INVESTIGATION OF THE EVOLUTION OF ATMOSPHERIC PARTICLES WITH INTEGRATION OF THE STOCHASTIC PARTICLE-RESOLVED MODEL PARTMC-MOSAIC AND ATMOSPHERIC MEASUREMENTS

BY

JIAN TIAN

DISCUSSION

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Doctoral Committee:

Associate Professor Nicole Riemer, Chair
Associate Professor Matthew West
Professor Gregory McFarquhar
Associate Professor Stephen Nesbitt
Abstract

Atmospheric aerosols are known to have strong impacts on human health, visibility and the climate system. They originate directly from either anthropogenic or natural emission, or can be also formed through gas-particle conversion processes. Aerosol particles in the atmosphere often represent a complex mixture of a wide variety of species, and the mixing state can change during the evolution of particles in the ambient environment, leading to significantly different effects on the climate system compared to freshly emitted condition.

With the recently-developed particle-resolved model PartMC-MOSAIC, the mixing state and other physico-chemical properties of individual aerosol particles can be tracked as the particles undergo aerosol aging processes. However, existing PartMC-MOSAIC applications have mainly been based on idealized scenarios, and a link to real atmospheric measurement has not yet been established. In this thesis, we extend the capability of PartMC-MOSAIC and apply the model framework to three distinct scenarios with different environmental conditions to investigate the physical and chemical aging of aerosols in those environments.

The first study is to investigate the evolution of particle mixing state and cloud condensation nuclei (CCN) activation properties in a ship plume. Comparisons of our results with observations from the QUANTIFY Study in 2007 in the English channel and the Gulf of Biscay showed that the model was able to reproduce the observed evolution of total number concentration and the vanishing of the nucleation mode consisting of sulfate particles. Further process analysis revealed that during the first hour after emission, dilution reduced the total number concentration by four orders of magnitude, while coagulation reduced it by an additional order of magnitude. Neglecting coagulation resulted in an overprediction of more than one order of magnitude in the number concentration of particles smaller than 40 nm at a plume age of 100 s. Coagulation also significantly altered the mixing state of the particles, leading to a continuum of internal mixtures of sulfate and black carbon. The impact of condensation on CCN concentrations depended on the supersaturation threshold at which CCN activity was evaluated. Nucleation was observed to have a limited impact on the CCN concentration in the ship plume we studied, but was sensitive to formation rates of secondary aerosol.
For the second study we adapted PartMC to represent the aerosol evolution in an aerosol chamber, with the intention to use the model as a tool to interpret and guide chamber experiments in the future. We added chamber-specific processes to our model formulation such as wall loss due to particle diffusion and sedimentation, and dilution effects due to sampling. We also implemented a treatment of fractal particles to account for the morphology of agglomerates and its impact on aerosol dynamics. We verified the model with published results of self-similar size distributions, and validated the model using experimental data from an aerosol chamber. To this end we developed a fitting optimization approach to determine the best-estimate values for the wall loss parameters based on minimizing the $\ell^2$-norm of the model errors of the number distribution. Obtaining the best fit required taking into account the non-spherical structure of the particle agglomerates.

Our third study focuses on the implementation of volatility basis set (VBS) framework in PartMC-MOSAIC to investigate the chemical aging of organic aerosols in the atmosphere. The updated PartMC-MOSAIC model framework was used to simulate the evolution of aerosols in air trajectories initialized from CARES field campaign conducted in California in June 2010. The simulation results were compared with aircraft measurement data during the campaign. PartMC-MOSAIC was able to produce gas and aerosol concentrations at similar levels compared to the observation data. Moreover, the simulation with VBS enabled produced consistently more secondary organic aerosols (SOA). The investigation of particle mixing state revealed that the impact of VBS framework on particle mixing state is sensitive to the daylight exposure time.
To My Dearest Family.
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Chapter 1

Introduction

1.1 Background and motivation

1.1.1 Atmospheric aerosol and its environmental effects

Atmospheric aerosols are a collection of small solid or liquid particles suspended in the air. Fig 1.1 shows an overview of the aerosol life cycle in the Earth’s system, including their formation, transformation, transport and climate impacts. Aerosols can originate from either anthropogenic or natural sources, including vehicle emission, mineral dust, volcanic eruption, biomass burning or sea spay (Valsaraj and Kommalapati, 2009). For example, incomplete combustion of fossil fuel in automobile exhaust and power plants can generate carbonaceous aerosols, including black carbon (BC) and organic carbon (OC) (Streets et al., 2004). Biogenic aerosols usually consist of plant debris, humic matter, and microbial particles. These directly emitted aerosols are also referred as primary aerosols. On the other hand, many aerosol species are formed through gas-particle conversion processes such as nucleation, condensation and heterogeneous and multiphase chemical reactions (Hallquist et al., 2009). In these processes, atmospheric gases undergo oxidation reactions that lower their vapor pressure and cause the gases to condense onto existing particles or spontaneously form particles themselves. Aerosols formed by these processes are referred as secondary aerosols. For example, sulfate particles are generated by oxidation of sulfur dioxide from gaseous precursors emitted from primary sources, such as volcanic eruptions. Secondary organic aerosols (SOA) are produced from volatile organic precursor gases from trees, plants, cars or industrial emissions (Carlton et al., 2009). Both primary and secondary aerosols are important constituents of the aerosol burden, and play important roles in the earth’s climate system.

Aerosols are known to have strong adverse impacts on human health (Pope, 2000), visibility (Watson, 2002), and the climate system (Lohmann and Feichter, 2005). First, inhalable particles which are particles less than 10 µm in size can make it past the body’s defenses and deep into the lungs. Fine particles with diameter less than 2.5 µm can penetrate deeper, and a significant proportion of these fine particles are
deposited in the trachea, bronchioles, and alveoli. As a result, aerosols can cause several health problems including aggravated asthma, lung cancer, and respiratory diseases. Pope and Dockery (2006) reviewed six substantial lines of research on particulate matter on human health and concluded that exposure to fine particulate air pollution has adverse effects on cardiopulmonary health. Tie et al. (2009) studied 52-year historical surface measurements of haze data in Guangzhou, China and found a close relationship between the incidence of increasing lung cancer and aerosol loading. Rohde and Muller (2015) reported that the observed air pollution is calculated to contribute to 1.6 million deaths/year in China, roughly 17% of all deaths in China. The health impact from aerosols are receiving more and more attention in recent years along with increasing aerosol concentrations, especially in urban areas with large populations.

Second, aerosols influence the visibility by scattering and absorbing incoming light. Scattering changes the direction of the photon’s propagation while absorption removes the photon from the beam by conversion to thermal or electronic energy in the particle or molecule. These two processes, collectively known as light extinction, both act to remove light from a beam and thus lead to a decreased visible range. Visibility degradation has become a severe problem of public concern in many areas in recent years, including Mexico City (Eidels-Dubovoi, 2002), Kaohsiung city (Lee et al., 2005), Beijing (Han et al., 2013), Los Angeles (Langridge et al., 2012), and even remote area in the US such as national parks (Mazurek et al., 1997).

Third, aerosols can affect climate radiative budget by either scattering and absorbing solar radiation
(direct effect) or acting as cloud condensation nuclei (CCN) to change cloud properties through aerosol-
cloud-interactions (indirect effect) (Haywood and Boucher, 2000). For most aerosol species, such as sulfate,
the main direct effect is scattering of a significant fraction of the incoming solar radiation back to space. On
the contrary, the main direct effect of black carbon is its strong absorption of solar radiation, which tends
to warm the air masses where black carbon resides. For the indirect effect, an increasing of aerosol loading
will increase the cloud droplet number concentration and reduce the cloud droplet size, which enhances the
cloud reflectivity and reduces solar radiation. This indirect effect is called Twomey effect or first indirect
effect (Twomey, 1974, 1977). Further, the smaller size of cloud droplets from increasing aerosol loading may
cause less efficient collision and coalescence among cloud droplets, which may decrease the production of
precipitation, lengthen the lifetime of clouds and increase the cloud water content and cloud coverage. This
indirect effect is called Albrecht effect or second indirect effect (Albrecht, 1989). The aerosol indirect effect
remains a significant source of uncertainty due to the complexity and number of the atmospheric interactions
involved, as well as the wide range of scales on which these interactions occur. The IPCC fifth assessment
report revealed that the radiative forcing from the aerosol indirect effect is $-0.9 \ \text{W m}^{-2}$ with the range
between $-0.1 \ \text{W m}^{-2}$ and $-1.9 \ \text{W m}^{-2}$ (IPCC, 2014).

Aerosol particles in the atmosphere often represent a complex mixture of a wide variety of species. We use
the term mixing state in this context to describe how the aerosol chemical species are distributed amongst
the particles of an aerosol population (Riemer and West, 2013). Figure 1.2 shows an example of an aerosol
population composed of two chemical species, with three different mixing states. A completely externally
mixed population contains only particles of one species, while a completely internally mixed population
contains identical particles which are a mixture of the two chemical species. Between those two extremes
there are intermediate states possible, as shown in the center panel of Figure 1.2.

![Figure 1.2: A schematic illustrating three mixing states of two bulk species (indicated by blue and red),
including a completely internally mixed aerosol population, a completely externally mixed aerosol population,
and an example of a population with a mixing state between those two extremes.](image)

The magnitude of aerosols’ climate effects significantly depends on the mixing state of aerosols (China
et al., 2013; Schill et al., 2015). For example, Jacobson (2000) reported an increase up to a factor of 2.9 for black carbon forcing from model estimates with internal mixed scenario compared to external mixed scenarios. Chandra et al. (2004) found that aerosol species may be coated over another species to form core-shell structure and have significantly different radiative impact than those of the externally-mixed or internally-mixed aerosols. Hand et al. (2005) investigated the optical properties of amorphous carbon spheres, or “tar balls”, and showed that they absorbed light in the UV and near-IR range of the solar spectrum. Liu and Wang (2010) indicated that changing the hygroscopicity parameter value of primary organic aerosols (POA) from 0 to 0.1 increased the number concentration of CCN at a supersaturation 0.1% by 40-80% over the POA source regions. Lack et al. (2012) showed that internal mixtures of BC and organic carbon (OC) enhanced absorption by up to 70% through a suite of multi-wavelength photo-acoustic optical measurements. Willis et al. (2015) conducted a box model study using mass-based BC measurements and showed an increase in single scattering albedo (SSA) of around 0.1 when mixing state at the point of emission was treated accurately, compared to the assumption of uniform mixing state.

Furthermore, the properties of atmospheric aerosols can evolve in ambient environment, leading to significantly different effects on climate system compared to fresh emitted condition. We will use the term “aging” in this context to represent the aerosol evolution. The aging process comprises of particle coagulation, condensation of secondary aerosol material and chemical processes. Abel et al. (2003) showed an increase of SSA in an African biomass burning plume from 0.84 to 0.9 in 5 hours. Jimenez et al. (2009) investigated the evolution organic aerosols (OA) and found that OA became increasingly oxidized, less volatile, and more hygroscopic, leading to the formation of oxygenated organic aerosol. Yang et al. (2012) studied the mixing state of carbonaceous particles using aerosol time-of-flight mass spectrometry and showed dramatic changes from fresh elemental carbon or biomass burning particles to aged ones with the addition of secondary components, mostly ammonium nitrate and secondary organic compounds during heavy haze events. Langridge et al. (2012) conducted airborne measurements on the Los Angeles plume and found that the changes to aerosol behavior with aging can impact visibility and climate forcing significantly. The dynamic behavior of particle properties further increases the difficulty in accurately assessing the climate effects of atmospheric aerosols.

1.1.2 Overview of atmospheric measurements on aerosol properties

Atmospheric measurements with integration of ground-based (or fixed-point) sampling and aircraft observations are used to quantify the evolution of aerosol particles in the ambient atmosphere. Moreover, they are essential to provide information from the real atmosphere which is crucial to evaluate the quality of
numerical models and to define model parameters which cannot be calculated solely from theory (Hendricks et al., 2012).

Earlier approaches on aerosol sampling mainly focused on the measurement of aerosol bulk properties, including mass and number concentrations. These measurements are routinely conducted in monitoring stations in various locations around the world. Most commonly used techniques for mass concentration measurements involve both of manual method such as filtration (Chow, 1995), and automated methods including beta gauge, piezoelectric crystals, and the oscillating element instruments (Williams et al., 1993). The condensation particle counter (CPC) measures the total aerosol number concentration larger than some minimum detectable size in real-time and at high time resolution. This works by growing particles by condensation in a supersaturated environment until they are sufficiently large to be detected optically (McMurry, 2000).

The ideal atmospheric aerosol measurement would produce data on the chemical composition of individual particles as a function of particle diameter. However, both size-resolved and composition-resolved measurements of aerosol properties have posed a big challenge over several decades in the science community. First, aerosols span a wide range of sizes in the atmosphere, typically from a few nanometers for nucleation mode particles to hundreds of micrometers for large coarse particles (Seinfeld and Pandis, 2006, Ch. 8.1). This broad size spectrum (around four to five orders of magnitude) will have a much larger mass spectrum with at least twelve orders of magnitude. Second, as mentioned in Section 1.1.1, aerosol particles in the atmosphere can have various mixing states, containing chemically differentiated particles emitted from different sources or products of different atmospheric chemical histories (Chow, 1995). These aerosol characteristics significantly increase the complexity to accurately performing atmospheric sampling.

Aerosol size-resolved measurements have been conducted using various instruments and approaches. An earlier approach is to use differential mobility analyzers (DMA) to classify particles according to their electrical mobility which depends on gas properties, particle charge, and the geometric particle size (Knutson and Whitby, 1975). Based on DMA and integrated with CPC for particle detection, several advanced instruments have been developed such as the differential mobility particle sizer (DMPS) (Williams et al., 2000) and scanning mobility particle sizer (SMPS) to measure size distributions of fine aerosols at a very high size resolution.

Aerosol chemical composition measurements have experienced two major stages. The first stage is offline method, where particle samples were collected and analyzed after a defined period of time using sampling techniques including filters, impactors and denuders. The samples can then be analyzed using microscopy techniques such as Transmission Electron Microscopy (TEM) to obtain the composition information (Fig-
These methods, however, suffer from several drawbacks including long sampling period and potential contamination during transport and analysis. To avoid these issues, online methods have been developed to automate the collection and analysis work. In recent years, with the introduction of aerosol mass spectrometer (AMS) (Nash et al., 2006), online sampling techniques have been widely used in in-situ measurements around the world. Based on Figure 1.4 (taken from Hallquist et al. (2009)), which shows the three-dimensional representation of the capability of existing aerosol instruments (including chemical resolution, completeness, and time and size resolution), AMS is able to provide aerosol chemical compositions at very high completeness (i.e., percent of aerosol mass analyzed). For example, the Aerodyne Aerosol Mass Spectrometer is one of the most popular instruments to provide real-time, quantitative and multidimensional data of atmospheric aerosols (Jayne et al., 2000; Canagaratna et al., 2007). The Aerodyne AMS uses an aerodynamic lens inlet technology together with thermal vaporization and electron-impact mass spectrometry to measure the real-time non-refractory chemical speciation and mass loading as a function of particle size of fine aerosol particles. It has been used in many field campaigns around the world (Figure 1.5) and the AMS field data have been used to validate models and investigate complex aerosol processes (Zhang et al., 2007; DeCarlo et al., 2008; Li et al., 2011a). Another popular instrument is Single Particle Laser Ablation Time-of-flight Mass Spectrometer (SPLAT-MS or SPLAT), which uses light scattering to generate reproducible single particle mass spectra and measure the particle size down to 50 nm at a high rate (Zelenyuk and Imre, 2005).

![Figure 1.3: High-resolution Transmission Electron Microscopy (TEM) showing the mixing and compositions of various cloud residues. Figure taken from Li et al. (2011b).](image-url)
Despite of the rapid development of aerosol measurement methods, we need to note that large errors can still be introduced from these measurements, including uncertainties of the instruments, calibration, sampling geography, and meteorological condition. The uncertainties are even larger for aircraft measurements, where there are issues from flow around the airframe, unknown transport efficiencies, and increase of aerosol temperature caused by the rapid deceleration of the air (McMurry, 2000; Hermann et al., 2001).
Numerical simulations on the evolution of aerosols

Numerical models can provide consistent, temporally and spatially resolved information about atmospheric aerosol properties and aerosol-related effects which are usually not accessible from measurements (Hendricks et al., 2012). In addition, numerical models can predict the evolution of aerosols in the atmosphere and estimate the corresponding effects on climate system. The robustness of numerical models on characterizing aerosol properties depends on the representation of aerosol mixing state, which has been observed to have strong influence on aerosol hygroscopicity (Lance et al., 2013; Holmgren et al., 2014; Jiang et al., 2016), optical properties (Lesins et al., 2002; McMeeking et al., 2011; Tan et al., 2016) and radiative forcing (Jacobson, 2000; Srivastava and Ramachandran, 2013; Klingmüller et al., 2014). The aerosol mixing state can be defined in terms of \( A \) classes of chemical species, where \( A \) could be sulfate, nitrate, black carbon, etc.. Therefore, the precise way to resolve the particle composition distribution is using a multivariate function on the \( A \)-dimensional mixing state space. Viewed in this way, the particle aging is represented by moving the particle composition distribution through this composition space.

