After calculating \( a \) and \( b \) the resulting curve is rotated around the X-axis to create a three-dimensional shape. The main idea of this connector is presented in Fig. 2. This type of connection is slightly more realistic than the previous one, especially when large values of \( Y_{\text{con}} \) are used. However, it is also more difficult to implement.

2.3. Quadratic connector

The most complex connector is based on the following quadratic function:

\[
y = ax^2 + b,
\]

(6a)

\[x \in [-l/2; l/2], \quad y \in [0; r_p].
\]

(6b)
The generation algorithm is very similar to the previous one. The quadratic connector is comparable to the linear connector, but its greatest advantage is that the bending point in \( y_{x-0} \) does not exist. Therefore, it is more similar to real structures (see Fig. 3). Note that every proposed connection type looks alike when \( Y_{\text{con}} = 1 \) or \( Y_{\text{con}} = 0 \) (providing that the particles are positioned in point contact only).

2.4. Overlap factor

It is one of the most common connection types, which was studied, for example, by Brasil et al. [4], Oh and Sorensen [5] and Mishchenko and Videen [10]. It is a well-known fact that the overlap factor \( C_{\text{ov}} \) has an undeniable impact on the morphological parameters of fractal-like aggregates. Because in our work such complex structures are not investigated, detailed study with discussion on this topic can be found elsewhere [4,5,11].
Furthermore, due to the additional overlap error $\delta C_{ov}$, that commonly persists in almost all TEM (transmission electron microscopy) images, in which three-dimensional structures are projected into a two-dimensional space, this type of connection should be at least considered to avoid any possible inaccuracies and errors \[12\]. The last, but not least, reason for understanding the importance of the overlap factor $C_{ov}$ is that it can be used for modeling the early stages of the sintering process \[13\]. In the paper we use the following definition of this parameter:

$$C_{ov} = 1 - \frac{l}{2r_{np}}$$  \hspace{1cm} (7)

in which $l$ is the distance between the centers of particles. Providing that there is no different neck ($Y_{con} = 0$), $r_{np}$ is exactly the same as the particle radius $r_p$. Otherwise, $r_{np}$ defines the hypothetical radius of the particle as if the half of the neck volume was transferred onto its surface (the position of the particle remains constant). In other words, when the total volume of the structure $V$ is conserved, the changes to the size of the neck do not affect the overlap factor $C_{ov}$ in spite of the fact that $r_p$ is diminished and both particles are theoretically no longer in point contact (part of the volume is moved to the neck). Sample shapes are presented in Figs. 4 and 5. In our work the overlap factor varies from $C_{ov} = 0.00$ to $C_{ov} = 0.98$. Detached spheres ($C_{ov} < 0$) and a single solid sphere ($C_{ov} = 1$), in which there is no clear distinction between different primary particles, were not investigated.

To model the sintering process both parameters $C_{ov}$ and $Y_{con}$ can be changed simultaneously. However, in our work we alter only one at a time to clearly distinguish its impact on the optical properties of investigated structures. The total volume $V$ is constant at every simulation step. The overlap factor changes from $C_{ov} = 0.00$ to $C_{ov} = 0.98$ with the step $\Delta C_{ov} = 0.02$. When $Y_{con} > 0$ the particle radius $r_p$ is decreased and the size of the connector $Y_{con}$ is adjusted accordingly to maintain the same volume $V$. It turned out to be very difficult to implement small necks (they are almost invisible, especially when $C_{ov} \geq 0$) and therefore, the starting point is as high as ca. $Y_{con} \approx 0.2$. Note that the second part of the process (i.e. when $Y_{con} = 1$) is identical

![Fig. 3](image3.jpg) The picture presents two monodisperse particles, denoted as $P_1$ and $P_2$ respectively, and a quadratic connector. $l$ is the distance between particle centers, $r_p$ describes their radius and $V_1$, $V_2$ represent their volume. $Y_{con}$ is a dimensionless parameter which describes the size of the connector. $V_c$ denotes the volume of the total intersection area (colored in gray). The shape on the right defines two particles and a single connector ($Y_{con} = 0.5$) decomposed into an array of dipoles.

