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Optical properties of black carbon aggregates with non-absorptive coating

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ABSTRACT

This study develops an idealized model to account for the effects of non-absorptive coating on the optical properties of black carbon (BC) aggregates. The classic fractal aggregate is applied to represent realistic BC particles, and the coating is assumed to be spherical. To accelerate the single-scattering simulation, BC monomers that were overlapped with coating sphere (not those completely inside the coating) are slightly moved to avoid overlapping. The multiple-sphere T-matrix method (MSTM) becomes applicable to calculate the optical properties of inhomogeneous particles with any coating amount, and is generally two orders of magnitude faster than the discrete-dipole approximation for particles we considered. Furthermore, the simple spherical coating is found to have similar effects on the optical properties to those based on more complicated coating structure. With the simple particle model and the efficient MSTM, it becomes possible to consider the influence of coating with much more details. The non-absorptive coating of BC aggregates can significantly enhance BC extinction and absorption, which is consistent with previous studies. The absorption of coated aggregates can be over two times stronger than that of BC particles without coating. Besides the coating volume, the relative position between the mass centers of BC aggregate and coating also plays an important role on the optical properties, and should obviously be considered in further studies.

1. Introduction

Black carbon (BC, or soot), emitted from incomplete combustion of fossil fuel, biofuel and biomass, is one of the strongest absorptive aerosols for solar radiation [1–4]. Once emitted into the atmosphere, BC particles quickly become inhomogeneous during the aging processes [5,6]. BC and its mixtures influence local and global climate directly by strongly absorbing the solar radiation [7,8]. Due to complex geometry and mixing structure, our understanding on BC optical properties is still limited [9], which makes BC, especially aged BC, one of the largest uncertainties in estimating aerosol radiative forcing [10–12].

BC particles normally exist in the atmosphere as aggregates with a large number of small spherical particles, and show really complex overall geometries [13]. Observations indicate that, during the aging process, BC aggregates with open cluster structures may collapse and become compact [14,15]. Meanwhile, those aggregates can mix with other aerosol components by absorption or condensation of gaseous species, coagulation with other aerosols and oxidation [7,16], and become inhomogeneous with coatings of water, sulfate or other non-absorptive materials [17]. With the significant variation on particle geometry and component, the optical properties of BC aggregates can be quite different during the aging. Both laboratory and numerical studies show that the absorption and scattering of BC aerosols can be greatly enhanced after coating or hygroscopic growth [5,18,19]. The enhancement leads to systematic errors in interpreting measurements of ambient BC concentrations [20], and brings significant uncertainties on estimating its radiative effects [21,22].

Numerical modeling becomes one of the most fundamental and important methods to improve our understanding on the effects of coating on BC optical properties. For homogeneous BC particles, the fractal aggregate is the most successful model to represent realistic particle geometries, and is widely accepted to estimate their optical properties [23,24]. However, due to the

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uncertainty and complexity on coated BC particles, quite different models with both simple and complex geometries were built [4,23–28]. The simplest models treat inhomogeneous particles as homogeneous ones by applying the effective medium approximations [2,19,29]. The core-shell spherical model, simplest inhomogeneous model, is also widely used, because the scattering properties can be easily given by the core-shell Mie theory [25,30,31,32]. However, those simple geometries are significantly different from the realistic particles. Meanwhile, some non-spherical and inhomogeneous models are built to give a better representation on particle geometries. Liu et al. add thin water film independently to each monomer, and consider fractal aggregate with core-shell monomers [30]. Dong et al. [25] and Liu et al. [29] introduce 'irregular' coating to fractal aggregates, and use the discrete dipole approximation (DDA) to calculate their optical properties. Those models do build numerical particles quite close to realistic ones, whereas the corresponding calculation for the optical properties is neither simple nor efficient. Thus, this study intends to develop a model that can not only better represent real coated BC particles but also be efficiently considered for light scattering simulations.

To further improve our understanding on the optical properties of aged BC, we build a simple model to account for the effects of non-absorptive coating on their optical properties. The paper is organized as follows. Section 2 introduces the model to represent inhomogeneous BC particles, and the numerical models to calculate their optical properties are compared. The effects of coating on BC optical properties are discussed in Section 3, and Section 4 concludes this work.

