The Effects of Morphology and Water Coating on the Optical Properties of Soot Aggregates

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ABSTRACT

Soot particles positively influence radiative forcing due to their strong absorption. Because of their chain-like structure, aggregated soot particles become more compact with the aging process, and the monomers or particles are always covered by water coatings. The optical parameters of two typical soot-water mixtures (i.e., an aggregate with core-shell monomers and a soot aggregate inside a water droplet) at 550 nm were investigated using the superposition T-matrix method, with a focus on the impact of the morphology and water coating of soot aggregates. For the soot aggregate with core-shell monomers, a relationship among the fractal dimension, relative humidity (RH) and monomer number was established and used to calculate optical parameters. The intensity of forward scattering declined with the increasing RH. The $C_{ext}$, $C_{sca}$, $C_{abs}$ and SSA are much more insensitive to RH under higher RH conditions (RH > 90%) than at a lower RH level. In addition, hygroscopic shrinkage and the thickness of water coating have stronger effects on the optical properties of larger aggregated soot at higher RH than lower RH. For another mixing state, the soot aggregate inside a water droplet, the morphology of the soot core plays an important role in the optical properties when the thickness of the water shell is small. When the diameter ratio of the water droplet to the aggregated soot ($D_{ratio}$) changes from 1.2 to 2.8, $C_{ext}$ difference increases from 0.23 µm$^2$ to 2.36 µm$^2$ for particles with $N = 100$ and 500, whereas the SSA difference decreases from 0.12 to 0.01. If the agglomerated structure of the soot core is not considered, the $C_{ext}$, $C_{sca}$ and SSA will be underestimated for a relatively small $D_{ratio}$ of 1.2. Ignoring the soot core in the water droplet could introduce large errors into the calculation of the optical parameters, and ignoring the structure of the aggregated soot core could enlarge the errors.

Keywords: Soot particle; Water coating; Optical property; The superposition T-matrix.

INTRODUCTION

Atmospheric soot aerosols are of both natural and anthropogenic origin and are emitted directly from incomplete combustion processes, such as burning of fossil fuel and biomass. In contrast to the majority of aerosol species (e.g., sulfate and nitrate) that cause negative radiative forcing, soot particles can heat the atmosphere and exhibit positive radiative forcing due to their strong absorption (Chung and Seinfeld, 2005; Ramanathan and Carmichael, 2008). Soot particles acting as cloud condensation nuclei (CCN) can also indirectly affect the radiative budget though modifying the efficiency of droplet freezing and contributing to the modulation of droplet growth and the onset of precipitation in convective clouds (Lohmann, 2002; Nenes et al., 2002).

According to the Intergovernmental Panel on Climate Change Fifth Assessment Report (IPCC-AR5), estimation of aerosol-cloud radiative forcing still carries large uncertainties, and the quantification of aerosols and clouds in climate models continues to be a challenge (Stocker et al., 2013). Therefore, clarifying the optical properties of the common soot particles existing in the nature is important for reducing the uncertainties proposed in the IPCC-5AR.

The optical properties of soot particles used in remote sensing and climate change studies are usually calculated using Mie scattering theory based on the traditional assumptions of spherical and homogeneous particles (Kaufman et al., 1997; Buseck, 2010). However, previous transmission electron microscope (TEM) analyses have indicated that soot particles commonly exist in the form of a fractal-like aggregate with a complex structure (Wentzel et al., 2003; Sachdeva and Attri, 2008; Li et al., 2010). The aggregated particles contain ten to hundreds of tiny and nearly spherical primary particles (also called monomers) with diameters ranging from 10 to 50 nm. Because freshly emitted soot aggregates are mostly characterized by loose...
of water coating of constituent monomers on the optical single-scattering properties of fractal soot aggregates using the core-mantle GMM method and found that the Maxwell-Garnett theory provided better approximations of the optical properties of water-coated fractal aggregates. However, previous studies only provided the optical properties of water-coated soot aggregates with different amounts of water for one or more specific morphologies. Because the shrinking and restructuring of agglomerated soot occur gradually as RH increases, it is more appropriate to simulate the soot aggregates whose structures and hygroscopic properties are gradually modified by the RH.