![Fig. 4](image4.jpg) The picture presents two overlapping, monodisperse particles denoted as $P_1$ and $P_2$ respectively. $l$ is the distance between their centers, $r_p$ describes their radius and $V_1$, $V_2$ represent their volume. $V_c$ denotes the volume of the total intersection area (colored in gray). The shape on the right depicts two overlapping particles ($C_{ov} = 0.5$) decomposed into an array of dipoles.

![Fig. 5](image5.jpg) Different values of the overlap factor are presented ($C_{ov} = 0.0$, $C_{ov} = 0.5$ and $C_{ov} = 1.0$ respectively). Structures are decomposed into arrays of volume elements (dipoles), required for the DDA simulations.

for all presented connector types and therefore, only one curve is needed. The full simulation process is presented in Fig. 6.

3. Accuracy of the simulations

In our study we used carbon black particles. The initial structure was composed of two spherically shaped monomers in point contact and a single connector. The particle radius was set to \( r_p = 25 \) nm, therefore the total volume of the structure was \( V \approx 130 \ 900 \) nm\(^3\). After the review by Bond et al. the refractive index of the material was assumed to be \( m = 1.85 + 0.71i \) [14] and the wavelength was \( \lambda = 532 \) nm. In our study we used the DDScat code, which is based on the DDA (discrete dipole approximation) method. Mostly because it is capable of simulating the amount of the light scattered by any shape providing that it is composed of a sufficient number of volume elements (dipoles) [9,8,15]. The initial structure was decomposed into ca. \( N_d \approx 65 \ 000 \) volume elements (dipoles) with the spacing \( d = 1.25 \) nm. The results were averaged over 512 orientations. As a solution, the FCDM (filtered couple dipole method) was used [16]. DDScat results can be considered as accurate providing that the following conditions are true [8]:

\[
|m|kd = \frac{2\pi|m|d}{\lambda} < 1, \quad (8a)
\]

\[
|m - 1| < 2. \quad (8b)
\]

In our case it was \( |m|kd \approx 0.03 \) and \( |m - 1| \approx 1.11 \) respectively. Additionally, to approximate the possible error our results were compared to different results calculated with an alternative light scattering code by Mackowski [17]. This code can be used when aggregates are composed of non-overlapping spheres only (i.e. \( C_{ov} = 0 \)), therefore our comparison was limited to two cases: a single sphere with the radius \( r_p = 25 \) nm and two monodisperse spheres with the same radius (\( r_p = 25 \) nm) positioned in point contact. In the first case, the absorption cross section calculated with the DDScat code was \( C_{abs} = 6.45 \times 10^{-4} \) nm\(^2\) and with the T-Matrix code was \( C_{abs} = 6.37 \times 10^{-4} \) nm\(^2\). Therefore, the relative error was \( E_{rel} = 1.24\% \). In the second case, the results were \( C_{abs} = 1.40 \times 10^{-3} \) nm\(^2\) and \( C_{abs} \approx 1.39 \times 10^{-3} \) nm\(^2\) respectively thus the value of the relative error was \( E_{rel} = 1.08\% \). The difference is not large hence we conclude that the light scattering results, calculated with the DDScat code, are reliable.

4. Results and discussion

The first simulation step was to determine the impact of the overlap factor \( C_{ov} \) on the absorption cross section \( C_{abs} \) of soot particles. The results are presented in Fig. 7. It can be clearly seen that \( C_{abs} \) is weakly dependent on \( C_{ov} \). In accordance with the work by Oltmann et al. the overlap parameter \( C_{ov} \) for freshly generated (under laboratory conditions) soot aggregates, derived from TEM images, is specified as \( C_{ov} \approx 0.25 \) [18]. Therefore, the relative error can be as high as \( 6\% \) if the aggregate model is composed of particles in point contact only. Note that the overlap factor \( C_{ov} \approx 0.25 \) could be overestimated due to the TEM technique, which requires a projection of three-dimensional structures into a two-dimensional plane [12]. This problem does not exist when more advanced methods, e.g. ET (electron tomography), are used [19,20]. The maximum value of the absorption cross section \( C_{abs} = 1.46 \times 10^{-3} \) nm\(^2\) can be found at \( C_{ov} \approx 0.18 \) and after this point, the structure gradually loses its absorption properties. The position of this peak is dependent on the total volume \( V \) and the optical properties of the structure, especially on the complex refractive index \( m \). When its value is altered, e.g. \( m = 1.57 + 0.56i \) [21], the peak changes its position to \( C_{ov} \approx 0.2 \). This phenomenon can be associated with the behavior of the electromagnetic wave that exists within the small gaps that occur close to the contact point of two touching spheres. When particles tend to overlap, i.e. \( C_{ov} > 0 \), these gaps disappear and the scattering behavior changes as well. When soot is considered, the maximum is located at \( C_{ov} \approx 0.18 \). After this point, the distinction between two separated particles vanishes slowly, the structure becomes more compact.
and finally, it changes to a single sphere with the radius \( r_p \approx 31.5 \) nm. During this process, the absorption cross section \( C_{\text{abs}} \) diminishes. The position of the absorption peak is not associated with the size of the generated dipole mesh. The simulations were repeated with a larger dipole spacing, i.e. \( d = 1.75 \) nm (they are not included in the paper due to their redundancy). The maximum value of \( C_{\text{abs}} \) occurs exactly at the same point and the relative error between both absorption cross sections is as small as \( \delta C_{\text{abs}} \approx 0.12\% \). The position of the peak is not associated with our decomposition procedure as well. Our meshes were compared to those generated with the internal procedure implemented in the DDScat program and no differences were observed.