However, the aerosol size distributions in most existing models are either represented by a number of sections or modes (Figure 1.6). This representation is a projection of the high-dimensional composition space to lower dimensions. Sectional models store the aerosol distributions in each grid cell which is determined by independent variable (including particle mass, diameter, etc.) space (Wexler et al., 1994; Adams et al., 1999; Korhonen et al., 2005; Luo and Yu, 2011). Modal models represent the particle distribution as a sum of modes, each having a lognormal (or similar) size distribution described by a small number of
parameters (Whitby and McMurry, 1997; Stier et al., 2005; Bauer et al., 2008; Korhola et al., 2014). For these representations, it then needs to be assumed that each particle consists only a single species (the “fully external-mixture assumption”), or within one bin or mode all particles have the same composition (the “fully internal-mixture assumption”). Both assumptions do not represent the reality of the aerosol particles found in the atmosphere. For example, Zhang et al. (2002) used both modal and sectional aerosol size representations to evaluate the impact of aerosol size representation on modeling aerosol-cloud interactions. Both representations were shown to have difficulty in predicting observed particle size distributions with normalized absolute difference over 100% in some scenarios. Mann et al. (2012) conducted an intercomparison of modal and sectional aerosol representations in 3-D global offline chemistry transport model and found that modal scheme led to a large bias when obtaining size distribution during cloud condensation nuclei (CCN) measurement.

Figure 1.6: Schematics of modal, sectional and particle-resolved representations of aerosol size distribution.

It is possible to extend sectional or modal models to handle multivariate particle composition distributions. Specifically, we can have a multi-dimensional distribution which is a function of several chemical species or other independent variables. Oshima et al. (2009) used a two dimensional bin structure to represent aerosol size distribution to study black carbon mixing state and its impact on CCN activation and optical properties. In this approach, 40 size bins and 10 BC dry mass fraction bins were used to construct the two dimensional framework. This framework was applied in later studies to investigate aerosol aging processes and radiative impact (Matsui et al., 2013, 2014a). Dergaoui et al. (2013) expanded the sectional approach by discretizing both the mass fraction of chemical species and size distribution into sections. Zhu et al. (2015) applied the same discretization approach and evaluated the impact of mixing state from condensation/evaporation, coagulation and nucleation. Although this approach provides a more detailed representation of aerosol mixing state, the storage and computational burden scale exponentially with number of species, since each species adds an additional dimension. For example, to resolve A model species...
with 20 size bins, it will require a total of $20^4$ bins to represent such a multi-dimensional distribution. The number of bins will become significantly larger when $A$ increases. Therefore, the fully-resolved multivariate sectional or modal models are too computationally expensive to make them feasible.

In contrast, for particle-resolved methods the storage and computational cost scale with the number of particles, not the dimension of the space that the particles are in. By explicitly resolving the high-dimensional particle composition space, particle-resolved methods is capable of representing aerosol mixing state and completely eliminating any errors associated with numerical diffusion. This method has been used in atmospheric science to investigate stochastic coagulation (Guias, 1997) and cloud microphysics (Shima et al., 2009; Arabas et al., 2015).

For this thesis we use the stochastic particle-resolved model PartMC-MOSAIC (Particle Monte Carlo model - Model for Simulating Aerosol Interactions and Chemistry). It was developed by coupling a Monte Carlo particle-resolved aerosol model (PartMC) (Riemer et al., 2009) with a comprehensive aerosol chemistry model (MOSAIC) (Zaveri et al., 2008). PartMC simulates particle emissions, dilution with the background, and Brownian coagulation stochastically by generating a realization of a Poisson process. Aerosol and gas-phase chemistry, particle phase thermodynamics, and dynamic gas-particle mass transfer are treated deterministically using the MOSAIC chemistry model. PartMC-MOSAIC explicitly resolves the composition of individual particles in a given aerosol population and is therefore uniquely suited to investigate the evolution of particle mixing state and the associated CCN activation and optical properties.

PartMC-MOSAIC has been used to simulate aerosol processes in the atmosphere for a wide range of topics, including the quantification of black carbon aging time scales (Riemer et al., 2010; Fierce et al., 2015), the impact of aerosol mixing state on cloud droplet formation (Ching et al., 2012), the heterogeneous oxidation of soot surfaces (Kaiser et al., 2011), and the sensitivity of cloud condensation nuclei activity to particle characteristics at emission (Fierce et al., 2013). It was also used as a modeling tool to explain the diurnal variations of aerosol hygroscopicity and the mixing state of light-absorbing carbonaceous material in the North China Plain (Liu et al., 2011; Ma et al., 2012).

1.2 Objectives

Existing PartMC-MOSAIC studies have mostly been applied to idealized environments. The goal of this thesis is to strengthen the link between PartMC-MOSAIC simulation and atmospheric measurements and experimental data. Specifically, this thesis focuses on developing and applying the PartMC-MOSAIC framework to three distinct scenarios with different environmental conditions. Substantial model development
was necessary for all the three studies.

1. Investigate the evolution of particle mixing state in a ship plume. This involved using a weighted particle scheme in PartMC-MOSAIC (DeVille et al., 2011) to reduce computational cost and including nucleation process during aerosol evolution. These capabilities were made available in PartMC-MOSAIC version 2.2.0. This is the first time where these new techniques were applied to a real-world scenario.

2. Study particle dynamics in a chamber environment. This required adding chamber-specific processes such as wall loss and sedimentation, as well as fractal particle treatment in PartMC framework. The development work has been completed as part of this thesis and will be available in the next PartMC release.

3. Simulate the chemical aging of organic aerosols in air parcel trajectories from CARES fields campaign. This included the implementation of volatility basis set (VBS) framework to predict secondary organic aerosol formation in PartMC-MOSAIC. This implementation has also been completed as part of this thesis.

Comprehensive model-measurement integrations and comparisons were conducted for all three studies. The overarching research questions are: is PartMC-MOSAIC able to capture the evolution of aerosol particles in different environments? What is the dominant process governing the particle evolution?

The scientific contribution of this work is twofold. First, it is a suite of process studies on the evolution of the physico-chemical properties of particles under various environments. Second, this work provides validation for PartMC-MOSAIC due to good agreement to atmospheric observations.

1.3 Organization of thesis

Chapter 2 summarizes the PartMC-MOSAIC model framework and the governing equations that form the basis of the model. Chapters 3 presents the application of PartMC-MOSAIC to an evolving ship plume which represents a real ambient atmospheric environment. We use PartMC-MOSAIC to investigate the evolution of particle mixing state, size distribution and cloud condensation nuclei (CCN) activation properties and examine the relative contribution from microphysical processes including nucleation, condensation and coagulation. This work was published as an article in the *Atmospheric Chemistry and Physics*, with the title “Modeling the evolution of aerosol particles in a ship plume using PartMC-MOSAIC” (Tian et al., 2014).

Chapter 4 discusses the application of PartMC to an aerosol chamber study, which is a closed measurement system. In this work we develop PartMC to include chamber-specific processes such as wall loss and
sedimentation, as well as fractal particle dynamic to account for the effects of particle morphology. This work is prepared as a journal article entitled “Application of the stochastic particle-resolved aerosol model PartMC to chamber experiments”, to be submitted to *Aerosol Science and Technology*.

In Chapter 5 we focus on the modeling of secondary organic aerosols (SOA). To do that we implement volatility basis set (VBS) scheme in PartMC-MOSAIC and apply the updated framework to ambient aerosol trajectories sampled during CARES field campaign in California during June 2000. The chapter is prepared as a journal article entitled “Particle-resolved modeling of secondary organic aerosol formation for the CARES field campaign: a volatility basis set approach” and to be submitted to *Journal of Geophysical Research-Atmosphere*. Chapter 6 summarizes our major findings, discusses its implications and proposes directions for future work.
Chapter 2

Methodology

2.1 PartMC-MOSAIC model overview

A detailed model description of PartMC-MOSAIC is given in Riemer et al. (2009). Here we review the most important features of the model. PartMC is a 0-D or box model, which explicitly resolves the composition of many individual particles within a well-mixed computational volume representing a much larger air parcel. During the evolution of the air parcel moving along a specific trajectory, the mass of each constituent species within each particle is tracked. The relative positions of particles within the computational volume are not tracked. The governing equations in PartMC-MOSAIC framework are presented in Section 2.2

Particle coagulation, emission and dilution with background air are implemented in a stochastic manner. Coagulation between aerosol particles is simulated in PartMC by generating a realization of a Poisson process with a Brownian coagulation kernel. For emission, a finite number of emitted particles is added to the computational volume at each timestep. Over time these finite particle samplings should approximate the continuum emission distribution. We also keep a finite sampling of background particles that dilutes into the computational volume, as well as sampling of particles that are diluted out of the volume. Emission and dilution are assumed to be memoryless, so that emission/dilution of each particle is uncorrelated with other emitted/diluted particles. So far we assume all the computational particles are spherical. The extension of this assumption to include fractal particles is discussed in Chapter 4.

A challenge of particle-resolved models is the large computational burden when simulating the evolution of particles under ambient conditions. Particle size distributions usually cover a very broad size range from a few nanometers to tens of micrometers, and typically the number concentrations of the small particles compared to the large particles differ by several orders of magnitude. Both sub-populations are important as the small particles dominate particle number concentration whereas the large particles dominate particle mass concentrations. Moreover, the most likely coagulation events involve interactions of small and large particles. It is challenging to represent such a particle distribution with a particle-resolved model, so that the large, rare particles are sufficiently resolved, while the overall number of computational particles is
still manageable. Here we used the method by DeVille et al. (2011) to reduce the computational cost and improve the model efficiency. This method is based on the notion that a single computational particle can correspond to some number of real particles, in other words, each computational particle is “weighted” by an appropriate factor. With this approach it is possible to span the large range of sizes and abundances of the particle population, which will prove importance for the ship plume study in Chapter 3.

PartMC is coupled with the state-of-the-art aerosol chemistry model MOSAIC (Model for Simulating Aerosol Interactions and Chemistry) (Zaveri et al., 2008). It treats gas-phase photochemistry, dynamic gas-particle mass transfer and particle phase thermodynamics deterministically. It uses a lumped structure photochemical Carbon Bond Mechanism (CBM-Z) as gas-phase chemistry scheme which contains 77 gas species (Zaveri and Peters, 1999). SOA (secondary organic aerosol) is treated based on the Secondary Organic Aerosol Model (SORGAM) scheme (Schell et al., 2001) which assumes that SOA compounds interact and form a quasi-ideal solution. The gas/particle partitioning of SOA compounds is parameterized according to Odum et al. (1996). The SOA treatment will be improved in this work as will be discussed in Chapter 5. The key aerosol species treated in MOSAIC include sulfate, nitrate, chloride, carbonate, methanesulfonic acid, ammonium, sodium, calcium, other inorganic mass (OIN), BC, primary organic aerosol and secondary inorganic aerosol. OIN are metal oxides, SiO$_2$ and other unmeasured and unknown inorganic species. The particle-resolved capability from coupling PartMC with MOSAIC allows particles to have different physical and chemical properties and therefore different computed physical quantities.

The details of the implementation and the model development as part of this thesis will be discussed in the following individual chapters. The current version of PartMC is available under the GNU General Public License (GPL) at http://lagrange.mechse.illinois.edu/mwest/partmc/, and the MOSAIC code is available upon request from R. A. Zaveri.

### 2.2 Coupled equations governing gas-particle interactions in PartMC-MOSAIC

Assuming that an aerosol particle contains mass $\mu_a > 0$ (kg) of species $a$, for $a = 1, \ldots, A$, the particle composition is described by the $A$-dimensional vector $\vec{\mu} \in \mathbb{R}^A$. The cumulative aerosol number distribution at time $t$ and constituent masses $\vec{\mu} \in \mathbb{R}^A$ is $N(\vec{\mu}, t) \ (m^{-3})$, which is defined to be the number concentration of aerosol particles that contain less than $\mu_a$ mass of species $a$, for all $a = 1, \ldots, A$. The aerosol number distribution at time $t$ and constituent masses $\vec{\mu} \in \mathbb{R}^A$ is $n(\vec{\mu}, t) \ (m^{-3} \ kg^{-A})$, which is defined by
\[
n(\bar{\mu}, t) = \frac{\partial^A N(\bar{\mu}, t)}{\partial\mu_1 \partial\mu_2 \ldots \partial\mu_A} \tag{2.1}
\]

We denote the concentration of trace gas phase species \(i\) at time \(t\) by \(g_i(t) \, (\text{mol m}^{-3})\), for \(i = 1, \ldots, G\), so the trace gas phase species concentrations are described by the \(G\)-dimensional vector \(\vec{g}(t) \in \mathbb{R}^G\). We assume that the aerosol and gas species are numbered so that the first \(C\) species of each undergo gas-to-particle conversion, and that they are in the same order so that gas species \(i\) converts to aerosol species \(i\), for \(i = 1, \ldots, C\). Besides, we further assume that aerosol species \(C + 1\) is water.

The complete set of differential equations governing the time evolution of the multidimensional aerosol size distribution with gas phase coupling in PartMC-MOSAIC is written in Eqs (2.2) and (2.3),

\[
\frac{\partial n(\bar{\mu}, t)}{\partial t} = \frac{1}{2} \int_{0}^{\mu_1} \int_{0}^{\mu_2} \cdots \int_{0}^{\mu_A} K(\bar{\mu'}, \bar{\mu} - \bar{\mu'}) n(\bar{\mu'}, t) n(\bar{\mu} - \bar{\mu'}, t) d\mu_1' d\mu_2' \ldots d\mu_A' \text{coagulation gain}
\]

\[
- \int_{0}^{\infty} \int_{0}^{\infty} \cdots \int_{0}^{\infty} K(\bar{\mu}, \bar{\mu'}) n(\bar{\mu}, t) n(\bar{\mu'}, t) d\mu_1' d\mu_2' \ldots d\mu_A' \text{coagulation loss}
\]

\[
+ \lambda_{\text{dil}}(t)(n_{\text{back}}(\bar{\mu}, t) - n(\bar{\mu}, t)) - \sum_{i=1}^{C} \frac{\partial}{\partial \mu_i} (c_i I_i(\bar{\mu}, \vec{g}, t) n(\bar{\mu}, t)) \text{dilution}
\]

\[
+ \frac{\partial}{\partial \mu_{C+1}} (c_w I_w(\bar{\mu}, \vec{g}, t) n(\bar{\mu}, t)) + \frac{1}{\rho_{\text{dry}}(t)} \frac{d\rho_{\text{dry}}(t)}{dt} g(t) \text{water transfer}
\]

\[
- \int_{0}^{\infty} \int_{0}^{\infty} \cdots \int_{0}^{\infty} I_i(\bar{\mu}, \vec{g}, t) n(\bar{\mu}, t) d\mu_1 d\mu_2 \ldots d\mu_A \text{gas-particle transfer} \tag{2.2}
\]

\[
\frac{dg_i(t)}{dt} = \lambda_{\text{dil}}(t)(g_{\text{back}, i}(t) - g_i(t)) + R_i(\vec{g}) + \frac{1}{\rho_{\text{dry}}(t)} \frac{d\rho_{\text{dry}}(t)}{dt} g_i(t) \text{chemical reactions}
\]

\[
- \int_{0}^{\infty} \int_{0}^{\infty} \cdots \int_{0}^{\infty} I_i(\bar{\mu}, \vec{g}, t) n(\bar{\mu}, t) d\mu_1 d\mu_2 \ldots d\mu_A \text{gas-particle transfer} \tag{2.3}
\]

In Eq. (2.2), \(K(\bar{\mu}_1, \bar{\mu}_2) \, (\text{m}^3 \text{s}^{-1})\) is the Brownian coagulation coefficient between particles with constituent masses \(\bar{\mu}_1\) and \(\bar{\mu}_2\), \(\lambda_{\text{dil}}(t) \, (\text{s}^{-1})\) is the dilution rate, \(n_{\text{back}}(\bar{\mu}, t) \, (\text{m}^{-3} \text{kg}^{-A})\) is the background number distribution, \(c_i\) (kg mol\(^{-1}\)) is the conversion factor from moles of gas species \(i\) to mass of aerosol species \(i\) (with \(c_w\) the factor for water), \(I_i(\bar{\mu}, \vec{g}, t) \, (\text{mol s}^{-1})\) is the condensation fluxes of gas species \(i\) (with \(I_w(\bar{\mu}, \vec{g}, t)\)
the flux for water). In Eq. (2.3), $g_{\text{back},i}(t)$ (mol m$^{-3}$) is the background concentration of gas species $i$, $R_i(g)$ (mol m$^{-3}$ s$^{-1}$) is the concentration growth rate of gas species $i$ due to chemical reactions in the gas phase, and $\rho_{\text{dry}}(t)$ (kg m$^{-3}$) is the dry air density.