This study focuses on the influence of morphology and water coating on the optical properties of two aggregated soot cases, an aggregate with core-shell (soot-water) monomers and a soot aggregate inside a water droplet. The diffusion-limited particle-cluster aggregation algorithm is used to generate aggregates with different monomer numbers, morphological structures and spherical monomer sizes. The superposition T-matrix method is adopted to calculate the optical properties of the aggregates. For the aggregate with core-shell monomers, both the hygroscopic growth of monomers in an aggregate and the morphological modification of the aggregate itself with increasing RH are considered in the hygroscopic model of soot aggregates. The second section describes the methods and models for simulating and computing the optical properties of aggregated soot. The optical results for the two aggregated soot cases are presented in the third section. The last section provides a summary and conclusions.

METHODS

Aggregate Generation

The fractal-like nature of aggregated soot can be mathematically expressed by the following statistical scaling law (Forrest and Witten, 1979):

$$N = k_f (R_g/a)^D_f$$

where $a$ is the radius of monomers, $N$ is the number of monomers contained in the considered aggregate, $k_f$ is the fractal prefactor and $R_g$ is the radius of gyration. A more consistent definition for $R_g$ is the mean square distance between the center of the aggregate and all points on the surface of the sphere, given by the following equations

$$R_g^2 = \frac{1}{N} \sum_{i=1}^{N} (r_i - r_0)^2 + a^2$$

(2)

$$r_0 = \frac{1}{N} \sum_{i=1}^{N} r_i$$

(3)

where $r_i$ and $r_0$ define the position of the $i$th monomer center and the center of the aggregate of $N$ identical spheres, respectively.

To conduct the superposition T-matrix method calculations, the positions of the monomers in a given aggregate are
needed. Following the study of Filippov et al. (2000), soot aggregates were generated using the sequential algorithm (SA) which is a tunable diffusion-limited particle-cluster aggregation (DLPDA) algorithm. In the SA algorithm, identical monomers are added one by one to an existing aggregate, and Eq. (1) is fulfilled exactly at each step for fixed values of fractal dimensions and pre-factors. Combining Eq. (2) with Eq. (1) for steps N-1 and N reveals that the center r_N of the next monomer must be situated on the surface of a sphere determined by the following equation:

\[(r_N - r_{N-1})^2 = \frac{N^2a^2}{N-1}(\lambda_f)_{N-1} = \frac{Na^2}{N-1} - \frac{N-1a^2}{\lambda_f} \]

where \(r_{N-1}^0\) is the center of mass of the first N-1 monomers.

Once a new monomer is placed randomly at the surface of the sphere without overlapping, the procedure is repeated for the next attaching monomer.

**Superposition T-matrix Method**

The superposition T-matrix method assumes that the T matrices of all monomers in the aggregate are known in their respective local coordinate systems with origins and that all these local systems have the same spatial orientation as the common reference frame. The scattered field of the superposition of individual contributions from each monomer can be expressed as:

\[E_{inc}^{\text{sc}}(r) = \sum_j E_{inc}^{\text{sc}}(r) \]

where r connects the origin of the common coordinate system and the observation point. The incident field in one monomer is the superposition of the external incident field \(E_{inc}(r)\) and the sum of partial fields scattered by other monomers in the aggregate

\[E_{inc}^{\text{sc}}(r) = E_{inc}(r) + \sum_j E_{inc}^{\text{sc}}(r), \quad j = 1, \ldots, N \]