Additionally, the asymmetry parameter \( g \) is enclosed. It defines the relationship between the light scattered in the forward and in the back direction and can be described by the following equation [22]:

\[
g = \langle \cos \theta \rangle,
\]

in which \( \theta \) denotes the scattering angle. The last studied parameter, the scattering albedo \( \omega \), is defined as [14]

\[
\omega = C_{\text{sca}}/C_{\text{ext}}.
\]

To have a better overview on the studied parameter, three different geometries, described in Fig. 8, were created and the value of the absorption cross section \( C_{\text{abs}} \) was calculated. The meshes of volume elements (dipoles) were generated accordingly to the previous study, i.e. the distance between dipoles was \( d = 1.25 \) nm and the results were averaged over 512 orientations. The structure composed of \( N_p = 5 \) primary particles was generated with the following fractal parameters: \( D_f = 1.8 \) and \( K_f = 1.3 \), which denote the fractal dimension and the fractal prefactor.

Fig. 7. Impact of the overlap factor \( C_{\text{ov}} \) on the optical properties of two connected soot particles. No necks are implemented, i.e. \( Y_{\text{con}} = 0 \). The total volume \( V \) is constant at every step of the simulation process.

Fig. 8. Impact of the overlap factor \( C_{\text{ov}} \) on the optical properties of structures characterized by the following morphological parameters: (A) \( N_p = 2 \), \( r_p = 10 \) nm, (B) \( N_p = 2 \), \( r_p = 40 \) nm, and (C) \( N_p = 5 \), \( r_p = 25 \) nm. No necks are implemented, i.e. \( Y_{\text{con}} = 0 \). The total volume \( V \) of every structure is constant at every step of the simulation process.
respectively. The aggregation algorithm was based on the procedure proposed by Filippov et al. [23,24]. Because of the small size of the structure, the PC (particle-cluster) method was used. The results show that the characteristic absorption peak always exists. However, its position can be slightly shifted when a different value of the particle radius $r_p$ or the number of primary particles $N_p$ is considered.

The next step was to investigate the impact of different connection types on the light scattering efficiencies. The particles were positioned in fixed positions and the total volume $V$ was constant. The results are presented in Figs. 9 and 10. It turned out to be difficult to investigate the impact of small connectors, i.e. $Y_{con} < 0.2$. Furthermore, for large fractal-like structures it is almost impossible to apply these changes, especially when the DDA technique is used. To implement the necking phenomenon, aggregates must be divided into a significant number of volume elements (dipoles) what usually results in increased simulation time. For large connections this problem does not apply and necks can be implemented relatively easily. The changes of the absorption cross section $C_{abs}$ are visible, however, they are almost independent of the connector type. The cylindrical, the linear and the quadratic connector can be used interchangeably, therefore, due to the algorithm complexity and the simulation time, we recommend the most basic one (i.e. the cylindrical connection). The absorption peak is positioned at $ca. Y_{con} = 0.8$. As in the previous study, it is dependent on the volume of the structure $V$ and its optical properties. For different refractive indices it might be shifted. For example, for $m = 1.57 + 0.56 i$ [21] the peak occurs at $Y_{con} = 0.85$. In our study also different structures were analyzed, as presented in Figs. 11 and 12. Although the values of the optical parameters may differ, the tendency remains the same and there are no differences between various connection types. We conclude that small necks, i.e. $Y_{con} < 0.2$, can be omitted.