The three studies outlined in Section 1.2 focus on expanding different aspects of the governing equations. Study 1 (ship plume study) extends the governing equation by adding nucleation process, and modifying the dilution scheme to account for marine boundary layer environment. Study 2 (chamber study) only focuses on the evolution of aerosols (Eq. 2.2), with adding chamber-specific processes including wall loss and sedimentation. In addition, the Brownian coagulation kernel is updated to include fractal particle dynamics. In study 3 (CARES trajectory study) the gas-particle transfer term in Eqs. 2.2 and 2.3 is modified using VBS framework that estimates additional SOA formation from semi-volatile POA emissions.
Chapter 3

Modeling the evolution of aerosol particles in a ship plume

This chapter presents the application of PartMC-MOSAIC to investigate the evolution of ship-emitted aerosol particles. Comparisons of the results with observations from the QUANTIFY Study in 2007 in the English channel and the Gulf of Biscay showed that the model was able to reproduce the observed evolution of total number concentration and the vanishing of the nucleation mode consisting of sulfate particles. Further process analysis focuses on the evolution of particles in the ship plume including coagulation, condensation and nucleation and their impacts on mixing state and cloud condensation nuclei (CCN) concentrations. The material of this chapter was published in Atmospheric Chemistry and Physics (Tian et al., 2014).

3.1 Background

Emissions from ocean-going ships have been receiving increased attention in recent years due to their adverse effects on coastal and global air quality (Ault et al., 2009; Endresen et al., 2003; González et al., 2011; Moldanová et al., 2009; Eyring et al., 2007), human health (Corbett et al., 2007; Winebrake et al., 2009) and the climate system (Capaldo et al., 1999; Eyring et al., 2010; Lawrence and Crutzen, 1999). Aerosol particles from ship exhaust represent a large fraction of global anthropogenic aerosol emissions (Agrawal et al., 2009; Dominguez et al., 2008) and influence significantly the radiative budget of the atmosphere both directly and indirectly (Capaldo et al., 1999).

Ship-emitted particulates are a mix of different particle types. These include combustion particles consisting mainly of black carbon, primary organic carbon (POC), sulfate and ash, and volatile particles forming from nucleation of sulfuric acid during plume expansion (Song et al., 2003; Cooper, 2003; Petzold et al., 2008). Their overall direct effect on the climate system is complex since BC causes a positive radiative forcing, while sulfuric acid particles cause a negative radiative forcing (Lauer et al., 2007; Kasper et al., 2007). While the different particle types are initially externally mixed, internal mixtures can form as a result of coagulation and condensation processes as the plume evolves, which may significantly alter the particles’ optical properties and hence the magnitude of the direct climate impact (Durkee et al., 2000b; Jacobson
et al., 2011). Particles from ship exhaust can also act as cloud condensation nuclei (CCN) and thus indirectly affect the climate by increasing cloud reflectivity (Twomey et al., 1968; Durkee et al., 2000b,a; Porch et al., 1999; Russell et al., 2000; Peters et al., 2012). The “ship tracks”, shown as the curvilinear cloud structures observed in satellite images of marine cloud fields, in fact represented the first evidence of an indirect effect by ship emissions (Conover, 1966; Coakley et al., 1987). Similar to the particles’ optical properties, their CCN properties may change during the plume evolution, which in turn impacts their indirect effect.

Many studies have been conducted in the past decade to characterize the ship emissions and their effects on climate through a combination of exhaust and plume measurements (Murphy et al., 2009; Frick and Hoppel, 2000; Petzold et al., 2008; Osborne et al., 2001; Sinha et al., 2003; Coggon et al., 2012). Healy et al. (2009) investigated the freshly-emitted ship exhaust particles on a single-particle level using an aerosol time-of-flight mass spectrometer (ATOFMS) at the Port of Cork, Ireland. They identified a unique ship exhaust particle type residing in the ultrafine mode and containing internally mixed elemental and organic carbon, sodium, calcium, iron, vanadium, nickel and sulfate. To quantify the in-plume mixing state Ault et al. (2010) conducted a series of individual ship plume measurements at the port of Los Angeles using a 4 m sampling mast at a site near the center of the main channel. The measurements characterized the size-resolved particle mixing state for individual plumes with plume ages ranging between 10–45 min. Their study showed enhanced sulfate concentration in ship plumes, probably due to vanadium-catalyzed sulfate-production reactions in the plume within minutes of emission.

The evolution of ship-emitted particles has also been investigated in a number of modeling studies. Russell et al. (1999) applied an externally mixed, sectional aerosol dynamic model to characterize condensational and coagulational particle growth during the Monterey Area Ship Tracks (MAST) experiment in 1994 and found that the sulfur content of fuels used in combustion processes had a direct impact on the CCN properties. Later Erlick et al. (2001) applied the same model as described in Russell et al. (1999) together with a delta-Eddington exponential-sum-fit radiation algorithm to simulate aerosol-cloud-interaction during two ship track events in the MAST experiment. The results suggested that both the marine clouds and ship tracks enhanced atmospheric absorption with respect to a clear sky. Song et al. (2003) used a Lagrangian photochemical plume model to explore the in-plume sulfur chemistry and new particle formation. Their findings stressed the importance of photochemistry for the production of sulfuric acid particles in plumes. von Glasow et al. (2003) introduced a plume expansion scheme in a time dependent photochemical model based on an updated version of the box model MOCCA (Model Of Chemistry Considering Aerosols) (Sander and Crutzen, 1996; Vogt et al., 1996) to treat the mixing of background and plume air. The evolution of particles in the plume was tracked by considering dilution and chemical processes, while coagulation was
neglected. The influence of semi-volatile background aerosol particles was found to be important for the in-plume gas phase chemistry, while including the soluble ship-produced aerosols was of little importance for in-plume heterogeneous reactions since dilution significantly reduced ship-derived particles on a very short time scale.

For this study we used a new modeling approach to represent the evolving particle distribution of ship-emitted aerosols, the stochastic particle-resolved aerosol model PartMC-MOSAIC (Particle Monte Carlo model-Model for Simulating Aerosol Interactions and Chemistry) (Riemer et al., 2009). This model explicitly resolves the composition of individual particles in a given aerosol population and is therefore uniquely suited to investigate the evolution of particle mixing states and the associated particle properties. The simulations were initialized with gas and particle information obtained from a test-rig study as part of the European research project HERCULES (High-efficiency Engine R&D on Combustion with Ultra-Low Emissions for Ships) in 2006 using a serial four-stroke marine diesel engine operating on high-sulfur heavy fuel oil (Petzold et al., 2008). We then tracked the particle population for several hours as it evolved undergoing coagulation, dilution with the background air, and chemical transformations in the aerosol and gas phase. We compared the results to aircraft measurements made in the English Channel and the Gulf of Biscay (France) in 2007 as part of the European program QUANTIFY (Quantifying the Climate Impact of Global and European Transport Systems).

New particle formation (nucleation) may play an important role in the evolution of the ship plume particle population (Song et al., 2003). Significant uncertainties are associated with modeling nucleation and growth, both regarding the quantification of the nucleation rates (Lucas and Akimoto, 2006; Yli-Juuti et al., 2011; Pierce and Adams, 2009; Verheggen and Mozurkewich, 2002), as well as regarding the mechanism responsible for particle growth (Spracklen et al., 2008; Kulmala et al., 2004; Westervelt et al., 2014). Here we use the parameterization by Kuang et al. (2008) to investigate when and to what extent nucleation impacts CCN concentration in the plume. This study does not attempt to exhaustively survey the range of currently proposed models for nucleation and subsequent particle growth.

The scientific contribution of this study is twofold. First, it is the first process study on the evolution of the particle-resolved mixing state in ship plumes quantifying the roles of coagulation and condensation in the plume and their impact on CCN properties of the particles. Second, this study provides validation for PartMC-MOSAIC due to good agreement to field observations. The structure of this chapter is as follows. Section 3.2 states the governing equations that form the basis of the model, and Section 3.3 describes the numerical methods. Section 3.4 shows the ship plume modeling results for the simulations. Section 3.5 summarizes our major findings.
3.2 Coupled equations governing gas-particle interactions

Our modeling framework considers a Lagrangian parcel, which simulates the evolution of aerosol particles and trace gases that are emitted by the ship in a volume of air moving along a specified trajectory at the center of the plume. After leaving the exhaust stack the air parcel is not further influenced by emissions. In addition to coagulation and aerosol and gas chemistry within the plume, the model treats mixing of the parcel with background air. Inherent to the parcel modeling approach is the assumption that the plume is immediately well-mixed. Within the air parcel we do not track the physical location of aerosol particles, and we assume homogeneous meteorological conditions and gas concentrations. Concentration gradients across the plume cannot be resolved with this approach and would require the use of a spatially-resolved 3D model framework.

Assuming that an aerosol particle contains mass $\mu_a > 0$ (kg) of species $a$, for $a = 1, \ldots, A$, the particle composition is described by the $A$-dimensional vector $\vec{\mu} \in \mathbb{R}^A$. The cumulative aerosol number distribution at time $t$ and constituent masses $\vec{\mu} \in \mathbb{R}^A$ is $N(\vec{\mu}, t)$ (m$^{-3}$), which is defined to be the number concentration of aerosol particles that contain less than $\mu_a$ mass of species $a$, for all $a = 1, \ldots, A$. The aerosol number distribution at time $t$ and constituent masses $\vec{\mu} \in \mathbb{R}^A$ is $n(\vec{\mu}, t)$ (m$^{-3}$ kg$^{-A}$), which is defined by

$$ n(\vec{\mu}, t) = \frac{\partial^A N(\vec{\mu}, t)}{\partial \mu_1 \partial \mu_2 \ldots \partial \mu_A} \quad (3.1) $$

We denote the concentration of trace gas phase species $i$ at time $t$ by $g_i(t)$ (mol m$^{-3}$), for $i = 1, \ldots, G$, so the trace gas phase species concentrations are described by the $G$-dimensional vector $\vec{g}(t) \in \mathbb{R}^G$. We assume that the aerosol and gas species are numbered so that the first $C$ species of each undergo gas-to-particle conversion, and that they are in the same order so that gas species $i$ converts to aerosol species $i$, for $i = 1, \ldots, C$. Besides, we further assume that aerosol species $C + 1$ is water.

The complete set of differential equations governing the time evolution of the multidimensional aerosol
size distribution with gas phase coupling in PartMC-MOSAIC is written in Eqs. (3.2) and (3.3),

\[
\frac{\partial n(\bar{\mu}, t)}{\partial t} = \frac{1}{2} \int_0^{\mu_1} \int_0^{\mu_2} \cdots \int_0^{\mu_A} K(\mu', \bar{\mu} - \mu') n(\bar{\mu}, t) n(\bar{\mu} - \mu', t) \, d\mu_1' \, d\mu_2' \cdots d\mu_A' \\
\text{coagulation gain}
\]

\[
- \int_0^\infty \int_0^\infty \cdots \int_0^\infty K(\mu, \mu') n(\bar{\mu}, t) n(\bar{\mu} - \mu', t) \, d\mu_1' \, d\mu_2' \cdots d\mu_A' \\
\text{coagulation loss}
\]

\[
+ \lambda_{\text{dil}}(t)(n_{\text{back}}(\bar{\mu}, t) - n(\bar{\mu}, t)) - \sum_{i=1}^C \frac{\partial}{\partial \mu_i} (c_i I_i(\bar{\mu}, \bar{\mu}, t) n(\bar{\mu}, t)) \\
\text{gas-particle transfer}
\]

\[
- \frac{\partial}{\partial \mu_{C+1}} (c_w I_w(\bar{\mu}, \bar{\mu}, t) n(\bar{\mu}, t)) + J_{\text{nuc}}(\bar{\mu}) \delta(\bar{\mu} - \bar{\mu}_{\text{nuc}}) \\
\text{nucleation}
\]

\[
+ \frac{1}{\rho_{\text{dry}}(t)} \frac{d\rho_{\text{dry}}(t)}{dt} n(\bar{\mu}, t) \\
\text{air density change}
\]

\[
\frac{dg_i(t)}{dt} = \lambda_{\text{dil}}(t)(g_{\text{back},i}(t) - g_i(t)) + R_i(\bar{\mu}) + \frac{1}{\rho_{\text{dry}}(t)} \frac{d\rho_{\text{dry}}(t)}{dt} g_i(t) \\
\text{chemical reactions}
\]

\[
- \int_0^\infty \int_0^\infty \cdots \int_0^\infty I_i(\bar{\mu}, \bar{\mu}, t) n(\bar{\mu}, t) \, d\mu_1 \, d\mu_2 \cdots d\mu_A - \frac{v_{\text{nuc}}\rho_i}{c_i} J_{\text{nuc}}(\bar{\mu}) \delta(i, i_{\text{SO}_4}) \\
\text{nucleation}
\]

In Eq. (3.2), \( K(\mu, \mu') \) (m^3 s^{-1}) is the Brownian coagulation coefficient between particles with constituent masses \( \bar{\mu} \) and \( \mu' \) (see Riemer et al. (2009)), \( \lambda_{\text{dil}}(t) \) (s^{-1}) is the dilution rate, \( n_{\text{back}}(\bar{\mu}, t) \) (m^{-3} kg^{-A}) is the background number distribution, \( c_i \) (kg mol^{-1}) is the conversion factor from moles of gas species \( i \) to mass of aerosol species \( i \) (with \( c_w \) the factor for water), \( I_i(\bar{\mu}, \bar{\mu}, t) \) (mol s^{-1}) is the condensation flux of gas species \( i \) (with \( I_w(\bar{\mu}, \bar{\mu}, t) \) the flux for water), \( J_{\text{nuc}}(\bar{\mu}) \) (m^{-3} s^{-1}) is the formation rate of particles by nucleation, \( \delta \) is the Kronecker delta function, \( \bar{\mu}_{\text{nuc}} \) represents the particle composition vector of each nucleated particle. In Eq. (3.3), \( g_{\text{back},i}(t) \) (mol m^{-3}) is the background concentration of gas species \( i \), \( R_i(\bar{\mu}) \) (mol m^{-3} s^{-1}) is the concentration growth rate of gas species \( i \) due to chemical reactions in the gas phase, \( \rho_{\text{dry}}(t) \) (kg m^{-3}) is the dry air density (with \( \rho_i \) the density of gas species \( i \)), and \( v_{\text{nuc}} \) (m^3) is the volume of each nucleated particle. The relevant references regarding the numerical implementation are provided in Section 3.3.

### 3.2.1 Model treatment of dilution

To model the dilution process we followed von Glasow et al. (2003) who proposed a Gaussian plume dispersion model for the evolution of the plume in the horizontal and vertical directions. The time-dependent plume
width \( w_{pl}(t) \) and height \( h_{pl}(t) \) are described by two power laws as:

\[
\begin{align*}
   w_{pl}(t) &= w_0 \left( \frac{t + t_0}{t_0} \right)^\alpha, \\
   h_{pl}(t) &= h_0 \left( \frac{t + t_0}{t_0} \right)^\beta,
\end{align*}
\]

(3.4) (3.5)

where \( w_0 \) and \( h_0 \) are the dimensions of the plume at the start of the simulation. Note that compared to the formulation in von Glasow et al. (2003) we introduced \( t_0 \) in the numerator to avoid a singularity for \( t = 0 \) in the expression for the dilution rate below. The coefficients \( \alpha \) and \( \beta \) are the plume expansion parameters in the horizontal and vertical, respectively. Assuming the plume cross section is semi-elliptic and is given as \( A_{pl} = \frac{\pi}{8} w_{pl} h_{pl} \), the dilution rate \( \lambda_{dil}(t) \) is:

\[
\lambda_{dil}(t) = \frac{1}{A_{pl}} \frac{dA_{pl}}{dt} = \frac{\alpha + \beta}{t + t_0}
\]

(3.6)

Previous ship plume studies have estimated the plume width and height at a plume age of 1 s to be approximately 10 m and 5.5 m, respectively (von Glasow et al., 2003; Durkee et al., 2000a; Ferek et al., 1998), and we used these values for \( t_0, w_0 \) and \( h_0 \), respectively. The parameters \( \alpha = 0.75 \) and \( \beta = 0.6 \) are the “best guesses” estimated from the expansion of ship tracks reported in the literature (von Glasow et al., 2003; Durkee et al., 2000a) and confirmed by observations reported in Petzold et al. (2008). von Glasow et al. (2003) evaluated the influence of mixing by varying \( \alpha \) between 0.62 and 1. The value of \( \alpha = 0.62 \) was deemed unrealistic as it caused a strong and persistent separation between plume and background air, which is not expected to occur in the marine boundary layer. Values of \( \alpha > 0.82 \) caused very strong mixing, most likely only valid in extremely turbulent conditions. From this von Glasow et al. (2003) concluded that \( \alpha = 0.75 \) was appropriate to characterize the plume dispersion. Petzold et al. (2008) derived the values of \( \alpha \) and \( \beta \) by fitting simulated excess CO\(_2\) as a function of plume age to the observed data. The result of \( \alpha = 0.74 \) to 0.76 agreed well with the “best guess” from von Glasow et al. (2003), while their result for \( \beta = 0.70 \) to 0.80 was somewhat higher. While we will use the values of \( \alpha = 0.75 \) and \( \beta = 0.6 \) for our base case, we will also explore the sensitivity to changes in these parameters in Section 3.4.2 below.