To make use of the information contained in the T matrix of the jth monomer, the fields incident on and scattered by this monomer are expanded to vector spherical wave functions centered at the origin of the jth local coordinate system. Combining the coordinate translations, the transformation matrix \(T^{ij}\) (from l to j) can be written as follows:

\[T^{ij} = \sum_{l=1}^N \begin{bmatrix} a^{il} \\ b^{il} \end{bmatrix}, \quad j = 1, \ldots, N \]

where \(T^{ij}\) transforms the coefficients of the incident field expansion centered at the lth origin (a^{il} and b^{il}) into the jth-origin-centered expansion coefficients of the partial field scattered by the jth monomer (p' and q'). Furthermore, the scattered-field expansions from the individual components can be transformed into a single expansion centered at the origin O of the common reference frame. The final joint-coordinate-system T-matrix is given by the following:

\[T = \sum_{j=1}^N \begin{bmatrix} RgA(kjr_{jl}) & RgB(kjr_{jl}) \\ RgB(kjr_{jl}) & RgA(kjr_{jl}) \end{bmatrix} \]

where \(k_j = 2\pi/\lambda\) is the wave number of the incident radiation with wavelength \(\lambda\), the vector \(r_{jl} = r_j - r_l\) or \(r_{jl} = r_{jl} - r_l\) connects the origins of the jth or lth local coordinate system and the common reference frame, and the vector spherical wave functions RgA and RgB are regular (finite) at the origin. The aggregate T-matrix can be used to compute the amplitude matrix for a fixed orientation of an aggregate and be input to the analytical procedures for the averaging scattering characteristics over orientations (Mackowski, 1994; Mackowski and Mishchenko, 1996).

In this paper, the superposition T-matrix method will be used to calculate the optical properties of fractal-like soot aggregates with water coatings. One of the corresponding implementations of the superposition T-matrix method is the FORTRAN-90 Multiple Sphere T-matrix (MSTM) code (Mackowski and Mishchenko, 2011). The latest version of the MSTM code was released in 2013 (available at http://www.eng.auburn.edu/users/dmckwski/scatcodes/). The new version of the MSTM has been extended to accommodate monomers that are located either internally or externally to other monomers. The only limitation is that the surfaces of the spherical monomers cannot overlap (Mackowski, 2013).

**Hygroscopic Growth and Morphology of Soot Aggregates**

To quantify the hygroscopicity of soot particles, the hygroscopic growth factor (HGF) is used to describe the relative size change of particles due to water uptake. HGF is defined as follows:

\[\text{HGF}(\text{RH}) = \frac{D_j(\text{RH})}{D_o} \]

where \(D_j(\text{RH})\) and \(D_o\) represent the particle diameter with a specific RH and a RH of 0%, respectively. The aggregate diameter is defined as the maximum projected length. The monomer radius of a fresh flame-generated soot aggregate is fixed as a typical value \(a_0 = 15\) nm, and \(k_f\) and \(D_f\) are set to 1.19 and 1.82, respectively, based on the study of Sorensen and Roberts (Sorensen and Roberts, 1997).

In the wet air, soot aggregates can exhibit marked shrinkage due to the surface tension of water and are thus significantly different from most aerosol particles which experiencing a hygroscopic growth under enhanced RH. In this paper, the HIGFs of soot aggregates with different \(D_f\) values (30, 80, 155, 240 and 360 nm) were obtained from the measurements (scatters in Fig. 1) of Khalizov (Khalizov et al., 2009). As
shown in Fig. 1, only the HGF for particles with $D_0 = 30$ nm increases with the increasing RH, while the HGFs for particles with $D_0 = 80, 155, 240$ or $360$ nm decrease with increasing RH. Therefore, the HGF for particles with $D_0 = 30$ nm can be used to quantify the hygroscopic growth of a soot monomer in an aggregate, and the observations for $D_0 = 80, 155, 240$ and $360$ nm can be employed to simulate the shrinkage of the soot aggregate. For a monomer in a soot aggregate, an empirical formula (solid line in Fig. 1) was determined by fitting the measurements for $D_0 = 30$ nm using the least squares fitting method to obtain the following HGF expression for a monomer:

$$\text{HGF}_{\text{monomer}}(\text{RH}) = \frac{a(\text{RH})}{a_0} = 0.979 \times \left(1 - \frac{\text{RH}}{100}\right)^{-0.0733} \quad (10)$$

