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Editorial

Preface: Morphology and Internal Mixing of Atmospheric Particles

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1. Introduction

The properties of atmospheric particles (often also termed aerosol) have been the subject of scientific studies for several decades because of their effects on air quality, health, visibility, propagation of electromagnetic radiation in the atmosphere, and climate. However, despite intense research efforts, several knowledge gaps remain to be filled, the reason being related to the complexity of the physical and chemical characteristics of these particles and of their dynamic interactions with the surrounding environment [1]. One of the frontier topics in this scientific endeavor is the subject of this special issue: the morphology and mixing of atmospheric aerosol at the single-particle level. With aerosol "morphology" and "mixing", here, we refer to three broad properties of a single particle suspended in the atmosphere: (1) the shape and size of a particle; (2) the geometrical distribution of components with different physico-chemical characteristics within a particle; and (3) the topology of a particle (e.g., the existence of convex or concave regions on the particle's surface, or fractal-like structures). Figure 1 shows some examples of the complex morphology and mixing state of atmospheric particles. These three properties affect important atmospheric processes; for example: (a) The shape and size of a particle affects its optical and aerodynamic properties, determining their effectiveness when interacting with electromagnetic radiation, their settling velocity, their ability to penetrate deeply into the lungs, and the sampling efficiency of instrumentation, inlets, or sampling lines. Even the simple concept of size becomes ill-defined (or ambiguous) for particles that have nontrivial shapes (e.g., different from spheres, spheroids, cylinders, or cubes); (b) The geometrical distribution of different components affects the particles' ability to interact with other atmospheric components, including water, and their effectiveness to scatter or absorb electromagnetic radiation. Therefore, particles with similar size and similar components' mass fractions, but different geometric distributions of these components, can have different cloud condensation and ice nucleation properties, can promote different heterogeneous reactions, can experience different aging processes, and can exert different radiative forcing; (c) The topology of the particle can affect its ability to nucleate water droplets and ice crystals, or favor the condensation of other material from the gas phase, determining, for example, the mass growth rate of secondary organic aerosol, and it can also affect heterogeneous chemical reactions and the particle toxicity. An important example where the topology has a key role is for fractal-like, combustion-generated soot particles (often also referred to as black carbon). These particles have a key role in determining the overall radiative forcing of anthropogenic aerosol [2–4]. Their initial structure is typically well described by a fractal formalism, and their mass scales with a measure of

their length through a power law—with an exponent different from that of convex objects [5]. This structure changes over time in the atmosphere and, therefore, the properties of these particles are very dynamic [3,6–11].

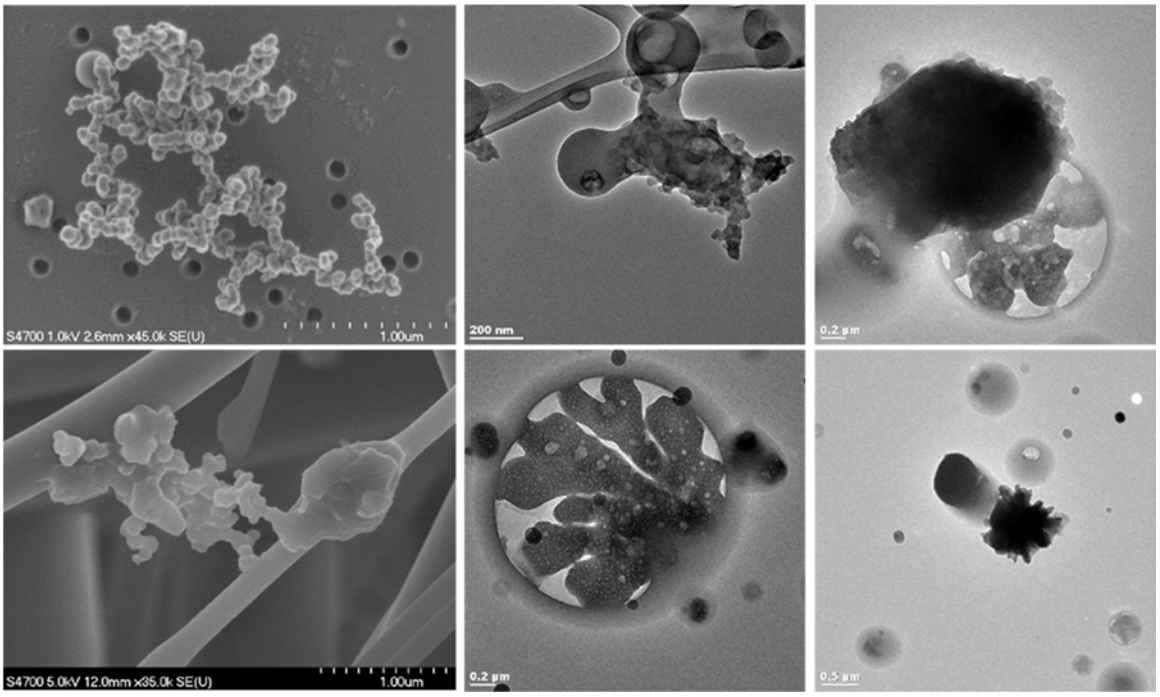

Figure 1. Complex morphology and internal mixing of atmospheric particles.