We further assume the top of the marine boundary layer to be impenetrable by the plume and define \( z_{MBL} \) as the height of the marine boundary layer. The total dilution rate used in our ship plume simulation
is then written as

\[ \lambda_{\text{di}(t)} = \begin{cases} \frac{\alpha + \beta}{t + t_0} & h_{\text{pl}}(t) < z_{\text{MBL}} \\ \frac{\alpha}{t + t_0} & h_{\text{pl}}(t) = z_{\text{MBL}} \end{cases} \]  

(3.7)

### 3.2.2 Treatment of nucleation

To model the nucleation process we follow the parameterization proposed by Kuang et al. (2008) based on the concentration of sulfuric acid. This uses a power law to quantify the production rate of nucleated particles as follows:

\[ J_{\text{nuc}} = K \cdot [H_2SO_4]^P, \]  

(3.8)

The values of prefactor \( K \) and exponent \( P \) in our model framework are \( 10^{-18} \) m\(^3\) s\(^{-1} \) and 2, respectively, based on least squares fitting between the measured formation rate and corresponding sulfuric acid vapor concentrations at different atmospheric environments as described in Kuang et al. (2008). The rate \( J_{\text{nuc}} \) quantifies the production of particles of diameter 1 nm, which initially consist of sulfuric acid.

### 3.3 Numerical implementation

The detailed description of the numerical methods used in PartMC-MOSAIC is given in Riemer et al. (2009). Here we briefly introduce the salient features of the model. PartMC (Particle-resolved Monte Carlo) is a 0-D or box model, which explicitly resolves the composition of many individual particles within a well-mixed computational volume representing a much larger air parcel. During the evolution of the air parcel moving along a specific trajectory, the mass of each constituent species within each particle is tracked. Emission, dilution, nucleation and Brownian coagulation are simulated with a stochastic Monte Carlo approach. The relative positions of particles within the computational volume are not tracked.

PartMC is coupled with the state-of-the-art aerosol chemistry model MOSAIC (Model for Simulating Aerosol Interactions and Chemistry) (Zaveri et al., 2008) which includes the gas phase photochemical mechanism CBM-Z (Zaveri and Peters, 1999), the Multicomponent Taylor Expansion Method (MTEM) for estimating activity coefficients of electrolytes and ions in aqueous solutions (Zaveri et al., 2005b), the Multi-component Equilibrium Solver for Aerosols (MESA) for intraparticle solid-liquid partitioning (Zaveri et al., 2005a) and the Adaptive Step Time-split Euler Method (ASTEM) for dynamic gas-particle partitioning over size- and composition-resolved aerosol (Zaveri et al., 2008), as well as a treatment for SOA (secondary...
organic aerosol) based on the SORGAM scheme (Schell et al., 2001). The CBM-Z gas phase mechanism treats a total of 77 gas species. MOSAIC treats key aerosol species including sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$), ammonium (NH$_4^+$), chloride (Cl), carbonate (CO$_3^{2-}$), methanesulfonic acid (MSA), sodium (Na), calcium (Ca), other inorganic mass (OIN), BC, POC, and SOA. OIN represents species such as SiO$_2$, metal oxides, and other unmeasured or unknown inorganic species present in aerosols. SOA includes reaction products of aromatic precursors, higher alkenes, α-pinene and limonene.

we used the method by DeVille et al. (2011) to reduce the computational cost and improve the model efficiency. This method is based on the notion that a single computational particle can correspond to some number of real particles, in other words, each computational particle is “weighted” by an appropriate factor. With this approach it is possible to span the large range of sizes and abundances of the particle population as will be demonstrated in Sect. 3.4.

We used model version PartMC 2.2.0 for this study. We initialized all simulations with $10^5$ computational particles. To capture the aerosol dynamics during early plume ages when the particle number concentration rapidly decayed owing to coagulation and dilution, we used a time step of 0.2 s for the first 600 s of simulation time, and a time step of 60 s for the remainder of the simulation.

3.3.1 Aerosol distribution functions

While the underlying multidimensional aerosol distribution is defined in Eq. (3.1), we often project this distribution in appropriate ways to better display the results. We take $N(D)$ to be the cumulative number distribution, giving the number of particles per volume that have diameter less than $D$. We then define the number distribution $n(D)$ by

$$n(D) = \frac{dN(D)}{d\log_{10} D}$$  \hspace{1cm} (3.9)

The underlying particle initial and background number size distributions used in our study were all superpositions of lognormal distributions, each defined by

$$n(D) = \frac{N}{\sqrt{2\pi} \log_{10} \sigma_g} \exp\left(-\frac{(\log_{10} D - \log_{10} D_g)^2}{2 (\log_{10} \sigma_g)^2}\right)$$  \hspace{1cm} (3.10)

where $N$ is the total number concentration, $D_g$ is the geometric mean diameter, and $\sigma_g$ is the geometric standard deviation.
To characterize the particle mixing state, we refer to the mass fraction of a species \( a \) as

\[
w_{a,\text{dry}} = \frac{\mu_a}{\mu_{\text{dry}}}
\]  

(3.11)

where \( \mu_a \) is the mass of species \( a \) in the particle, and \( \mu_{\text{dry}} \) is the total dry mass of the particle. We can then define a two-dimensional number distribution that is a function of both particle composition and diameter. The two-dimensional cumulative number distribution \( N_{a,\text{dry}}(D, w) \) is the number of particles per volume that have a diameter less than \( D \) and a dry mass fraction less than \( w \) for certain species \( a \). Here \( a \) could be BC, POC, sulfate, nitrate, etc. The two-dimensional number distribution \( n_{a,\text{dry}}(D, w) \) is then defined by

\[
n_{a,\text{dry}}(D, w) = \frac{\partial^2 N_{a,\text{dry}}(D, w)}{\partial \log_{10} D \partial w}
\]  

(3.12)

Similarly, we can define a two-dimensional number distribution \( n_{\text{coag}}(D, k) \) based on the number of coagulation events \( k \) that a given particle has experienced during the simulation time. Let \( N_{\text{coag}}(D, k) \) be the cumulative number distribution describing the number of particles per volume with diameter less than \( D \) and that have experienced less than \( k \) coagulation events, \( n_{\text{coag}}(D, k) \) can be written as

\[
n_{\text{coag}}(D, k) = \frac{\partial N_{\text{coag}}(D, k)}{\partial \log_{10} D \partial k}
\]  

(3.13)

To investigate changes in the CCN properties of the aerosols, we use the hygroscopicity parameter \( \kappa \) to define a two-dimensional cumulative number distribution \( N_{\kappa}(D, \kappa) \) in terms of diameter and hygroscopicity parameter. Then the two-dimensional number distribution is written as

\[
n_{\kappa}(D, \kappa) = \frac{\partial^2 N_{\kappa}(D, \kappa)}{\partial \log_{10} D \partial \log_{10} \kappa}
\]  

(3.14)

### 3.3.2 CCN activity module

The unique feature of PartMC-MOSAIC to provide particle-resolved mixing state information enables us to calculate the critical supersaturation \( S_{c,i} \) that an individual particle requires to activate. The procedure is as follows. The per-particle water activity \( a_{w,i} \) is given by:

\[
\frac{1}{a_{w,i}} = 1 + \kappa_i \frac{V_{\text{dry},i}}{V_{w,i}}
\]  

(3.15)
where $\kappa_i$ is a single, dimensionless hygroscopicity parameter to relate particle dry diameter to CCN activity (Ghan et al., 2001; Petters and Kreidenweis, 2007), $V_{\text{dry},i}$ is the dry particle volume and $V_{w,i}$ is the volume of water in the particle. For an aerosol particle $i$ containing several non-water species, the $\kappa_i$ value for the particle is the volume-weighted mean of the individual $\kappa$ value of each constituent species (Petters and Kreidenweis, 2007). Table 3.1 lists $\kappa$ values for individual aerosol components used in this study. The equilibrium saturation ratio $S(D_i)$ over an aqueous particle $i$ is given by the Köhler equation:

$$S(D_i) = a_{w,i} \exp \left( \frac{4\sigma_w M_w}{RT \rho_w D_i^3} \right)$$ (3.16)

where $\sigma_w$ is the surface tension of the solution–air interface, $M_w$ is the molecular weight of water, $R$ is the universal gas constant, $T$ is the temperature, and $D_i$ is the particle wet diameter. Combining Eqs. (3.15) and (3.16) and using wet and dry diameters $D_i$ and $D_{\text{dry},i}$ to represent their respective volumes, we obtain the $\kappa$-Köhler equation based on Petters and Kreidenweis (2007):

$$S(D_i) = \frac{D_i^3 - D_{\text{dry},i}^3}{D_i^3 - D_{\text{dry},i}^3 (1 - \kappa_i)} \exp \left( \frac{4\sigma_w M_w}{RT \rho_w D_i^3} \right)$$ (3.17)

To calculate the critical supersaturation, we set $\partial S(D_i)/\partial D_i$ to zero and numerically solve for the critical wet diameter $D_i$, then use Eq. (3.17) to obtain the critical supersaturation $S_{c,i}$ for each particle.

Table 3.1: List of hygroscopicity values for model species.

<table>
<thead>
<tr>
<th>Species</th>
<th>Hygroscopicity, $\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{SO}_4$</td>
<td>0.9</td>
</tr>
<tr>
<td>$\text{NH}_4\text{HSO}_4$</td>
<td>0.65</td>
</tr>
<tr>
<td>$\text{NH}_4\text{NO}_3$</td>
<td>0.65</td>
</tr>
<tr>
<td>$\text{NaCl}$</td>
<td>1.12</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>–</td>
</tr>
<tr>
<td>POC</td>
<td>0.001</td>
</tr>
<tr>
<td>SOA species</td>
<td>0.1</td>
</tr>
<tr>
<td>BC</td>
<td>0</td>
</tr>
<tr>
<td>Ash</td>
<td>0.1</td>
</tr>
</tbody>
</table>
3.3.3 Setup of case study

Measurements of the particle and gas phase of the raw engine exhaust served as initial input parameters for our model runs. To evaluate our model, the output was compared to measurements performed in a single ship plume and in a ship corridor study. The two campaigns, HERCULES and QUANTIFY SHIPS are briefly described in the following section.

The initial concentrations of gases and particles as well as particle size distribution and composition were obtained from the HERCULES study in 2006 during which a serial four stroke marine diesel engine was used on a test rig (Petzold et al., 2008, 2010). The heavy fuel oil was composed of 86.9 weight-% carbon, 10.4 weight-% hydrogen, 2.21 weight-% sulphur, and some minor constituents. We used the exhaust data under 75 % engine load condition for our model inputs. These exhaust conditions are expected to be similar to the ones encountered in the QUANTIFY SHIPS study, therefore the aerosol population and the gas phase concentrations present in the engine exhaust served as input for the model.

During the QUANTIFY SHIPS field study in June 2007, airborne measurements of a single ship plume (June 14, 2007) as well as aged aerosol in highly frequented sea lanes (June 11, 2007) were performed. During the single-plume study the plume was crossed several times during the time interval of approximately one hour. As in-plume total particle number concentrations we considered the maximum measured concentration during one plume crossing ($D > 4$ nm). Size distributions of both the polluted and the clean marine boundary layer were determined using a combination of instruments capable of measuring in different size ranges. The research domain with the flight path for June 11 is shown in Figure 3.1. The location of the shipping corridor is marked. In addition to the size distributions observed in the shipping corridor, we also used measurements of gas phase species (NO, NO$_y$, O$_3$, SO$_2$, and CO) to qualitatively compare to our simulations. Last but not least, the following meteorological parameters in the well-mixed marine boundary layer were measured and used for the model runs: a relative humidity of $RH = 90 \%$, a temperature $T = 289$ K and a boundary layer mixing height $z_{MBL} = 300$ m. These parameters were obtained from observations on June 14, 2007. The mixing height was derived from the vertical potential temperature profile.

Table 3.2 shows the initial and background conditions of the gaseous species obtained from the measurements during the HERCULES and QUANTIFY study, respectively. From the HERCULES measurements only the total amount of non-methane hydrocarbons (NMHC) was known. We partitioned the total mixing ratio of NMVOCs to different categories based on the composition fractions provided in Eyring et al. (2005), including (1) hexanes and higher alkanes, (2) ethene, (3) propene, (4) toluene, (5) xylene, (6) trimethylbenzenes and (7) other alkene. We then converted these mixing ratios to model surrogate species mixing ratios as listed in Table 3.2 suitable for the use in CBM-Z. Note that CBM-Z is a carbon bond mechanism, and
the model species represent the mixing ratios of constituent groups regardless of the molecule to which they are attached (Stockwell et al., 2012). The background inorganic gas phase mixing ratios in Table 3.2 were obtained by averaging the values along the segment of the flight track as marked in Figure 3.1. This segment was outside the shipping corridor, and sampled at low enough altitude. The background NHMC concentrations were estimated from measurements by Penkett et al. (1993). They were taken on July 8, 1988, while approaching the UK from the West (with similar time and location to the QUANTIFY measurements). The measured species were converted to CBM-Z species including PAR, ETH, OLET, OLEI, TOL and XYL.

Table 3.3 shows the total number concentration, count median diameter and geometric standard deviation, the parameters determining the initial, background and ship corridor size distributions. The initial aerosol size distribution from the test rig study was composed of three distinct modes with one volatile nucleation mode and two larger combustion modes. The volatile mode consisted of 100% sulfate, while BC, POC and ash were present in the two combustion modes. The background aerosol distribution was tri-modal with Aitken, accumulation and coarse modes. We assigned the fractions of sulfate, ammonium, nitrate, POC, BC and sea salt to these three modes based on O’Dowd and De Leeuw (2007).

We initialized our model with $10^5$ computational particles and followed the air parcel as it evolved for 14 h to predict the aged plume and to compare to measurements from the ship corridor. For the base case,
Table 3.2: Gas phase initial and background conditions.

<table>
<thead>
<tr>
<th>MOSAIC Species</th>
<th>Symbol</th>
<th>Initial (ppb)$^a$</th>
<th>Background (ppb)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitric Oxide</td>
<td>NO</td>
<td>8.8·10$^5$</td>
<td>1.86·10$^{-2}$</td>
</tr>
<tr>
<td>Nitrogen Dioxide</td>
<td>NO$_2$</td>
<td>3.7·10$^4$</td>
<td>3.95·10$^{-2}$</td>
</tr>
<tr>
<td>Nitric Acid</td>
<td>HNO$_3$</td>
<td>3.29·10$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Ozone</td>
<td>O$_3$</td>
<td></td>
<td>3.39·10$^1$</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>CO</td>
<td>3.4·10$^4$</td>
<td>1.05·10$^2$</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>SO$_2$</td>
<td>4.7·10$^5$</td>
<td>1.55·10$^{-1}$</td>
</tr>
<tr>
<td>Hydrogen Chloride$^c$</td>
<td>HCl</td>
<td>3.09·10$^5$</td>
<td>5.99·10$^{-1}$</td>
</tr>
<tr>
<td>Paraffin carbon</td>
<td>PAR</td>
<td>3.09·10$^5$</td>
<td></td>
</tr>
<tr>
<td>Ethene</td>
<td>ETH</td>
<td>2.94·10$^4$</td>
<td></td>
</tr>
<tr>
<td>Terminal Olefin Carbons</td>
<td>OLET</td>
<td>3.38·10$^4$</td>
<td></td>
</tr>
<tr>
<td>Internal Olefin Carbons</td>
<td>OLEI</td>
<td>1.55·10$^3$</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>TOL</td>
<td>2.56·10$^4$</td>
<td></td>
</tr>
<tr>
<td>Xylene</td>
<td>XYL</td>
<td>6.06·10$^3$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Initial data are obtained from HERCULES measurement in 2006 under 75 % engine load condition (Petzold et al., 2008, 2010). The attribution of non-methane hydrocarbons is based on Table 2 in Eyring et al. (2005).

$^b$ Background data are obtained from European program QUANTIFY in 2007. NO$_x$ to NO$_y$ ratio is 0.15 based on Table 2 in Shon et al. (2008) in the marine boundary layer.

$^c$ Value from Table 2 in Keene et al. (2007).

$^d$ If no value is listed the species is initialized with 0 ppb.

the simulation started at 2 p.m. LT, similar to the measurement time of the single plume study on 14 June in 2007. During the plume evolution we considered the following processes: dilution with the background air, coagulation of the particles, chemical transformations in the aerosol and gas phase, and phase transitions.

Coagulation and condensation may physically or thermodynamically change the particles’ composition and phase state, and consequently alter the CCN activation properties. To quantify the impact of coagulation and condensation, we carried out two additional simulations, one where coagulation was not simulated (referred to as “only cond.”), and one where chemical transformations were not simulated (referred to as “only coag.”).

We also simulated a sensitivity case by setting the model starting time to 6 a.m. LT instead of 2 p.m., to investigate conditions with a longer exposure to sunlight and hence more opportunity for secondary aerosol mass formation. Analogous to the base case we performed three runs: “cond.+coag.”, “only cond.”, and “only coag.”.
On a process level, a nucleation event can impact CCN concentration in several ways: (1) nucleation produces a large number of additional particles, which can grow into CCN directly if enough condensable material is present; (2) if the condensable material is limited, then the competition for this material between the large near-CCN-active particles and the nucleated small particles could actually lead to less CCN; and (3) the nucleated particles can coagulate with other particles, which could potentially render them CCN-active, increasing the CCN concentration. To investigate the impact of new particle formation on CCN properties in the ship plume, we additionally performed simulations including nucleation as described in Sect. 3.2.2, and the results for the number concentrations, the size distributions, and the resulting CCN spectra will be discussed in Section 3.4.2, 3.4.3 and 3.4.5, respectively.