However, for the soot aggregate, the HGF significantly decreases with increasing $D_0$ (or monomer number $N$), and it is difficult to fit a regression model for the aggregate HGF using the single variable factor RH. Therefore, in this paper, we attempted to establish the relationship among $D_f$, RH and $N$ using the following steps. 1) Simulating the fresh soot aggregates ($k_s = 1.19$ and $D_f = 1.82$) with $N$ ranging from 3 to 100 using the DLPCA algorithm (1000 samples for a fixed $N$), $N = 3, 11, 24$ and 52 could be deduced from the averaged $D_0 = 80, 155, 240$ and $360$ nm, respectively. 2) Taking Eq. (10) into consideration, for each $N$ ($N = 3, 11, 24$ or 52), 1000 cases of aggregates with a fixed $k_s = 1.19$ were generated by the DLPCA algorithm for each value of $D_f$ from 1.82 to 3 in steps of 0.01 and for a certain level of RH from 0% to 90%. 3) Then, the $D_f$ value for a certain level of RH was obtained by matching the $D_f$(RH) means of 1000 cases to the corresponding HGFs observed by Khalizov. The scatterplots in Fig. 2 depict the matched $D_f$ values for different RHs and different $D_0$ (or $N$). 4) Finally, a fitting binary nonlinear model could be fit as follows:

$$D_f(\text{RH}, N) = 1.82 \times \left(1 - \frac{\text{RH}}{100}\right)^{-0.1125} \left(\frac{0.1814}{N}\right)^{0.1125} \quad (11)$$

which is used to describe the impact of RH on the morphology of soot aggregates.

RESULTS AND DISCUSSION

Soot Aggregate with Core-Shell Monomers

Based on the fractal-like aggregated soot (Fig. 3) generated by the DLPCA algorithm and the electromagnetic scattering by the soot calculated from the superposition T-matrix method, we investigated the influence of aggregate morphology and monomer water-coatings on the optical properties of soot aggregates with core-shell (soot-water) monomers. Two complex refractive indices of $1.75 + 0.44i$ and $1.33 + 0.00i$ at a wavelength of 550 nm from the OPAC (Optical Properties of Aerosols and Clouds) package (Hess et al., 1998) were used to represent soot and water, respectively. The morphology of soot aggregates varied with RH (Figs. 3(d)–3(f)), and the shrinking process followed Eq. (11). Each soot monomer of an aggregate exists in a core-shell form (Fig. 3), and its hygroscopic growth rule is determined by Eq. (10). Due to the limitations of the superposition T-matrix approach, we assumed that there was no overlap between neighboring monomers.

Fig. 4 depicts the scattering phase functions (SPFs) of soot aggregates with water-coated monomers for different $N$ and RH at 550 nm. The SPF is the P11 element of the scattering matrix, and it satisfies the normalization condition. As shown in Fig. 4, the scattering intensities decrease in the forward scattering directions when RH increases. However, for most aerosol particles, particularly water-soluble particles, their forward scattering intensities generally increase with RH due to the increase in their diameter. To some extent, this increase indicates that ignoring the morphological

![Fig. 1. Experimental results for the hygroscopic growth factor of soot aggregates for different $D_0$ and RH, and the fitting curve for $D_0 = 30$ nm.](image-url)
Fig. 2. Matched fractal dimensions ($D_f$) for different $D_0$ and RH and the fitting curves.

Fig. 3. Fractal soot aggregates characterized by different values of $N$ and RH. (a)–(d): Fresh particles with $N = 100$, 200, 300 and 400, respectively. (e) and (f): Shrinking particles with $N = 400$ and RH = 90% and 98%.

Fig. 4. Scattering phase functions of soot aggregates with core-shell monomers for different monomer numbers and under different RH conditions.
change of soot aggregates with RH can introduce uncertainties into radiative calculations of ambient soot particles. In the backward scattering directions, the SPFs of larger soot aggregates (e.g., $N = 300$ and 500) also decline with increasing RH. Moreover, the aggregate shrinking and the monomer’s water-coating thickening have a much more important role in the SPFs of larger particles (e.g., $N = 500$) than for smaller ones (e.g., $N = 100$), particularly in the forward scattering region.