The rest of the simulation process is presented in Figs. 13 and 14. The connector size is always at its maximum $Y_{con} = 1$ and the overlap factor varies from $C_{ov} = 0.00$ to $C_{ov} = 0.98$ with the step $\Delta C_{ov} = 0.02$. Due to the shrinking phenomenon (the particle centers are no longer in fixed positions) the absorption efficiency decreases gradually from $C_{abs} = 1.48 \times 10^{-3} \mu m^2$ to $C_{abs} = 1.34 \times 10^{-3} \mu m^2$.

Next, the normalized light scattering patterns for a different connector size for two different polarization

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**Fig. 9.** Impact of the connection size parameter $Y_{con}$ on the absorption cross section $C_{abs}$ and the extinction cross section $C_{ext}$ of two connected soot particles. The total volume $V$ is constant at every step of the simulation process.

**Fig. 10.** Impact of the connection size parameter $Y_{con}$ on the scattering albedo $\omega$ and the asymmetry parameter $g$ of two connected soot particles. The total volume $V$ is constant at every step of the simulation process.
Fig. 11. Impact of the connection size parameter $Y_{con}$ on the absorption cross section $C_{abs}$ of structures characterized by the following morphological parameters: (A) $N_p = 2, r_p = 10$ nm, (B) $N_p = 2, r_p = 40$ nm, and (C) $N_p = 5, r_p = 25$ nm. The total volume $V$ of every structure is constant at every step of the simulation process.

Fig. 12. Impact of the connection size parameter $Y_{con}$ on the extinction cross section $C_{ext}$ of structures characterized by the following morphological parameters: (A) $N_p = 2, r_p = 10$ nm, (B) $N_p = 2, r_p = 40$ nm, and (C) $N_p = 5, r_p = 25$ nm. The total volume $V$ of every structure is constant at every step of the simulation process.

Fig. 13. Impact of the overlap factor $C_{ov}$ on the optical properties of two monodisperse soot particles when the connector size is at its maximum $Y_{con} = 1$. The total volume $V$ is constant at every step of the simulation process.
states, i.e. HH (horizontal) and VV (vertical), were compared and the results are presented in Fig. 15. The difference between different connector types is barely visible. Therefore, only the cylindrical connector is presented. The greatest alteration in the light intensity can be observed between the quadratic and the cylindrical connector at the angle $\theta = 180^\circ$ for the VV polarization. However, the relative error at this point is lower than $\delta I = 5\%$ and can be considered as non-existent. Note that small connections do not alter the scattering patterns significantly and can be omitted.

Finally, we decided to check whether our results are valid when different wavelengths $\lambda$ are considered. We were interested in the visible spectrum only and the results are presented in Fig. 16. They show that the impact of $C_{ov}$ and $Y_{con}$ is similar for many wavelengths $\lambda$. The relative error for the linear connector is always lower than $\delta C_{abs} < 0.6\%$ and for the quadratic connector it is not larger than $\delta C_{abs} < 0.1$. Therefore, they are almost indistinguishable and for this reason only the cylindrical connector is presented.

5. Conclusions

In our work we investigated the impact of the overlap factor $C_{ov}$ and different connection types on the optical properties of two $N_p=2$ and five $N_p=5$ monodisperse soot particles. The total volume $V$ was constant at every simulation step. When only the overlap factor $C_{ov}$ is considered, the changes of $C_{abs}$ are visible and should not be avoided (Fig. 7). The absorption cross section $C_{abs}$ is at its maximum when $C_{ov} \approx 0.18$ and then soot aggregates gradually loose their absorption properties. Additionally, small necks, i.e. $Y_{con} < 0.2$, can be neglected. When particles are positioned in point contact and the neck between them grows gradually, $C_{abs}$ also increases. Different connector types behave similarly, therefore they can be used interchangeably (Figs. 9 and 15). We recommend the most
simple one, i.e. the cylindrical connector (Fig. 1). When the connector size is at its maximum $Y_{\text{con}} = 1$ and the overlap factor changes from $C = 0.00$ to $C = 0.98$, the absorption cross section $C_{\text{abs}}$ decreases gradually (Fig. 13).

References