Due to the stochastic nature of PartMC-MOSAIC, for each simulation we conducted an ensemble of 10 runs and averaged the results of these runs to obtain more robust statistics. To quantify the variability within this ensemble, we show the 95% confidence interval for the size distributions in Figures 3.5 and 3.6 below.

3.4 Results and discussion

In this section we present the results of our base case simulation of the ship plume (start at 2 p.m. LT), and contrast it with the sensitivity case (start at 6 a.m. LT). To provide context, we begin by discussing the simulated evolution of selected trace gas species and bulk aerosol species. We then show the comparison of measured and modeled total number concentrations from a single plume event, as well as the comparison of measured and modeled size distributions from the shipping corridor. Finally, we quantify the role of coagulation and condensation for the evolution of aerosol mixing state and their impacts on CCN properties.

3.4.1 Evolution of gas and bulk aerosol species

Figure 3.2 shows the evolution of key trace gas mixing ratios and bulk aerosol species concentrations in the ship plume as it evolves for 14 h. For our base case (start at 2 p.m. LT), dilution reduced the concentrations of the primary emitted species by several orders of magnitude within the first 15–20 min of simulation time. Ozone was diluted in from the background air. For the base case the transition from day to night occurred at about 6 h after the simulation started. The NO₂ mixing ratio was further decreased after 6 h. While during nighttime the reaction of NO₂ with OH ceases, N₂O₅ and NO₃ are formed. In addition, reactions of NO₃ with aldehydes, alkanes, and DMS deplete NOₓ further.

The OH mixing ratio reached about 0.03 ppt after 2 h of simulation and decreased later in the afternoon.
The HNO₃ mixing ratio reached quickly its background value within the first 10 min, then showed a slight increase during daytime as a result of photochemical processes, and a subsequent decrease due to reaction with sea salt to form sodium nitrate.

Similar to the primary gaseous species, sulfate and BC started out with high initial mass concentrations and their concentrations decreased very quickly due to dilution. There was no net formation of sulfate mass during plume aging since dilution dominated the evolution of total sulfate mass concentration. Note that our predicted sulfate concentration may be underestimated since we did not include vanadium-catalyzed sulfate production reactions in our model, as proposed by Ault et al. (2010). The SOA concentrations increased only by about 0.01 µg m⁻³. The lack of production of secondary aerosol mass was a result of the low mixing ratios of oxidants (such as OH, O₃ and NO₃) in the plume, so that oxidation reactions were largely limited. Our finding is consistent with the results reported in Hobbs et al. (2000), where they did not observe any appreciable increase of the aerosol mass concentration in the ship plume with similar initial conditions and sun light exposure time.

The sensitivity case (start at 6 a.m. LT) shows a maximum OH mixing ratio to be 15 times higher than in the original run, and the corresponding SOA mass concentration was enhanced by a similar magnitude. An increase of sulfate mass concentration was observed after 4 h of simulation, leading to a net production of sulfate mass concentration in the plume of about 2 µg m⁻³. Likewise, the nitrate mass concentration increased to about 6 µg m⁻³. This shows as expected that the production of secondary aerosol species is largely determined by the exposure time to sunlight during daytime.

No observations are available that followed the evolution of a particular plume for several hours, hence a quantitative comparison to our simulation results is not possible. However, mixing ratios of NO, NOₓ, O₃, SO₂, and CO were measured in the shipping corridor on June 11 2007. These can be used for qualitative comparison with our model results. Observed peak values of NO, NOₓ, and SO₂ mixing ratios were 4 ppb, 12 ppb, and 4 ppb, respectively. Observed mixing ratios for O₃ and CO were approximately 35 ppb and 105 ppb, respectively. These values are comparable with the model results after approximately 7 h of simulation time of the sensitivity run (right column in Figure 3.2). The mixing ratios of NO and O₃ of the base case are somewhat lower because this case extends into the nighttime.
Table 3.3: Aerosol initial, background and ship corridor conditions.\(^a\)

<table>
<thead>
<tr>
<th>Initial</th>
<th>(N) (m(^{-3}))</th>
<th>(D_g) (nm)</th>
<th>(\sigma_g)</th>
<th>Composition by Mass (hygroscopicity, (\kappa))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile Mode</td>
<td>(2.29 \times 10^{15})</td>
<td>15</td>
<td>1.66</td>
<td>100% SO(_4) (0.9)</td>
</tr>
<tr>
<td>Combustion Mode 1</td>
<td>(4.36 \times 10^{14})</td>
<td>38</td>
<td>1.40</td>
<td>11.7% BC + 88.3% POC</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.0009)</td>
</tr>
<tr>
<td>Combustion Mode 2</td>
<td>(3.11 \times 10^{10})</td>
<td>155</td>
<td>1.25</td>
<td>27.6% Ash + 8.4% BC + 64.0% POC</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.014)</td>
</tr>
<tr>
<td>Background</td>
<td>(N) (m(^{-3}))</td>
<td>(D_g) (nm)</td>
<td>(\sigma_g)</td>
<td>Composition by Mass(^b) (hygroscopicity, (\kappa))</td>
</tr>
<tr>
<td>Aitken Mode</td>
<td>(9.6 \times 10^8)</td>
<td>40</td>
<td>1.7</td>
<td>9% SO(_4) + 2% NH(_4) + 1% NO(_3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+ 82% POC + 2% BC + 4% Sea salt (0.07)</td>
</tr>
<tr>
<td>Accumulation Mode</td>
<td>(2.3 \times 10^8)</td>
<td>200</td>
<td>1.25</td>
<td>22% SO(_4) + 6% NH(_4) + 1% NO(_3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+ 64% POC + 1% BC + 6% Sea salt (0.163)</td>
</tr>
<tr>
<td>Coarse Mode</td>
<td>(3.2 \times 10^6)</td>
<td>900</td>
<td>1.8</td>
<td>1% NO(_3) + 5% POC + 94% Sea salt (0.999)</td>
</tr>
<tr>
<td>Ship corridor</td>
<td>(N) (m(^{-3}))</td>
<td>(D_g) (nm)</td>
<td>(\sigma_g)</td>
<td>Composition by Mass</td>
</tr>
<tr>
<td>Aitken Mode</td>
<td>(7.7 \times 10^{10})</td>
<td>60</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Accumulation Mode</td>
<td>(1.8 \times 10^8)</td>
<td>220</td>
<td>1.25</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Initial aerosol size distribution and chemical composition data are obtained from HERCULES measurement in 2006 under 75\% engine load condition (Petzold et al., 2008, 2010). Parameters are defined in Eq. 3.10. Background and ship corridor aerosol size distribution data are obtained from European program QUANTIFY in 2007. Note that the ship corridor data is with background distribution excluded.

\(^b\) Background aerosol compositions are estimated from Figure 5 in O’Dowd and De Leeuw (2007).
Figure 3.2: Evolution of gas and bulk aerosol species in the ship plume over a period of 14 h for the base case starting from 2 p.m. (left column) and sensitivity case starting from 6 a.m. (right column).
3.4.2 Evolution of total number concentration in a single plume

Figure 3.3 compares our predicted particle number concentrations to those measured in a ship plume during the single plume study on 14 June 2007. For this figure, only particles in the 10–2000 nm size range were considered, consistent with the size range observed by the SMPS instrument.

Due to the short encounter time with the ship plume, we assumed that the measurements were conducted at the ship plume center line. The measurements were taken within the first hour after the ship emissions entered the atmosphere, representing a relatively fresh plume. The horizontal error bars on the measured values show the estimated errors in determining plume ages. The estimated relative errors in number concentration are less than 8%, and are not visible in this graph due to the logarithmic scaling of the ordinate. As described in Sect. 3.3.3 we initialized the model simulations with data from the HERCULES study, indicated here with the red dot.

The modeled time series of number concentration shows a sharp decrease at the beginning due to dilution and coagulation, and then the model results approach the measurements well when coagulation is included (solid red line). When coagulation was not simulated, the total particle number concentration was overestimated by a factor of ten (blue line). A list of error metrics, including mean bias, mean error, mean normalized bias and mean normalized error, is provided in Table 3.4 for the comparison of simulated and measured data.
Table 3.4: Error metrics for comparison of measured and simulated aerosol number concentrations. The “only cond.”, “only coag.” and “cond.+coag.” entries correspond to simulated number concentrations.

<table>
<thead>
<tr>
<th></th>
<th>only cond.</th>
<th>only coag.</th>
<th>cond.+coag.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Bias</td>
<td>$2.77 \times 10^{11}$ m$^{-3}$</td>
<td>$1.41 \times 10^{10}$ m$^{-3}$</td>
<td>$1.87 \times 10^{10}$ m$^{-3}$</td>
</tr>
<tr>
<td>Mean Error</td>
<td>$2.77 \times 10^{11}$ m$^{-3}$</td>
<td>$1.58 \times 10^{10}$ m$^{-3}$</td>
<td>$1.96 \times 10^{10}$ m$^{-3}$</td>
</tr>
<tr>
<td>Mean Normalized Bias</td>
<td>1096.44%</td>
<td>41.38%</td>
<td>59.55%</td>
</tr>
<tr>
<td>Mean Normalized Error</td>
<td>1096.44%</td>
<td>51.81%</td>
<td>65.11%</td>
</tr>
</tbody>
</table>

observed number concentrations. Note that since the plume encounter times during the measurements were very short, neither size distribution nor chemical composition data could be obtained from the single plume study.

To explore the sensitivity to the choice of the dispersion parameters $\alpha$ and $\beta$, we conducted four sensitivity runs: Two sensitivity runs use the base case value of $\alpha = 0.75$, but combine it with $\beta = 0.7$ (lower end from the range in Petzold et al. (2008)) and $\beta = 0.5$, respectively. Two additional sensitivity runs use the base case value of $\beta = 0.6$, combined with $\alpha = 0.87$ and $\alpha = 0.62$, respectively (same range of values used in von Glasow et al. (2003)). The simulated number concentration from the sensitivity runs were added to Figure 3.3 as broken lines. The parameter combination ($\alpha = 0.62$, $\beta = 0.6$) results in a consistent overprediction of the number concentration by a factor of about 3, while the combination ($\alpha = 0.87$, $\beta = 0.6$) underpredicts the number concentration after a plume age of 30 min. Differences due to variations of $\beta$ are most noticeable during the first 20 min of the plume. Given the simplicity of the model assumptions, we do not attempt to perform a fitting procedure, but conclude from this exercise that using parameter set of our base case ($\alpha = 0.75$, $\beta = 0.6$) captures the observed data reasonably well. Importantly, the spread caused by varying $\alpha$ and $\beta$ is less than the difference between the base case runs with and without coagulation.

Fig. 3.4 shows the evolution of the base-case number concentration when nucleation was simulated. When including only the particles from the observed 10–2000 nm size range, the results are the same as for the corresponding case without nucleation (Fig. 3.4a). However, nucleation did affect the number concentration of particles smaller than 10 nm. Fig. 3.4b shows the evolution of number concentration for particles in the 10–2000 nm range, as well as for those below 10 nm, for the entire 14 h of simulation period. The concentration of nucleated particles (which are assigned the size of 1 nm when they enter the simulation) reached the maximum of $10^{12}$ m$^{-3}$ at 4 pm LT (2 hours after simulation), then gradually decreased to around $10^{10}$ cm$^{-3}$ at 8 pm LT. The concentration of 10–2000 nm particles, however, did not increase, which indicated that the nucleated particles did not grow to sizes larger than 10 nm during the plume evolution.
3.4.3 Evolution of particle size distributions in the shipping corridor

The aerosol population measured in the shipping corridor can be thought of as the superposition of many ship plumes of different, however unknown, ages. This makes it difficult to compare the size distribution measurements quantitatively to the model results, which simulate only one specific plume. Here we attempt to use the observations for a qualitative comparison to see if the PartMC-MOSAIC results are consistent with the observations.

Figure 3.5 displays the in-plume aerosol number distributions for the base case. The red, green and blue curves represent the measured aerosol distributions for initial, background and ship corridor conditions, while the five black curves are the predicted distributions at plume ages of 100 s, 1200 s, 1 h, 5 h and 14 h, respectively. All model results are the averages of an ensemble of 10 runs. The error bars represent the 95% confidence intervals, only shown for the size distribution at 100 s as an example. These are vanishingly small for small particle sizes and are somewhat larger for the size range above 500 nm. This is a result of the fact that fewer computational particles are used to represent the population at larger sizes (even though we used the weighted particle algorithm as described in Sect. 3.3).

To distinguish the effects of coagulation and condensation on particle size distributions, we show the results without simulating coagulation (Fig. 3.5a, “only cond.”), without simulating condensation (Fig. 3.5b, “only coag”), and the case including all processes (Fig. 3.5c, “cond.+coag.”).

Fig. 3.5a shows that particle number concentration was significantly reduced due to dilution within the first 100 s, and simultaneously large particles from background were diluted into the plume so that an accumulation and a coarse mode in the size distributions were formed. However, it is obvious that the
Figure 3.5: Measured aerosol number distributions for background, initial and ship corridor and modeled results for (a) neglecting coagulation, (b) neglecting condensation and (c) including condensation and coagulation at plume ages of 100 s, 1200 s, 1 h, 5 h and 14 h for base case (starting from 2 p.m.). The error bars represent 95% confidence intervals from 10 ensemble runs (only shown for size distribution at 100 s as an example).

The shape of the size distribution observed in the shipping corridor could not be reproduced when coagulation was neglected. The predicted number concentration of small particles was overestimated compared to the ship corridor measurement. For example, at 14 h, the model result overpredicted the number concentration of particles with sizes 30 nm by at least one order of magnitude compared to the observed value. When coagulation was additionally included (Fig. 3.5c), the depletion of the small particles in the volatile mode was captured and the modeled and observed size distributions agreed qualitatively better.

Fig. 3.5b (condensation not simulated) shows a very similar pattern compared to Fig. 3.5c, which confirms that the impact of condensation on the size distributions was small for this case due to the short daylight exposure time and consequently limited amount of photochemical production of secondary aerosol mass, as
already pointed out in the discussion of Fig. 3.2. Therefore, in this case, coagulation and dilution were the driving processes that shaped the size distributions.

To investigate the impact of daylight exposure time further, Fig. 3.6 shows the in-plume particle size distributions for the simulation of the sensitivity case, with a simulation start of 6 a.m. The size distributions of plume ages smaller than 1 h were similar to those for the base case. However in the more aged plume (at 5 h and 14 h), condensation of secondary aerosol set in, which shifted the particles to larger sizes. Condensation in this case greatly altered the size distribution, as shown in Fig. 3.6a and 3.6c. As in Fig. 3.5, we see that including coagulation led to particle size distributions that are qualitatively in better agreement with the observations.
Figure 3.7: Measured aerosol number distributions for background, initial and ship corridor and modeled results with nucleation for (a) base case (from 2 pm) (b) sensitivity case (from 6 am) at plume ages of 100 s, 1200 s, 1 h, 5 h and 14 h. The error bars represent 95% confidence intervals from 5 ensemble runs (only shown for size distribution at 100 s as an example).

Overall, Figs. 3.5 and 3.6 demonstrate that dilution and coagulation were two major processes dominating the evolution of particles in ship plumes. While dilution significantly reduced the overall in-plume number concentrations, coagulation reduced the number concentrations of the small volatile particles. Moreover, the condensational growth of particles was sensitive to the start of the simulation time. An earlier starting time with a longer, and more intense sun exposure enhanced the production of secondary aerosol mass. Generally, our model results are qualitatively consistent with the observations in the shipping corridor.

The evolution of the size distributions with nucleation enabled is shown in Fig. 3.7 for both the base case (Fig. 3.7a) and the sensitivity case (Fig. 3.7b). Note that we extended the diameter axis down to 1 nm to capture the full range of sizes. In both cases, nucleated particles formed a distinct mode below 10 nm, and the number concentrations in this mode gradually decreased due to coagulation and dilution, and moved to larger sizes due to condensation during the plume evolution. While for the base case the nucleated particles form a distinct mode that remains below 10 nm in size, for the sensitivity case they grow beyond this size, which has an appreciable impact on CCN concentrations as shown in Section 3.4.5.
3.4.4 Impact of coagulation and condensation on particle mixing state

To elucidate how the mixing state evolved over the course of the simulation of the base case, we show the two-dimensional number distribution as a function of dry diameter and dry mass fraction of BC and sulfate in Fig. 3.8 and Fig. 3.9 at plume ages of 100 s, 1 h and 5 h. The simulation results for the three cases “only cond.”, “only coag”, and “cond+coag” are placed next to each other for comparison. The definition of the two-dimensional number distribution function is given in Sect. 3.3.1.

BC initially resided in the two combustion aerosol modes and also to a small extent in the background aerosol mode. Without coagulation (“only cond.”, Figs. 3.8a, d, and g), the three particle source types were at all times distinctly separated shown as horizontal bands in the two-dimensional number distribution plot. However, when coagulation was included (Figs. 3.8b, c, e, f, h and i), a continuum of internal mixing states was established very quickly with BC dry mass fraction ranging from 0 to 12%.

When condensation was not simulated (“only coag.”), the initial range of BC mass fractions from 0 to 12% was maintained (Figs. 3.8b, e, and h). When condensation was simulated, the maximum BC mass fraction decreased over time to values as low as 9% after 5 h of simulation, as seen in Fig. 3.8i. For the sensitivity case (not shown) this is even more pronounced, and the maximum BC mass fraction decreased to values as low as 5%.