In addition to the SPF, other optical parameters such as the extinction cross section ($C_{\text{ext}}$), absorption cross section ($C_{\text{abs}}$), scattering cross section ($C_{\text{sca}} = C_{\text{ext}} - C_{\text{abs}}$), single scattering albedo ($SSA = C_{\text{sca}}/C_{\text{ext}}$) and asymmetry parameter ($g$), are also crucial optical parameters for atmospheric radiation studies. Fig. 5 presents these optical parameters of different soot aggregates with water-coated monomers as functions of RH, which were also calculated by using the superposition T-matrix method. These optical parameters all positively correlate with $N$. When the $N$ increases from 100 to 500, the $C_{\text{ext}}$, $C_{\text{sca}}$, $C_{\text{abs}}$, $SSA$ and $g$ for a given

\[ \text{Fig. 5. Optical parameters of soot aggregates with core-shell monomers as a function of RH.} \]
RH = 90% increase by 0.06 µm², 0.041 µm², 0.018 µm², 0.096 and 0.31, respectively. For a constant $N$, $C_{ext}$, $C_{sca}$, $C_{abs}$ and SSA are not sensitive to RH at RH < 90%, but increase significantly when RH ranges from 90% to 98%. For $N = 400$, the increments of $C_{ext}$, $C_{sca}$, $C_{abs}$ and SSA are 0.01 µm², 0.001 µm², 0.009 µm² and 0.13 at RH of 0%–90%, and reach to 0.021 µm², 0.003 µm², 0.018 µm² and 0.16 at RH of 90%–98%, respectively. It is because the electromagnetic interaction led by the superposition of the scattered field among the monomers of the compact aggregate with a larger $D_f$ is much stronger than that of a loose aggregate with a smaller $D_f$. The probability of absorption increases with the shrinkage of an aggregated particle. In addition, the growing thickness of the water coating can enlarge the monomer and increase its scattering capacity. Therefore, the $C_{ext}$, $C_{sca}$ and $C_{abs}$ monotonically increase with increasing RH. The $g$ goes up and down with the increasing RH, which is mainly determined by the monomer number $N$.

**Soot Aggregate inside a Water Droplet**

In a moist atmosphere, the aging process can eventually result in a soot aggregate immersing in a water droplet (shown as Model A in Fig. 6), a common consequence of soot/water interactions in the cloud formation process. The effect of enhanced absorption by water droplets containing soot cores has been studied in many previous literatures (Chung and Seinfeld, 2005). The soot cores inside water droplets are usually assumed to be spherical particles in climate and remote sensing applications. Thus, using the extended Mie theory for coated spheres (Mackowski et al., 1990), or using the classical Mie theory combined with an effective medium approximation (Bohren, 1986), the optical properties of spherical soot inside water droplets can be easily computed. However, the above two methods can not work for the aggregated soot inside water droplets. In this study, we investigated the optical properties of soot aggregates as cores inside water droplets, and then analyzed the effects of soot morphology and water coating on the optical parameters.

We assumed that a soot aggregate continues to shrink until the fractal dimension $D_f$ reaches to the value of $D_f$ (RH = 98%, $N$) in Eq. (11). Based on this assumption, the soot aggregates with $D_f = D_f$ (RH = 98%, $N$) inside water droplets were generated using the DLPCA algorithm for a different $N$ and $D_{ratio}$, where $D_{ratio}$ is defined as the ratio of the water droplet diameter $D_p$ (water_droplet) to the aggregated soot diameter $D_p$ (soot) (Fig. 6). The optical properties were simulated using the superposition T-matrix method. The SPFs of soot aggregates internally mixed with water droplets are presented in Fig. 7. For the aggregated soot core composed of 100, 300 or 500 spherical monomers, the forward scattering intensities at the scattering angles

![Fig. 6. Models of water droplets with soot cores (Model A and B), pure water droplets (Model C) and spherical soot particles (Model D).](image)

![Fig. 7. Scattering phase functions of Model A particles as a function of the scattering angle at different values of $N$ and $D_{ratio}$.](image)
between 0° and 30° increased with increasing $D_{\text{ratio}}$. To evaluate the impacts of the shape of the soot core and the thickness of the water shell on the optical parameters of a water droplet with an aggregated soot core, we computed and compared the optical properties at 550 nm of the following four models (Fig. 6).