In this special issue, the authors discuss several of these aspects and present recent advances in this field, including ambient and laboratory characterizations, as well as theoretical and numerical treatments. In the next section, we will briefly summarize the individual contributions to this issue, categorized into three broad topics: (1) sampling and laboratory techniques; (2) analyses of atmospheric particles; and (3) theoretical and numerical studies.

2. Summary of This Special Issue

2.1. Sampling and Laboratory Techniques

Chen et al. [12] report a detailed study of the modification of the particle morphology deposited on different substrates and subjected to various conditions during storage, handling, and analysis. For their study, they generated, collected, and analyzed three types of particles: sodium chloride, sulfuric acid, and soot coated with sulfuric acid. Depending on substrates and conditions, they observe that morphological changes of the deposited particles could vary from negligible to severe. They, therefore, recommend caution during each step of the specimen lifetime from the collection to the analysis. They also provide specific conditions and sampling media that can work better for the specific problem and particle type investigated.

Bhandari et al. [13] analyze fresh soot particles generated in the laboratory using acetylene and methane flames, before and after a thermodenuder. Thermodenuders are often used to estimate the effect that coating material has on the soot particles' optical properties through the "lensing" effect. Freshly generated soot has typically a fractal-like (lacy) structure, but such a structure can collapse to a more compact one upon aging. Compaction, as coating, affects the soot optical properties as well. If the goal of using a thermodenuder is to assess the effect of coating only, then the thermodenuder itself should cause minimal or no compaction. The study verifies that indeed that is the case.

Kulkarni et al. [14] demonstrate a laboratory-based experimental method to investigate the immersion freezing of ice residuals using two continuous-flow diffusion chambers and a pumped counterflow virtual impactor. Ice is nucleated in immersion freezing mode in the first diffusion chamber. The larger ice crystals are separated and sublimated using the virtual impactor and a heat exchanger. The ice residuals are transferred to the second ice chamber to investigate the immersion freezing properties of ice residuals. The results from this study show that not all the ice residuals nucleate ice in the second chamber. The transformation of morphology and chemical composition of ice residuals during the freezing–sublimation process can influence the freezing properties of the ice residuals.

Brus et al. [15] present laminar flow tube measurements of sulfuric acid diffusion coefficients as a function of relative humidity, temperature, and concentration. They use a chemical ionization mass spectrometer to monitor sulfuric acid concentrations at different positions along the flow tube and calculate the effective sulfuric acid diffusion coefficient from the wall loss rate. They apply a computational fluid dynamics model to investigate the laminar flow in the tube. The authors find that the effective sulfuric acid diffusion coefficients linearly decrease with increasing relative humidity, while they show a power dependence with respect to temperature. They further use clustering kinetics simulations to investigate the effective diffusion coefficients. They suggest that the attachment of sulfuric acid molecules with base molecules may be responsible for a higher temperature dependence.

2.2. Analyses of Atmospheric Particles

Kiriya et al. [16] report a study of aerosol surface area during a field study in Japan, in 2015–2016. Often size distributions are reported in terms of number concentrations per size bin; the authors here, instead, study the aerosol surface area distributions. The motivation is that the surface area might be particularly important for the toxicity of the particles and their ability to react with humans' and animals' cells and other pollutants. They find that the surface area correlated with the black carbon concentrations. Freshly emitted black carbon particles are typically fractal-like aggregates of small monomers and have a relatively large surface area. This surface area can decrease over time due to aging and coating processes. Therefore, the authors interpret their result as evidence that the black carbon transported to the site was mostly uncoated.

Mahish et al. [17] report an analysis of different methods used to calculate cloud condensation nuclei spectra and assess the effect of various assumptions and simplifications, including those regarding the mixing state of atmospheric aerosol. For their analysis, they use a large dataset collected at the Southern Great Planes site in Oklahoma from the U.S. Department of Energy, Atmospheric Radiation Measurement program. They first make a baseline estimate of the cloud condensation nuclei spectra with k-Köhler theory and using all the data available without averaging. Then, they compare several estimates using different assumptions and they find the best agreement with their baseline when they include size-dependent internal mixture hygroscopicity information.