An analogous evolution of the sulfate mixing state was observed. A continuum of internal mixtures from 0 to 100% of sulfate dry mass fraction formed due to coagulation (Figs. 3.9b, e, h and c, f, i), while for the simulation without coagulation the particles from different sources remained externally mixed (Figs. 3.9a, d, and g). When condensation was not simulated, (“only coag.”, Figs. 3.9b, e, and h), the range of sulfate mass fractions completely filled the range from 0 to 100% as the population evolved.

An interesting feature of the sulfate mixing state is that after 1 h, the previously horizontal lines representing the particles from various sources became “tilted” (Figs. 3.9d, f, g and i). This tilt formed because secondary aerosol mass condensed on the particles, and the resulting change in sulfate dry mass fraction was relatively larger for small particles compared to large particles. For the volatile-mode particles the tilt was the result of ammonia partitioning into the aerosol phase and thereby reducing the sulfate dry mass fraction. In our simulation ammonia originated from the evaporation of ammonium nitrate present in the background particles. For the combustion-mode particles the tilt was due to the condensation of sulfuric acid, thereby increasing the sulfate dry mass fraction. This two-way condensation effect on sulfate mixing state was observed for both cases when condensation was included. A similar behavior could also be observed for the BC mixing state (e.g. Figs. 3.8d and g). Note that other secondary aerosol species form as well and contribute to a change in mixing state, such as secondary organic aerosol and aerosol nitrate, however for
Figure 3.8: Two-dimensional number distributions $n_{\text{BC,dry}}(D, w)$ after 100 s, 1 h and 5 h of simulation for the base case. The two-dimensional number distribution is defined in Eq. (3.12).

brevity we do not include these results as figures.
Figure 3.9: Two-dimensional number distributions \( n_{SO_4,\text{dry}}(D, w) \) after 100 s, 1 h and 5 h of simulation for the base case. The two-dimensional number distribution is defined in Eq. (3.12).
3.4.5 Cloud condensation nuclei activity

We will now address the question to what extent the changes in aerosol mixing state translated into changes in CCN activity. For this purpose it is convenient to display the number distribution $n_\kappa(D,\kappa)$ based on Eq. (3.14), as established in Fierce et al. (2013). Also shown in these graphs are the lines of constant critical supersaturation, which are a function of particle size and hygroscopicity parameter. For a given environmental supersaturation threshold the particles with critical supersaturations equal to or smaller than the threshold will activate, i.e. these are the particles to the right of the corresponding critical supersaturation line. Fig. 3.10 shows these number distributions for 0 s, 100 s, 1 h and 5 h for the base case simulation, including condensation and coagulation. Initially ($t = 0$ s), three distinct bands represented the volatile and the two combustion modes. The position of each band was determined by the initial size distribution and composition of each mode determining the overall hygroscopicity. The volatile-mode particles, which contained 100% sulfate, had the largest hygroscopicity, while hydrophobic combustion-1-mode particles, consisting of POC and BC, were most difficult to activate initially.

At $t = 100$ s, the space between the three bands had begun to fill out due to coagulation and the associated change of mixing state. As a result, for a subset of the combustion mode particles the hygroscopicity parameter increased. After 1 h and 5 h, the average $\kappa$ values of the aerosol population increased further, indicating that a larger fraction of the particles had the potential to become a CCN for a certain supersaturation threshold. Note that particles larger than 0.2 $\mu$m represented mainly the background particles, as shown in Fig. 3.5.

Fig. 3.11 shows the CCN concentration versus critical supersaturation $S$ ranging from 0.01% to 1% for 0 s, 1 h, 5 h, and 14 h for the base case. The three different curves at each time represent the cases where coagulation was not simulated (“only cond.”, blue), where condensation was not simulated (“only coag.”, green) and where both condensation and coagulation was simulated (“cond.+coag.”, red). As the simulation time progressed, the “cond.+coag.” case showed consistently larger CCN concentrations than the “only coag.” case, but only for supersaturations above a certain threshold (e.g. $S = 0.4\%$ for $t = 1$ h). This is due to the fact that more particles are closer to the activation threshold in the case of higher supersaturations, so adding some hygroscopic material by condensation can have an impact on CCN concentration. Note that this threshold changed with time. At $t = 1$ h it was $S = 0.4\%$, while for $t = 5$ h and $t = 14$ h it was lowered to $S = 0.2\%$. This is consistent with Fig. 3.10, which shows that the overall population moved up (i.e. reached higher $\kappa$-values) in the diagram over time.

The total number concentrations for the “only cond.” case were about one order of magnitude larger than for the cases that included coagulation. This means that there were more particles available that could act...
Figure 3.10: Two-dimensional number distribution $n_\kappa(D, \kappa)$ (base case, condensation and coagulation included) at 0 s, 100 s, 1 h and 5 h. The 2-D distribution is defined in Eq. (3.14).

as CCN, but at the same time they all competed for condensable material. The “only cond.” case resulted in smaller CCN concentrations than the other two cases for $S$ less than about 0.7%. This is because most of the combustion particles remained too hydrophobic in the absence of coagulation, and also because there was not enough condensable material available to render these particles hygroscopic enough to activate at supersaturations below 0.7%. However, the CCN concentration of the “only cond.” case exceeded the other two cases for $S$ larger than 0.7% when the growth due to condensation was sufficient to enable activation.

We conclude from Fig. 3.11, that coagulation increased the particle hygroscopicity of initially hydrophobic particles. Coagulation therefore may enhance the CCN number concentrations, while decreasing the total particle number concentration. Condensation can further enhance the hygroscopicity of particles, leading to an increase of total CCN number concentration if those particles are near the activation threshold.

Interestingly, the three cases resulted in the same CCN concentration for supersaturation thresholds below 0.2%. The particles that formed CCN at these low supersaturations were mostly background particles
Figure 3.11: CCN number concentrations as the function of critical supersaturation at 0 s, 1 h, 5 h and 14 h for the base case.

from the accumulation and coarse mode, which have already low critical supersaturations when they enter the simulation. For the base case, the aging of combustion particles by coagulation or condensation was not sufficient to increase their hygroscopicity to the extent that they could activate at such low supersaturation levels.

Similar CCN spectra resulted for the sensitivity case (Fig. 3.12). However, condensation had a larger impact in this case due to the increased formation of secondary aerosol mass compared to the base case. This can be seen most clearly for low supersaturation thresholds (lower than 0.2%) after 14 h of simulation. For example, at $S = 0.2\%$, the CCN concentration for the “cond.+coag.” case was six times that of the “only coag.” case, and 3.5 times that of the “only cond.” case.

Fig. 3.13 shows the comparison of the CCN spectrum with and without nucleation for the base case. Coagulation and condensation were included for these simulations. When nucleation is included, the CCN concentration remains unchanged for supersaturations below 0.6%. For higher supersaturations, the simulation with nucleation yields somewhat higher CCN concentrations. For example, at 5 h, nucleation increased the CCN(0.6) concentration from 2422 cm$^{-3}$ to 2496 cm$^{-3}$ for the base case, and from 3053 cm$^{-3}$ to 3200 cm$^{-3}$ for the sensitivity case. This is consistent with the findings described above.

For the sensitivity case, including nucleation led to much larger differences after several hours of simulation. This can be seen in Fig. 3.14d ($t = 14$ h), where the CCN concentration for supersaturations above
0.3% increased by about one order of magnitude when nucleation was included. Interestingly, for this time, we also observe that for supersaturation lower than 0.3% the CCN concentration decreased when nucleation was included. This counterintuitive result is a reflection of competition for condensable material between the larger near-CCN-active particles and the nucleated particles.

It has been reported that the typical supersaturation for marine stratocumulus is around 0.1% (Hoppel et al., 1996; Martucci and O’Dowd, 2011). Our results suggest that the impact of ship-emitted particles on marine cloud formation will significantly depend on the time of the day that these particles are exposed to the marine boundary layer.
Figure 3.13: CCN number concentrations as the function of critical supersaturation at 0 s, 1 h, 5 h, and 14 h for the base case, comparing the simulation with nucleation enabled to the simulation with nucleation disabled.

Figure 3.14: CCN number concentrations as the function of critical supersaturation at 0 s, 1 h, 5 h, and 14 h for the sensitivity case, comparing the simulation with nucleation enabled to the simulation with nucleation disabled.
3.5 Conclusions

In this chapter we presented the application of the stochastic aerosol model PartMC-MOSAIC to investigate the evolution of aerosol mixing state and associated changes of CCN properties in a ship plume. This work provides the first validation study of PartMC, and we showed that the model results agreed well with observed particle number concentrations.

From our process analysis we conclude that for our base case dilution and coagulation were the two major processes influencing the particle distribution and the resulting CCN activation properties. Dilution reduced the in-plume total particle number concentration by about four orders of magnitude within 15 min from simulation start. Coagulation further reduced the particle number concentration by another order of magnitude and preferentially depleted small volatile particles. To adequately capture the evolution of the size distribution, it was essential to include coagulation.

Moreover, coagulation amongst the particles and condensation of secondary aerosol material altered the particle mixing state in the fresh plume, leading to internally mixed aerosols containing BC and sulfate within the first 1–2 min after emission, which evolved further over the course of the simulation. This impacted the CCN properties even for conditions when only small amounts of hygroscopic secondary aerosol mass were formed, as it applied for our base case simulation. However, the impact depended on the supersaturation threshold. For the base case, at the end of the 14-h simulation neglecting coagulation (but simulating condensation) did not have any impact of the CCN concentration below supersaturation values of 0.2%. For supersaturations between $S = 0.2\%$ and $S = 0.7\%$ neglecting coagulation resulted in a reduction of the CCN concentration, for example by 37% and 28% for supersaturation thresholds of 0.3% and 0.6%, respectively. For supersaturations larger than 0.7% neglecting coagulation resulted in an overestimation of CCN concentration, about 75% for $S = 1\%$. On the other hand, neglecting condensation, but simulating coagulation, did also not impact the CCN concentrations below 0.2%. It resulted in an underestimation of CCN concentrations for larger supersaturations, e.g. 18% for $S = 0.6\%$. From this we conclude that, for the base case conditions, coagulation had a larger impact on CCN concentrations than condensation.

This picture changed somewhat for conditions with higher formation rates of secondary aerosol mass. This can be seen for low supersaturation thresholds (lower than about 0.3%) after 14 h of simulation. For example, at $S = 0.2\%$, neglecting coagulation resulted in a 70% decrease of CCN concentrations, whereas neglecting condensation resulted in a 83% decrease. While neglecting condensation resulted in lower CCN concentrations over the whole range of supersaturations, neglecting coagulation led to a large increase in CCN concentrations for supersaturations larger than 0.3%. For example, for $S = 0.6\%$ the CCN concentration for the “only cond.” case is seven times that of the “coag.+cond.” case.
We also explored the role of new particle formation for the evolution of the ship plume aerosol population using the nucleation parameterization by Kuang et al. (2008). For the base case the influence of nucleation on CCN concentration was limited because there was not enough condensable material available to grow the particles formed by nucleation to CCN-relevant sizes. For the sensitivity case, after the newly-formed particles were exposed to about 10 hours of growth, the CCN concentration was increased by about one order of magnitude when nucleation was included as long as the supersaturation threshold was sufficiently high, in our case higher than 0.3%.
Chapter 4

Application of PartMC model to chamber experiments

This chapter discusses the development of PartMC model to represent the aerosol evolution in an aerosol chamber, with the intention to use the model as a tool to interpret and guide chamber experiments in the future. We added chamber-specific processes to our model formulation such as wall loss due to particle diffusion and sedimentation, and dilution effects due to sampling. We also implemented a treatment of fractal particles to account for the morphology of agglomerates and its impact on aerosol dynamics. We verified the model with published results of self-similar size distributions, and validated the model using experimental data from an aerosol chamber. This work was a collaboration with Dr. Benjamin Brem who took the measurements in 2012. At that time Dr. Brem was a graduate student in the research group of Prof. Mark Rood and Prof. Tami Bond at Department of Civil and Environmental Engineering in University of Illinois at Urbana-Champaign. This chapter is prepared as a journal article for submission to Aerosol Science and Technology.

4.1 Introduction

Stochastic particle methods are widely used across different communities in science and engineering. Gillespie (1975) set a milestone in applying this technique to the evolution of physical particle populations by developing the exact Stochastic Simulation Algorithm to simulate the collision of cloud droplets. Since then many studies have developed this method further (e.g. Eibeck and Wagner (2001), Gillespie et al. (2009) and Roh et al. (2011)). Variants of this method have been used to investigate the evolution of specific particle systems, for example for industrial aerosol applications (e.g. Wells et al. (2006) and Shekar et al. (2012)), for application in astrophysics (e.g. Ormel and Spaans (2008) and Okuzumi et al. (2009)), and for applications in atmospheric sciences (e.g. Shima et al. (2009) and Riemer et al. (2009)).

This study applies the stochastic particle-resolved model PartMC (Riemer et al., 2009) to the simulation of aerosol particles in an aerosol chamber. PartMC was developed to simulate the evolution of aerosol particles in an air parcel in the atmosphere. Atmospheric aerosol particles typically consist of a complex
mixture of different chemical species, with their sizes ranging from a few nanometers to tens of micrometers (Pöschl, 2005; Seinfeld and Pandis, 2006; Kolb and Worsnop, 2012). The particle-resolved approach is auspicious for modeling such a system as it allows for explicitly resolving the full composition space without any a priori assumptions about particle composition. Since the per-particle composition governs the aerosols’ optical properties and their ability to form cloud droplets these details are important for determining the aerosol impact on climate (Zaveri et al., 2010).

PartMC simulates stochastically particle emissions from different sources into the air parcel, dilution of parcel air with background air, and Brownian coagulation of particles by generating a realization of a Poisson process. Using the “weighted flow algorithm” by DeVille et al. (2011) improves the model efficiency and reduces ensemble variance. The PartMC model was coupled with the state-of-the-art aerosol chemistry model MOSAIC (Zaveri et al., 2008) to treat gas chemistry, particle phase thermodynamics, and dynamic gas-particle mass transfer. So far PartMC-MOSAIC has been used to simulate aerosol processes in the atmosphere for a wide range of topics. For example, we applied the model to quantify black carbon aging time scales (Riemer et al., 2010; Fierce et al., 2015), and the impact of aerosol mixing state on cloud droplet formation (Ching et al., 2012). Other model applications included the heterogeneous oxidation of soot surfaces (Kaiser et al., 2011), and the characterization of the aerosol evolution in ship plumes (Tian et al., 2014).

The contributions of this study are the verification and validation of PartMC to simulate aerosol processes in a chamber environment. The term verification refers to the comparison of simulation results to theoretical benchmark data (Thacker et al., 2004; Battjes and Stive, 1985), while the term validation refers to the comparison of simulations results to experimental data (Oreskes et al., 1994; Nowak, 2013). This not only necessitated implementing chamber-specific loss processes such as wall loss and sedimentation, but also representing fractal-like agglomerates and developing an objective optimization procedure to estimate required model parameters. As such, this study lays the foundation for using PartMC as a tool to interprete and design aerosol chamber experiments in the future. This chapter is organized as follows. Section 4.2 states the governing equation for the evolution of the population in the chamber environment and treatments of wall loss and fractal particle dynamics in our PartMC model. Section 4.3 presents the verification of the coagulation code using self-preserving size distributions. Section 4.4 presents the code validation procedure using results from chamber experiments, and Section 4.5 summarizes our findings.
4.2 Numerical implementation

4.2.1 Governing equation for the chamber environment

Our aim was to simulate the evolution of an aerosol particle population after being introduced into an aerosol chamber. To isolate the impact of coagulation and wall loss on the size distribution evolution, additional particle emissions are not introduced after the start of the simulation. Further, we only consider the evolution of a single, non-volatile aerosol species in the chamber, excluding gas-to-particle conversion and aerosol chemistry in our current model framework. The relevant processes are therefore coagulation, dilution, and wall loss. The differential equation governing the time evolution of the aerosol size distribution \( n(\mu, t) \) in the chamber environment is written as follows:

\[
\frac{\partial n(\mu, t)}{\partial t} = \frac{1}{2} \int_0^\mu K(\nu, \mu - \nu)n(\nu, t)n(\mu - \nu, t)d\nu - \int_0^\infty K(\mu, \nu)n(\mu, t)n(\nu, t)d\nu - n(\mu, t)\lambda_{\text{dil}}(t) - n(\mu, t)(\alpha_{\text{D}}^\mu(t) + \alpha_{\text{S}}^\mu(t))
\]

(4.1)

In Eq. (4.1), \( K(\mu, \nu) \) (m\(^3\) s\(^{-1}\)) is the coagulation coefficient between particles with constituent masses \( \mu \) and \( \nu \), \( n(\mu, t) \) (m\(^{-3}\)) is the aerosol number distribution at time \( t \), \( \lambda_{\text{dil}}(t) \) (s\(^{-1}\)) is the dilution rate, and \( \alpha_{\text{D}}^\mu \) and \( \alpha_{\text{S}}^\mu \) (s\(^{-1}\)) are the wall loss rate coefficients due to diffusion and sedimentation, respectively.