**Model A.** A compact soot aggregate with $D_f = D_f(RH = 98\%, N)$ completely imbedded in a spherical water droplet. Moreover, the aggregated soot core and the water droplet are concentric.

**Model B.** The same as Model A, but the soot aggregate is substituted by a homogeneous spherical soot particle with the same volume.

**Model C.** A pure water droplet with a volume identical to that of Model B.

**Model D.** A pure spherical soot particle with a volume identical to that of the soot core in Model B.

Fig. 8 depicts the SPFfs for Models A–D for $N = 300$ and 500 and $D_{\text{ratio}} = 1.2, 2.0$ and 2.8. Large SPF differences are apparent between Model B and Model D. In the forward scattering direction, the water shell enhances the scattering intensity of the initial particle but also reduces the backward scattering intensity, indicating that the water shell plays a significant role in the scattering intensity of the initial soot particle, even if the thickness of the water shell is very small (e.g., $D_{\text{ratio}} = 1.2$). At a fixed monomer number of the aggregated soot core in Model A, the differences in the SPF among Models A–C become insignificant with an increase in the $D_{\text{ratio}}$, particularly at the middle scattering angles ranging from 60° to 120°. A comparison of the SPFfs of Model A with those of Model B in Fig. 8 indicates that the assumption of a spherical soot core inside the water droplet can lead to an underestimation in the forward scattering directions but an overestimation in the middle scattering directions. A comparison of the SPFfs of Model A with those of Model C demonstrates that directly ignoring the soot core in a water droplet overvalues the forward scattering intensities and undervalues the middle scattering ones.

The variations of $C_{\text{ext}}$, $C_{\text{sca}}$, $C_{\text{abs}}$, SSA and $g$ for Model A particles with different values of $N$ and $D_{\text{ratio}}$ are shown in Fig. 9. Nearly all of these five optical parameters increase with both $N$ and $D_{\text{ratio}}$. A large $D_{\text{ratio}}$ can lead to significant discrepancies in $C_{\text{ext}}$ and $C_{\text{sca}}$ among Model A particles with different $N$, but makes the discrepancies in SSA and $g$ insignificant. For Model A particles, the respective differences in $C_{\text{ext}}$ and $C_{\text{sca}}$ between $N = 100$ and 500 are 0.23 µm² and 0.16 µm² at $D_{\text{ratio}} = 1.2$, and reach 2.36 µm²...

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**Fig. 8.** Scattering phase functions as a function of the scattering angle for Models A (red solid lines) and B–D (black dashed lines).
and 2.29 µm², respectively, at D_ratio = 2.8. Meanwhile, the respective differences in SSA and g between N = 100 and 500 are 0.12 and 0.32 at D_ratio = 1.2, and drop to 0.01 and 0.05, respectively, at D_ratio = 2.8. Cabs of the Model A particle with a fixed N is not sensitive to a change in D_ratio. When the thickness of the water shell is sufficiently large (e.g., D_ratio > 2.7), the influence of particle size on the SSA of Model A particles can almost be ignored. The results of Cext, Csca, Cabs, SSA and g for the Model A particles with N = 300 and 500 and the corresponding Models B–D calculations are listed in Tables 1 and 2, respectively. The differences in optical parameters among Models A–D are remarkable. The water shell plays a significant role in these optical parameters, particularly in the SSA of the initial soot particle. Our findings are also consistent with the SPF results mentioned above. If the agglomerated structure of the soot core is not considered, Cext, Csca and SSA will be underestimated for a relatively small D_ratio = 1.2. When the D_ratio increases to 2.8, Cext and Csca will be underestimated for N = 300 but overestimated for N = 500. The calculation errors will also be further enlarged if we neglect the soot core in the water droplet.
In this paper, we first established a relationship and reconstruction process of aggregated soot with increasing RH. The assumption is not appropriate for describing the shrinking be a function of RH and the diameter of the particle, but the T-matrix method. The hygroscopic shrinkage for soot aggregates. We then used the DLPCA algorithm to investigate the radiative properties of soot components of the initial aggregated soot, and can further introduce large uncertainties into simulations of soot optical properties when the thickness of the water shell is small. In addition, the water shell can significantly change the optical parameters of the initial soot particle, even if its thickness is very small.