Xu et al. [18] discuss a single particle study using electron microscopy and spectroscopy on samples collected in the Northeast of China. They characterize the particles based on their elemental composition, mixing, and morphology. From their analysis, they suggest that coal combustion in low-efficiency stoves, used for household heating, is a dominant source in the area. The authors also suggest that biomass burning is of secondary importance, although not negligible. They conclude that the anthropogenic emissions from rural regions can be transported to urban areas and substantially add to the local pollution, contributing to regional haze episodes.

Wang et al. [19] investigate the morphology and mixing state of individual atmospheric particles in the megacity of Beijing during the 2015 China Victory Day parade, using transmission electron microscopy coupled with energy dispersive X-ray spectrometry. They classify particles into two broader groups and within each group, they define different subcategories (primary: mineral dust, soot, and organic; and secondary: homogeneous mixed S-rich, and organic coated S-rich particles) based on their morphology and mixing state. They find that secondary particles dominate (~79%) the

total particle population. They also observe that the average diameter of secondary particles increases with increasing relative humidity. They suggest that organic coated S-rich particles may be formed by condensation of secondary organic aerosol on seed S-rich particles.

Fraund et al. [20] present a microspectroscopy analysis of single particles collected in the Amazon basin from three sites with different proximity from the city of Manaus. The authors quantitatively combine two complementary microspectroscopy techniques, Scanning Transmission X-ray Microscopy/Near-Edge Fine Structure Spectroscopy and Scanning Electron microscopy/Energy Dispersive X-ray Spectroscopy. They estimate the particle-specific mass fraction and calculate the bulk and individual particle diversity parameters. They utilize the mass fraction data for k-means clustering analysis to identify several particle classes. They use the diversity parameter to quantify the mixing state (i.e., the mixing state index) of the particle population. The mixing state index varies from 0 (completely externally mixed) to 1 (completely internally mixed). The results of this study suggest that the background site contains less cluster variety and fewer anthropogenic clusters than samples collected at the sites nearer the city.

2.3. Theoretical and Numerical Studies

Sorensen et al. [21] provide a detailed review of the power of Q-space analysis that offers general insights on the optical properties of particles and allows the discovery of patterns useful for the interpretation of these properties. After a general introduction of the basic concepts using Mie and Rayleigh scattering theories, the authors expand the analysis to the more complex topic of the optical properties of irregular particles. Particle types discussed include dust, abrasive powders, fractal aggregates, and ice crystals, covering a wide range of sizes, shapes, and index of refractions, and making the work relevant to several branches of science, even beyond purely atmospheric applications. For their discussion, the authors use experimental and theoretical data (e.g., numerical methods such as T-matrix and the discrete dipole approximation). Among several interesting findings, what stands out is the clear distinction between fractal and nonfractal particles, especially at some regimes.

Chin et al. [22] present a numerical modeling analysis of how the mixing state of black carbon affects its atmospheric removal through nucleation scavenging. Nucleation scavenging, where a water droplet grows by condensation on a particle, is possibly the most important mechanism for the removal of black carbon from the atmosphere, determining the lifetime of this type of particle. Because black carbon strongly absorbs solar radiation, an understanding of its lifecycle is key to accurately modelling the effect of aerosol on climate. For their work, the authors use a detailed particle-resolved model that can follow the aerosol mixing (internal and external) at the single-particle level. Based on their analysis, they suggest that typically employed models that ignore (or simplify) the intricacy of the single-particle mixing, can significantly overestimate the scavenged black carbon mass fraction, especially for lower supersaturation conditions.

Hughes et al. [23] apply the machine learning approach to predict the global distribution of the aerosol mixing state and its implications on hygroscopicity, as quantified by a mixing state metric. Machine learning is an emerging tool in atmospheric science; it utilizes a set of algorithms to recognize patterns in large datasets and make predictions. Global climate models use a simplified representation of aerosol mixing state, which can introduce large uncertainties. In this study, the authors utilize a large ensemble of particle-resolved box model simulations and the machine learning approach to determine mixing state matrices and identify the regions where the external and internal mixing state assumption can be applied in global climate models. They find that the mixing state metric varies between 20% and 100%. They also report how the mixing state metric varies with particle diameter, geographical location, and season. This study shows how machine learning can be applied to link detailed particle-resolved models to large-scale global climate models.

3. Conclusions

This special issue assembles a dozen contributions discussing a wide range of aspects on the morphology and mixing state of individual particles by internationally recognized experts in the field. The results and techniques discussed and proposed in this special issue will be of interest to experimentalists as well as global climate modelers, and guide the improvement of numerical simulations of past and future climate changes. However, we also hope that these results will be useful to other research communities, including those that study air quality, visibility, particle toxicity, combustion processes, atmospheric optics, and chemistry, and possibly those that study particles for technological applications. Finally, we hope that the research presented here will spark new ideas and indicate future research directions.

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