4.2.2 Wall loss treatment

A challenge for chamber studies arises from quantifying wall losses due to particle diffusion and sedimentation to the chamber wall. Misestimation of these wall losses can result in inaccurate interpretation of the experimental results as for example shown for secondary aerosol yield measurements by Matsunaga and Ziemann (2010). Modeling wall loss is difficult because of the complexity of the wall loss rate dependence, which could include aerosol particle size, structure and material of the chamber, electric charge distribution, and turbulence in the chamber. Past studies have proposed detailed formulations to quantify the wall loss rate (Crump and Seinfeld, 1981; McMurry and Rader, 1985; Park et al., 2001; Verheggen and Mozurkewich, 2006). They often introduce parameters that are difficult to constrain and that might vary between different experiments. Therefore, inverse approaches which use size distribution measurements to constrain these
unknown parameters are often conducted to obtain the functional forms of wall-loss rate (Pierce et al., 2008).

In this study we followed the method by Naumann (2003), which provides a detailed formalism of size-dependent wall loss due to particle diffusion and sedimentation. Based on Naumann (2003), the wall loss rates due to diffusion and sedimentation are shown in Eq. (4.2) and Eq. (4.3), respectively.

\[
\alpha_D^\mu = \frac{D(R_{me,\mu})A_D}{\delta_D V} \quad (4.2)
\]

\[
\alpha_S^\mu = 4\pi \rho R_{m,\mu}^3 g D(R_{me,\mu})A_S \frac{3kTV}{(4.3)}
\]

In Eq. (4.2), \(D(R_{me,\mu}) \text{ (m}^2 \text{s}^{-1})\) is the diffusion coefficient for particle \(\mu\), \(R_{me} \text{ (m)}\) is the particle mobility equivalent radius, \(A_D \text{ (m}^2)\) is the diffusional deposition area, \(\delta_D \text{ (m)}\) is diffusional boundary layer thickness, and \(V \text{ (m}^3)\) is the volume of the chamber. \(\delta_D\) has the following formulation based on Fuchs (1964) and Okuyama et al. (1986),

\[
\delta_D = k_D \left( \frac{D}{D_0} \right)^a \quad (4.4)
\]

where \(k_D \text{ (m)}\) and \(a\) are chamber-specific parameters and their values will vary between different experimental set-ups, \(D_0 \text{ (m}^2 \text{s}^{-1})\) is the unit diffusion coefficient. In Eq. (4.3), \(R_m\) is particle mass-equivalent radius, and \(A_S\) is the sedimentation area.

### 4.2.3 Fractal particle treatment

Irregular, fractal-like particles, including soot (Moldanová et al., 2009; Lapuerta et al., 2006) and soot-inorganic mixtures (Wentzel et al., 2003), are ubiquitous in both natural environments and technical applications. In addition, fractal-like agglomerates can also be formed from packing of spherical primary particles (Eggersdorfer and Pratsinis, 2014). These particles exhibit significantly different dynamics and optical properties from those of spherical particles (Wu and Friedlander, 1993; Pranami et al., 2010; Sorensen, 2001; Chen et al., 1990), such as enhanced coagulational growth due to the increased collision cross section. In this study we implemented the formalism of fractal particles described in Naumann (2003). As we will show later, this is essential to successfully model the evolution of the observed size distributions.
The number of monomers \( N \) in a fractal-like agglomerate can be related to the particle geometric radius \( R_{\text{geo}} \) by

\[
N = \frac{1}{f} \left( \frac{R_{\text{geo}}}{R_0} \right)^{d_f}
\]  

(4.5)

where \( f \) is the volume filling factor quantifying how much available volume will be occupied by spherical monomers, \( R_0 \) (m) is the radius of primary particles, \( d_f \) is the fractal (or Hausdorff) dimension which determines the growth rate of fractal agglomerates due to collision processes (Wu and Friedlander, 1993), \( R_{\text{geo}} \) (m) is the effective geometrical radius of a fractal particle, which is defined as the radius of the particle’s closest convex envelope. Let \( m(R_{\text{geo}}) \) (kg) be the particle mass, \( R_{\text{geo}} \) can be related to \( m(R_{\text{geo}}) \) by

\[
R_{\text{geo}} = R_0 \left( \frac{3f m(R_{\text{geo}})}{4\pi \rho R_0^3} \right)^{\frac{1}{d_f}}
\]

(4.6)

In order to obtain the diffusion coefficient \( D \) to calculate the Brownian coagulation rate, \( R_{\text{geo}} \) will first be converted to mobility equivalent radius in continuum regime \( R_{\text{me},c} \) (m) using a convenient mathematical form based on the Kirkwood-Riseman (KR) theory (Kirkwood and Riseman, 1948)

\[
R_{\text{me},c} = h_{KR} R_{\text{geo}} = (-0.06483d_f^2 + 0.6353d_f - 0.4898) R_{\text{geo}}
\]

(4.7)

where \( h_{KR} \) is Kirkwood-Riseman ratio. The mobility equivalent radius \( R_{\text{me}} \) that covers the entire dynamic regime can then be obtained by

\[
R_{\text{me}} = R_{\text{me},c} \frac{C(R_{\text{me}})}{C(R_{\text{eff}})}
\]

(4.8)

Eq. (4.8) will be solved iteratively to obtain \( R_{\text{me}} \). Eqs. (4.6), (4.7) and (4.8) allow the conversion between measured mobility size distribution (e.g., from differential mobility analyzer or scanning mobility particle sizer) and corresponding mass distribution. In Eq. (4.8), \( R_{\text{eff}} \) is the effective radius, and \( C \) is a correction function considering the transition from the continuum to the free molecular regime. \( R_{\text{eff}} \) is given by
\[ R_{\text{eff}} = \frac{S_{\text{acc}}}{4\pi R_{\text{me,c}}} \]  

\[ S_{\text{acc}} = 4\pi R_0^2 N^{d_s/3} \left[ (d_s - 2) \left( \frac{z}{N} \right)^{1-\gamma} - d_s + 3 \right] \]

where \( d_s \) is the surface fractal dimension, which has the value of 3 when \( d_f \leq 2 \), and \( 6/d_f \) when \( 2 \leq d_f \leq 3 \). \( z \) and \( \gamma \) are the scaling factor and exponent with values of 1 and 0.86, respectively.

The correction function \( C \) in Eq. (4.8) has the form of

\[ C(R) = 1 + A \frac{l}{R} + Q \frac{l}{R} \exp \left( -b \frac{R}{l} \right) \]

where \( A = 1.142 \), \( Q = 0.588 \) and \( b = 0.999 \) are constant parameters with values determined empirically (Allen and Raabe, 1985; Cheng et al., 1988), \( l \) is the mean free path of carrier gas molecules.

After obtaining \( R_{\text{me}} \) from Eq. (4.8), the diffusion coefficient \( D \) of fractal particles will be calculated as

\[ D = \frac{kTC(R_{\text{me}})}{6\pi\eta R_{\text{me}}} \]

where \( k \) (J K\(^{-1}\)) is Boltzmann constant, \( T \) (K) is temperature, and \( \eta \) (kg m\(^{-1}\) s\(^{-1}\)) is the gas viscosity.

Then the Brownian coagulation kernel \( K(\mu, \nu) \) can be written as

\[ K(\mu, \nu) = \frac{4\pi[D(R_{\text{me},\mu}) + D(R_{\text{me},\nu})][R_{\text{geo},\mu} + R_{\text{geo},\nu}]}{1 + G_{\mu\nu}} \]

\[ G_{\mu\nu} = \frac{4[D(R_{\text{me},\mu}) + D(R_{\text{me},\nu})]}{R_{\text{geo},\mu} + R_{\text{geo},\nu}} \sqrt{8kT(m_{\mu} + m_{\nu})} \]

In this study, we assume the primary particles constructing the fractal agglomerates to be non-overlapping, equal-size spheres (constant \( R_0 \)) with homogeneous density, which is a common assumption in theoretical analyses (Ulrich and Subramanian, 1977; Koch and Friedlander, 1990). Furthermore, we assume that \( d_f \) and \( f \) will not change during the evolution of particles, although studies have argued that the fractal dimension may change as the size distribution of fractal agglomerates evolves (Kostoglou and Konstandopoulos, 2001; Artelt et al., 2003). We will justify these assumptions in Section 4.4.2.
4.3 Model verification of fractal treatment

When Brownian coagulation is the dominant mechanism for particle growth, particle size distributions assume an asymptotic shape after sufficiently long time, independent of the initial size distribution (Friedlander and Wang, 1966; Friedlander, 2000). These so-called self-preserving size distributions are represented by graphing the dimensionless particle number density function $\psi(\eta)$ as a function of the dimensionless particle volume $\eta$ (Eq. 4.16).

![Figure 4.1: Self-preserving size distributions in free molecular regime (left panel) and continuum regime (right panel) obtained from PartMC simulations (symbols) and the Vemury and Pratsinis (1995) code (lines) at different fractal dimensions ($d_f$). The error bars represent 95% confidence intervals from 10 ensemble run. The self-preserving size distribution is defined in Eq. 4.16.](image)

In this study, the implementation of the fractal particle treatment in PartMC was verified by comparing the simulated self-preserving size distributions to those from theoretical results reported in Vemury and Pratsinis (1995) in both free molecular and continuum regimes. The detailed formalism is provided as follows.

Let $n(v, t)$ (m$^{-3}$) be the aerosol size distribution, $c_n$ (m$^{-3}$) be the total number concentration and $c_v$ be the total volume concentration (m$^3$ m$^{-3}$), for particle with volume of $v$ at time $t$, we have

$$\frac{n(v, t)dv}{c_n} = \psi \left( \frac{v}{\bar{v}} \right) d \left( \frac{v}{\bar{v}} \right)$$  \hspace{1cm} (4.15)

where $\bar{v} = c_v/c_n$. Define $\eta = v/\bar{v} = c_n v/c_v$, we will obtain

$$\psi(\eta) = \frac{n(v, t)c_v}{c_n^2}$$  \hspace{1cm} (4.16)

which form does not change with time (self-preserving).
The dimensionless time $\tau_f$ in free molecular regime is defined as

$$\tau_f = \left( \frac{6kTR_0}{\rho} \right)^{1/2} N_0 t$$

(4.17)

where $N_0$ (m$^{-3}$) is the initial total number concentration. The dimensionless time $\tau_c$ in continuum regime is

$$\tau_c = \frac{2kT}{3\eta} N_0 t$$

(4.18)

Based on Naumann (2003), the Brownian coagulation kernels $K(\mu, \nu)$ in the limits of the two dynamic regimes are written in Eqs. (4.19) and (4.20), respectively.

$$K(\mu, \nu)_{\text{(free)}} = \sqrt{\frac{6kTR_0}{\rho}} \left( \frac{1}{N^1_{\mu}} + \frac{1}{N^1_{\nu}} \right)^{f^{2/dt}} \left( N^1_{\mu} + N^1_{\nu} \right)^{2}$$

(4.19)

$$K(\mu, \nu)_{\text{(cont)}} = \frac{2kT}{3\eta h_{KR}} \left( \frac{1}{N^1_{\mu}} + \frac{1}{N^1_{\nu}} \right)^{\left( N^1_{\mu} + N^1_{\nu} \right)}$$

(4.20)

Note that although Eqs. (4.19) and (4.20) are slightly different from those in Vemury and Pratsinis (1995) (with additional $f^{2/dt}$ term in Eq. (4.19) and $1/h_{KR}$ term in Eq. (4.20)), the shape of the self-preserving size distributions described in Eq. (4.16) will not change in the long time regime since the coagulation rates are enhanced by the same, constant factor (assuming $dt$ does not change with time).

We followed the same scenario set-up and model initialization as discussed in Vemury and Pratsinis (1995) as well as in Naumann (2003) and used $10^5$ computational particles to initialize the simulation. Because of the stochastic nature of PartMC, for each case we conducted an ensemble of ten runs with different random seeds, and averaged the results of these runs to obtain more robust statistics.

The results of $\psi(\eta)$ versus $\eta$ are shown in Fig. 4.1 for both of the free molecular and continuum regimes. The error bars represent the 95% confidence intervals from ten ensemble PartMC runs. In addition, Fig. 4.2 shows the decay of normalized number concentrations versus dimensionless time $\tau_f$ and $\tau_c$ in the two dynamic regimes for various $dt$ values. $\tau_f$ and $\tau_c$ are defined in Eqs. 4.17 and 4.18, respectively. Perfect agreement is...
observed, confirming the successful implementation of fractal particle treatment in PartMC.

Figure 4.2: Normalized number concentration decay as a function of dimensionless time obtained from PartMC simulations (symbols) and the Venmury and Pratsinis (1995) code (lines) for various $d_f$ values in free-molecular regime (left panel) and continuum regime (right panel). The dimensionless time is defined in Eq. 4.17 for free molecular regime and Eq. 4.18 for continuum regime.

4.4 Model validation

4.4.1 Chamber measurements

Experiments were conducted in a 209 L, cylindrical, stainless steel chamber (Fig. 4.3) that was electrically grounded. The chamber was filled the first minutes of each experiment with dried, poly-disperse, charge neutralized ammonium sulfate aerosol that was generated by atomizing an aqueous 0.0001 g cm$^{-3}$ ammonium sulfate solution with a constant output atomizer (TSI 3076, Fig. 4.3a). The atomizing pressure was set at 241 kPa (35 psi). Before entering the chamber and dilution with particle-free dry air, the aerosol was dried with a custom silica gel diffusion dryer and charge neutralized with a custom neutralizer (BMI Inc.) containing four Polonium 210 ionizer plates (500 µC each, Amstat Corp., Staticmaster 2U500). Particles with an aerodynamic diameter greater than 500 nm were removed with a greased two stage Berner type impactor (Berner et al., 1979) before entering the chamber.

After filling the chamber with atomized aerosol, the atomizer setup was disconnected from the chamber and the evolution of the size distribution was measured every 7 minutes with a modified scanning mobility particle sizer instrument (SMPS, TSI Instruments, 3934, Fig. 4.3b). This instrument consisted of a Polonium 210 (Amstat Corp., Staticmaster 2U500) neutralizer, a Differential Mobility Analyzer (DMA, TSI3071A) and
a Condensation Particle Counter (CPC, TSI 3022A) operating in low flow mode (0.3 L min\(^{-1}\)). Modification of the original instruments configuration was the use of an HEPA filtered recirculating sheath airflow that was set to 2.4 L min\(^{-1}\). Actual air flow rates were checked and adjusted by comparing them to a Primary Standard Airflow Calibrator (Gilian Gilibrator) for each experiment. The voltage up-scan time was set to 300 s, whereas the down-scan time was set to 60 s. These settings allowed a sizing range of particle diameters between 15.4 and 1000 nm. The delay time and sizing accuracy of the SMPS system was evaluated by performing up- and down-scans for 200±5 nm and 350±6 nm mono-disperse polystyrene latex (PSL) spheres (Thermo Scientific, 3200A/3350A). The aerosol instrument manager software (TSI AIM Version 9.0, TSI Inc.) was used to collect and process the data from the SMPS system. The embedded multiple particle charge correction inversion algorithm from the TSI aerosol instrument manager software accounted for multiple charged particles.

The experimental conditions of datasets used as initialization and comparison with PartMC simulations are tabulated in Table 4.1. Experiments 1 and 2 were conducted with a chamber filling time of 6 minutes, whereas Experiment 3 had a filling time of 10 minutes. The evolution of the particle size distribution was tracked in each experiment for a minimum of 5 hours. The relative humidity and temperature monitored near the inlet and at the outlet of the chamber ranged from 3.2 to 9.1% and from 19.5 to 22.2°C, respectively.
Table 4.1: Initial conditions for ammonium sulfate experiments from UIUC chamber measurements.

<table>
<thead>
<tr>
<th>ID</th>
<th>Initial conc. (cm(^{-3}))</th>
<th>Initial mean diam. (µm)</th>
<th>Initial standard dev. (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.275 ( \times ) (10^5)</td>
<td>114</td>
<td>53.9</td>
</tr>
<tr>
<td>2</td>
<td>3.548 ( \times ) (10^5)</td>
<td>93.2</td>
<td>53.8</td>
</tr>
<tr>
<td>3</td>
<td>1.196 ( \times ) (10^6)</td>
<td>71.5</td>
<td>48.9</td>
</tr>
</tbody>
</table>

for all experiments. Filter samples were collected at the end of each experiment by emptying the barrel onto 47 mm PTFE Membrane Filters (FGLP04700, Fisher, Inc.). These samples were then used for scanning electron microscopy (SEM) imaging to obtain the microstructure of particles.

### 4.4.2 Determination of model parameters

Including wall loss and fractal dynamics introduces five unknown parameters in the governing equation, namely two parameters in Eq. 4.4 (prefactor \(k_D\) and exponent \(a\)), and three in Eq. 4.5 (\(d_f\), \(R_0\) and \(f\)). As we will show in section 4.4.2, we use SEM images to estimate the parameters \(R_0\) and \(f\). We determine the remaining three parameters by a global optimization procedure as described in section 4.4.2.

#### Determination of parameters \(f\) and \(R_0\)

Fig. 4.4 shows the SEM images of the filters at the end of experiment 1, after about 6 hours of evolution. The particles show as bright agglomerates, some of which are highlighted with red circles on Fig. 4.4. Note that the fibrous and the darker agglomerated structures are the teflon filter. The images reveal that over the course of the experiment the dry ammonium sulfate particles formed agglomerates consisting of spherical primary particles.