In a moist atmosphere, the aging process can change the shape of agglomerated soot particles, and cause them to be covered by a water shell. We modeled two states of soot mixing states with water: a soot aggregate with core-shell covered by a water shell. We modeled two states of soot shape of agglomerated soot particles, and cause them to be smaller. In addition, the water shell can significantly change the optical properties when the thickness of the water shell is small. In addition, the water shell can significantly change the optical parameters of the initial soot particle, even if its thickness is very small.

CONCLUSIONS

In a moist atmosphere, the aging process can change the shape of agglomerated soot particles, and cause them to be covered by a water shell. We modeled two states of soot mixing states with water: a soot aggregate with core-shell (soot-water) monomers and a soot aggregate inside a water droplet. The DLPCA algorithm was used to generate these aggregates, and the impacts of the morphological structure and water coating on their optical properties at a wavelength of 550 nm were numerically studied using the superposition T-matrix method.

The hygroscopic growth factor is commonly assumed to be a function of RH and the diameter of the particle, but this assumption is not appropriate for describing the shrinking and reconstruction process of aggregated soot with increasing RH. In this paper, we first established a relationship (equation) among $D_r$, RH and $N$ to address the problem of hygroscopic shrinkage for soot aggregates. We then used this model to investigate the radiative properties of soot aggregates with core-shell monomers. For this mixing state, forward scattering intensities decline with the growing RH, in contrast to the effect on water-soluble particles. When RH < 90%, the $C_{ext}$, $C_{sca}$, $C_{abs}$ and SSA are insensitive to the RH for an aggregate with a fixed number of monomers, but these parameters significantly increase when the RH > 90%. For $N = 400$, the increments of $C_{ext}$, $C_{sca}$, $C_{abs}$ and SSA in the range of 90–98% RH are factors of 2, 3, 2 and 1.23 higher, respectively, than the values in the range of 0–90% RH. In addition, the shrinking of the aggregate and the thickening of the monomer’s water-coating more strongly affect large particles than small ones.

For a soot aggregate inside a water droplet, our results indicate that the scattering intensities of particles with aggregated soot cores are larger than those with spherical soot cores in the forward scattering directions and smaller in the middle scattering directions. $C_{ext}$, $C_{sca}$, $C_{abs}$ and $g$ all increase with $N$ and $D_{ratio}$. The differences in $C_{ext}$ and $C_{sca}$ between particles with $N = 100$ and 500 become large when $D_{ratio}$ value ranges from 1.2 (0.23 µm$^2$ and 0.16 µm$^2$, respectively) to 2.8 (2.36 µm$^2$ and 2.29 µm$^2$, respectively), while the difference in SSA changes from 0.12 to 0.01 with the increase in $D_{ratio}$. Generally, the morphology of the soot core plays an important role in the optical properties when the thickness of the water shell is small. In addition, the water shell can significantly change the optical parameters of the initial soot particle, even if its thickness is very small.

Soot aerosols are special particles due to their complex structures and strong absorption. Our results suggest that water vapor can change the morphology, size and chemical components of the initial aggregated soot, and can further introduce large uncertainties into simulations of soot optical properties. Therefore, assumptions about soot-water mixtures in humid air should be mad with caution in studies of aerosol radiative forcing and remote sensing.

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