2. BC aggregates with coating and their optical properties

The geometry of homogeneous BC is normally constructed following the well-known framework of the fractal aggregate, and it describes BC particles using the statistical scaling rule [33]:

$$N = k_f \left(\frac{R_g}{a} \right)^{D_f} \tag{1}$$

where N is the number of monomers in an aggregate, and a is the monomer radius. k_f and D_f are the fractal prefactor and fractal dimension, respectively, and they indicate the overall structure of the aggregates. R_g, the gyration radius, is defined as a measure of the aggregate overall spatial size, and it can be calculated by

$$R_g^2 = \frac{1}{N} \sum_{i=1}^{N} (\boldsymbol{r_i} - \boldsymbol{r_o})^2 \tag{2}$$

where $\mathbf{r_i}$ is the position vector of the ith monomer center, and $\mathbf{r_o}$ indicates the position vector of the aggregate mass center. As D_f or k_f increases, the aggregate tends to be more compact. For example, aggregates with D_f close 1 correspond to those with a lacy chain-like structure, and compact aggregates have D_f almost 3. We keep using the fractal aggregates to define homogeneous BC particles. This study fixes the values of k_f and a to be 1.2 and 15 nm, respectively, which are both typical observed values [33]. To represent fresh (lacy/open clusters) and aged (compact particles) BC aggregates, we consider two D_f values of 1.8 and 2.8 for comparison [16,26]. A tunable particle-cluster aggregation algorithm is used to generate aggregates with given geometric parameters (N, a, D_f, and k_f) [27,34–36].

The geometries of fractal aggregates are widely applied, whereas models for coated ones are still under discussion. Some models oversimplify particle geometries for the sake of computational convenience [30,35,36]. Meanwhile, some complex geometries are developed to represent realistic particles, whereas the computational burden for the single-scattering simulation limits the applications of those models [25,29]. To build a realistic particle model for efficient optical simulation, the simplest three-dimension geometry, sphere, is "coated" to the soot fractal aggregate. Actually, some microscopic images of aged BC particles do show spherical coating geometry [16,25].

To form an inhomogeneous particle, we first generate a fractal aggregate and a spherical coating with given sizes separately. Secondly, the coating sphere is randomly placed "in the aggregate" with a given distance between their mass centers. It should be noticed that the coating sphere should be enlarged to offset the volume occupied by the monomers inside and to reach the required coating volume. Last, the BC monomers that are completely inside or outside of the coating sphere are kept, whereas those that are partially inside and partially outside (overlapping) are slightly moved to the outside of the coating sphere. Therefore, we can generate such an inhomogeneous BC particle with only spherical elements but without overlapping ones, and both aggregate and coating sizes can be arbitrary. The size of BC aggregate, i.e. N, and the volume fraction of the BC aggregate or coating to the inhomogeneous particle, i.e. f_BC or f_coating, are used to specify particle overall 'size'. f_coating is given by:

$$f_{coating} = 1 - f_{BC} = \frac{V_{coating}}{V_{coating} + V_{BC}} \tag{3}$$

where V_BC and V_coating are the volume of the BC aggregate and coating, respectively.

The 2D images in Fig. 1 show the typical examples of monomer movements to avoid overlapped spheres. The gray and blue spheres represent BC monomers and coating, respectively, and the red spheres indicate the moved monomers. The left and middle panels show 2D particles before and after the move. The top row is for an aggregate with relatively lacy structure (e.g., D_f=1.8), and, with enough space outside the coating sphere, we can simply move the overlapped monomers to the outside and to be attached with the coating sphere. For aggregates with compact structure (e.g., D_f=2.8), the outside of the coating sphere is mostly occupied by other monomers, and we may move the monomers outward until all overlapping avoided. This is illustrated by the 2D images in the bottom row of Fig. 1. Considering the small monomer size (radius of 15 nm in this study), the distance moved to avoid overlapping is small compared with the wavelength we consider (i.e., 550 nm). The influence of such movement on optical

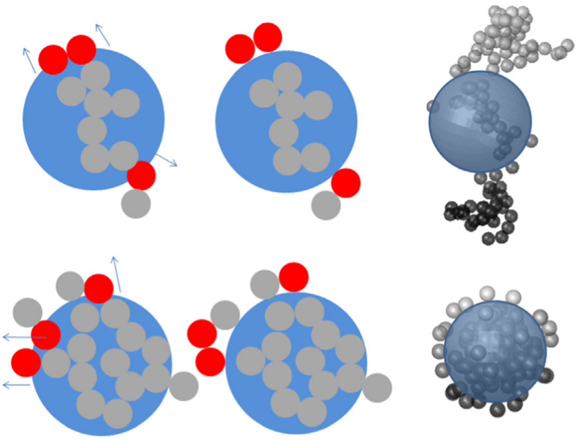

Fig. 1. Procedures to generate a fractal aggregate with a spherical coating and no overlapping monomers, and two examples of coated BC aggregates (100 monomers) with fractal dimension of 1.8 and 2.8. Gray and blue spheres represent BC and coating, respectively, and the red ones are the moved monomers. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)