SEM images have been analyzed using the image analysis software (ImageJ version 10.2, NIH) to estimate the values of the radius of primary particles \(R_0\) and the volume filling factor \(f\). The primary particles are not mono-disperse, but show a size distribution with median diameter of about 90 nm. Fig. 4.5 shows the histogram of the size distribution of 130 particles identified from the SEM images. Since in the current model implementation the primary particles size is set to a constant value during the entire simulation time, we tested the sensitivity of the predicted size distribution to different \(R_0\) values.

Fig. 4.6 shows the comparison of number distribution at \(t = 280\) min from experiment 1 using three different \(R_0\) values: 15 nm (the smallest), 45 nm (median) and 80 nm (around maximum). All other parameters are set to the same values for the three simulations. The three curves almost overlap with each other, with a maximum percentage difference (between \(R_0 = 15\) nm and 80 nm) of 24% at particle diameter
Figure 4.4: Scanning electron microscope (SEM) images of particle filter from experiment 1 at different resolutions. The stripes represent the fibers of the filter.

Figure 4.5: Histogram of primary particle size distribution obtained from the analysis of SEM images as shown in Fig. 4.4.

of 100 nm, and 5% at 200 nm. Compared to measurement uncertainty of 40% at 100 nm and 15% at 200 nm (quantified based on Fig. 4.8), we conclude that varying $R_0$ values has only a small effect on the simulation results. Therefore, we set $R_0$ value to be 45 nm, which is the median radius from the sample.

The volume filling factor $f$ accounts for the fact that the spherical primary particles can only occupy as much as 74% of the available volume. Given the closely packed structure as shown in Fig. 4.4, we assumed that around 70% of the available volume will be occupied by the monomers (close to the extreme case),
corresponding to a $f$ value of 1.43. Similarly to the sensitivity test regarding $R_0$, we tested the sensitivity to the choice of parameter $f$. Fig. 4.7 shows the number distribution comparison from simulation results using $f = 1.0, 1.35, 1.43$ and $2.0$, representing that the monomers occupy 100%, 74%, 70% and 50% of the available volume, respectively. The value $f$ of 1.0 is in fact physically impossible, however we include it as a limiting case. The maximum percentage difference (between $f = 1.0$ and 2.0) is again small, with 25% at particle diameter of 100 nm and 15% at 200 nm. In addition, the SEM images provided a constraint to the selection of $f$ value that $f$ should be close to its minimum value. Therefore, a fixed $f$ value of 1.43 was chosen for the model simulation.

**Optimization procedure**

With the determination of $R_0$ and $f$ values in the previous section, the governing equation described in section 4.2 now has three unknown parameters left: $k_D$ and $a$ in Eq. (4.4) for the wall loss calculation, and $d_f$ in Eq. (4.5) for the fractal formalism. To find the appropriate values for these unknown parameters, inverse approaches using non-linear least-square fitting optimization on size distribution measurements were often conducted (Pierce et al., 2008). We apply the similar approach in this study. To determine the combination of free parameters that gives the best agreement between simulation and measurements, we produce an ensemble of simulations for which we vary the parameters systematically between simulations. The best fit is determined when a chosen error metric is minimized.

In particular, we varied $k_D$ from 0.025 to 0.095 with increments of 0.005, $a$ from 0.22 to 0.27 with
Figure 4.7: Particle number distributions obtained from PartMC simulation on experiment 1 at 280 min using $f = 1.0$, 1.35, 1.43 and 2.0, respectively.

increments of 0.01, and $d_i$ from 1.5 to 3.0 with increments of 0.1. These values are within the ranges reported in previous studies (Bunz and Dlugi, 1991; Naumann, 2003). This amounts to a total of 14,400 simulations with $15 \times 6 \times 16$ cases, and each case is repeated 10 times with different random seeds.

Our error metric, $\epsilon$, is based on a weighted $\ell^2$-norm of the difference in the discretized number size distributions of simulation and measurement at time $j$:

$$
E_j^2 = \sum_{i=1}^{N_{bin}} \frac{1}{\sigma_{i,j}^2} (n_{sim,i,j} - n_{mea,i,j})^2,
$$

where $n_{sim,i,j}$ and $n_{mea,i,j}$ are the simulated and measured number concentration densities in size bin $i$ at time $j$, respectively, and $N_{bin}$ is the number of size bins. The weighting factor $\sigma_{i,j}^2$ is the uncertainty that arises from both of the measurement and the simulation. Similar to the approach in Moore et al. (2010), the total uncertainty at time $j$ for $i^{th}$ size bin is

$$
\sigma_{i,j}^2 = \sigma_{flow,i,j}^2 + \sigma_{size,i,j}^2 + \sigma_{count,i,j}^2 + \frac{1}{N_{run}} \sigma_{partmc,i,j}^2.
$$

The measurement results have estimated uncertainties of 1.5% for flow rate ($\sigma_{flow}$), and of 5% for determining the particles size ($\sigma_{size}$). In addition, Poisson statistics was applied to approximate the raw count uncertainty ($\sigma_{count}$). To quantify the stochastic error of the PartMC simulations, we performed each run repeatedly with different random seeds and calculated mean and standard deviations. The number of repeats is denoted by
Table 4.2: Optimal parameters obtained by minimizing the error between simulated and observed results. Rows 1–3 show the results for applying the optimization procedure individually to each experiment. Rows 4–6 show the results for applying the optimization procedure to all three experiments combined.

<table>
<thead>
<tr>
<th>ID</th>
<th>$k_D$</th>
<th>$a$</th>
<th>$d_f$</th>
<th>error</th>
<th>$\epsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (indiv.)</td>
<td>0.06</td>
<td>0.26</td>
<td>2.2</td>
<td></td>
<td>6.8926</td>
</tr>
<tr>
<td>2 (indiv.)</td>
<td>0.06</td>
<td>0.22</td>
<td>2.2</td>
<td></td>
<td>7.3177</td>
</tr>
<tr>
<td>3 (indiv.)</td>
<td>0.04</td>
<td>0.25</td>
<td>2.4</td>
<td></td>
<td>14.1940</td>
</tr>
<tr>
<td>1 (comb.)</td>
<td>0.06</td>
<td>0.26</td>
<td>2.3</td>
<td></td>
<td>8.0859</td>
</tr>
<tr>
<td>2 (comb.)</td>
<td>0.06</td>
<td>0.26</td>
<td>2.3</td>
<td></td>
<td>9.6211</td>
</tr>
<tr>
<td>3 (comb.)</td>
<td>0.06</td>
<td>0.26</td>
<td>2.3</td>
<td></td>
<td>14.9126</td>
</tr>
</tbody>
</table>

$N_{\text{run}}$ in Eq. 4.22, which was set to ten in our case. The standard deviation of the size distribution obtained from the ensemble runs is the uncertainty from PartMC, denoted by $(\sigma_{\text{partmc}})$, which is divided by $N_{\text{run}}$ to obtain the uncertainty in the mean.

The best fit is obtained by minimizing the root mean square of the relative errors over the entire simulation period, $\epsilon$:

$$
\epsilon = \sqrt{\frac{1}{N+1} \sum_{j=0}^{N} E_j^2},
$$

(4.23)

where $N$ is the total number of time steps.

4.4.3 Results

With datasets from three experiments available, we first performed the optimization procedure for each dataset individually to explore to what extent the obtained values for $k_D$, $a$, and $d_f$ vary between datasets. The results are shown in the first three rows of Table 4.2. While the parameter values are not identical for the three experiments, they remain in a relatively small range, which suggests that all three experiments can be modeled by using the same set of free parameters. This statement is justified by performing the optimization procedure on all three experiments combined, which results in an error increase of only 18% on average (rows 4–6 of Table 4.2). In the following we will present the results of the individual optimization first, and then discuss the combined optimization.

Bunz and Dlugi (1991) indicated that $k_D$ is proportional to the laminar boundary layer and can vary between different experiments. Our best-estimates for $k_D$ are about 10 times higher than the value reported in Bunz and Dlugi (1991). For the parameter $a$ Bunz and Dlugi (1991) reported a value of 0.25 from previous theoretical derivations and 0.274 from their experiments. Our optimal values for $a$ are between 0.22 and 0.26 and close to these literature values. The optimal fractal dimensions range between 2.2 and 2.4, clearly

64
below the value of 3 for spherical particles.

Fig. 4.8 shows the evolution of measured and simulated number size distributions at 7 min, 70 min and 210 min for experiment 1 using the best-estimate values of the parameters for this experiment. The shaded areas indicate the estimated uncertainty based on Eq. (4.22) with the width of $3 \times \sigma$, i.e. we expect 95% of the values to be within the bounds of the shaded range. Note that the maximum values on the vertical axes changes between the three panels to ensure better readability. For the entire simulation time of about 3.5 hours, the simulated distributions match the experimental results very well. This is further proved by displaying the time evolution of several key parameters of measured and simulated size distributions, including mean diameter, standard deviation and skewness, as shown in Fig. 4.9. For comparison, we also included the simulated size distribution when spherical particles are assumed throughout the entire simulation (blue trace in Fig. 4.8). This simulation result does not capture the measured distribution, confirming our strategy to include the treatment for fractal particles.

![Figure 4.8](image)

Figure 4.8: Experimental and simulated time evolutions of number distributions from experiment 1 at 7 min, 70 min and 210 min (left to right). Shaded areas represent $3 \times \sigma$ as described in Eq. (4.22). The blue curve represents the simulated distribution assuming $d_t = 3$. The parameters $k_d$, $a$, and $d_t$ were determined based on experiment 1 only.

![Figure 4.9](image)

Figure 4.9: Time evolution of experimental and simulated mean diameter, standard deviation of size and skewness of size distribution (left to right) from experiment 1. The parameters $k_d$, $a$, and $d_t$ were determined based on experiment 1 only.

Fig. A.1 and Fig. A.2 in Appendix A show the results for all three experiments. Except for one occasion (experiment 3, after 7 min) all model results are within the range of the uncertainties. Overall, the good agreement between PartMC simulations and chamber measurement indicates that the updated model is able to capture the evolution of particles in a chamber environment undergoing Brownian coagulation and wall
losses.

A potential concern with an optimization procedure as used in this work is that different combinations of free parameters may result in errors of similar magnitude. To investigate this, we show in Fig. 4.10 for experiment 1 the dependence of $\epsilon$ on each of the three parameters individually, while keeping the other two constant and equal to their optimal values. These curves should exhibit a clear minimum within the range of parameters used, which then indicates the optimal parameter combination. Fig. 4.10 confirms this for experiment 1, and an overview for all three experiments is shown in Fig. A.3. We do see some flattening in the curve of experiment 2 when $k_d$ is varied, which indicates that the fitting results are not sensitive to the values of parameters within the given range. From these figures we also learn that the fractal dimension $d_f$ is always the dominant factor determining $\epsilon$ compared to $k_D$ and $a$.

We further quantified the relative importance of particle loss due to coagulation and wall loss with two additional sensitivity runs for which coagulation and wall loss were disabled, respectively (see Fig. A.4). For experiment 1, after around 5 hours, wall loss and coagulation accounted for an additional 5% and 20% of particle loss, respectively, hence both processes are indeed important in shaping the aerosol size distribution.

Lastly, since we obtained similar optimal values for the three individual experiments, we performed one overall optimization procedure of all three experiments together. The best-estimate values for $k_D$, $a$ and $d_f$ for the combined optimization procedure based on experiments 1, 2 and 3 are $k_D = 0.06$, $a = 0.26$ and $d_f = 2.3$. As expected, the combined optimization increases the error somewhat, namely by 17%, 31% and 5% for experiments 1, 2, and 3, respectively, as listed in Table 4.2, rows 4–6. Still, the simulated size distributions remained within the range of the uncertainties as demonstrated in Fig. A.5, the time series for simulated size distribution parameters agreed well with the measured ones (Fig. A.6), and the optimal combination of parameters corresponds to a unique minimum in the error function (Fig. A.7). We conclude that one set of parameter values ($k_D = 0.06$, $a = 0.26$ and $d_f = 2.3$) is sufficient to successfully simulate all three experiments.
4.5 Conclusions

We extended the stochastic particle-resolved model PartMC to allow for the representation of fractal particle structure and for wall loss to simulate the evolution of coagulating particle populations in a chamber environment. Including wall loss and fractal dynamics in the governing equation introduced five unknown parameters. We constrained two of them (radius of the primary particles \( R_0 \) and volume filling factor \( f \)) using SEM images and determined the remaining three parameters (wall loss parameters \( k_D \) and \( a \), and fractal dimension \( d_f \)) by a global optimization procedure. We show that excellent agreement between modeled and measured size distributions can be achieved if the optimization procedure is applied to each experiment individually. Further, we can successfully simulate the measured size distributions by using the same set of parameters for all three experiments obtained from applying the optimization procedure to all three experiments combined.

The scientific contribution of this study is a successful verification and validation of the PartMC model. It sets up a model framework that can be further applied to more complex experiments, for example to investigate the evolution of aerosol mixing state when secondary aerosol material is coating the particles.

Currently the model uses a constant value of fractal dimension throughout the simulation period. From the comparison of the model results to the experimental data we conclude that using a constant \( d_f \) value is a good approximation for simulating coagulating particle populations in these experiments. We plan to implement a time- and size-dependent fractal dimension in the future to better quantify particle restructuring during more complex mixing and coating processes. This can be easily achieved by adding fractal dimension as an additional entry in particle-resolved representation using PartMC model. At the same time, this would necessitate more detailed particle size measurements to constrain the rate of change of \( d_f \) during the evolution of particles in the chamber.
Chapter 5

Secondary organic aerosol formation during the CARES field campaign

The previous two chapters focused on the physical aging of aerosols. In this chapter we will investigate the chemical aging of aerosols in ambient environment. Specifically, we use PartMC-MOSAIC to characterize the formation of secondary organic aerosol during CARES field campaign which was conducted during June 2010. This required the implementation of the “volatility basis set framework” to take into account the semi-volatile nature of primary emissions and the subsequent chemical oxidation in the atmosphere. This work was a collaboration with Dr. Jerome Fast and Dr. Joseph Ching from Pacific Northwest National Laboratory, who processed the data for model input and observation. This chapter is prepared as a journal article for publication in the Journal of Geophysical Research.

5.1 Background

5.1.1 Secondary organic aerosol and its role in the atmosphere

Organic aerosols (OA) are ubiquitous in the atmosphere and typically comprise a major fraction of submicron aerosol mass in ambient air (refer to Figure 1.5) (Saxena and Hildemann, 1996; Andreae and Crutzen, 1997; Kanakidou et al., 2005; Zhang et al., 2007). Based on the sources and formation mechanisms, OA can be classified into two categories: primary organic aerosols (POA) and secondary organic aerosols (SOA). POA come from direct emissions including fossil fuel combustion, meat cooking and biomass burning (Rogge et al., 1993a; Mohr et al., 2009; Paglione et al., 2014; Zheng et al., 2014). SOA are produced from atmospheric oxidation processes that convert volatile organic compounds (VOCs) to nonvolatile or semi-volatile species, which may subsequently nucleate to form new particles (Zhang et al., 2004) or condense onto existing particles through gas-to-particle partitioning (Pankow, 1994; Odum et al., 1996; Seinfeld and Pankow, 2003; Kroll and Seinfeld, 2008; Hallquist et al., 2009). The VOC precursors can be of anthropogenic or biogenic origin. Recent studies have shown that SOA can further be formed via other processes such as heterogeneous reactions on particle surfaces (Knopf et al., 2005), oligomerization in aqueous phase (Liu et al., 2012) and chemical reactions in cloud/fog/rain droplets (Ervens et al., 2011).
SOA are observed to be a major component in atmospheric environments. On the global scale, SOA represent around 60% of the overall OA loading (Kanakidou et al., 2005). This number can be even larger on the regional scale, including both urban and remote areas. For example, Turpin and Huntzicker (1995) showed that SOA can contribute to as much as 80% of OA mass during peak oxidation conditions in Los Angeles area. Xu et al. (2015) conducted ambient OA measurement in Atlanta and revealed that the seasonal SOA fraction in total OA varied between 47% to 79%. Jimenez et al. (2009) summarized results from aerosol mass spectrometry (AMS) measurements on locations in the Northern Atmosphere and indicated that SOA can make up a fraction of over 90% of OA mass concentration in remote areas. The ubiquity and dominance of SOA exert significant impacts on human health and climate radiative system. Baltensperger et al. (2008) conducted analyses of the lung cells after exposure to SOA and observed moderate increase of necrotic cell death due to high molecular weight SOA. Gaschen et al. (2010) performed similar experiments and analysis as Baltensperger et al. (2008) and found decreased phagocytic activity in human macrophages exposed to SOA from α-pinene. Scott et al. (2014) investigated the direct and indirect effects of biogenic SOA using a combination of global aerosol microphysics model and an offline radiative transfer model. The presence of biogenic SOA was observed to increase the global annual mean CCN concentration by 3.6–21.1% at 0.2% supersaturation, and pose a global annual mean first aerosol indirect effects between $-0.22 \text{ W m}^{-2}$ and $-0.77 \text{ W m}^{-2}$. Overall, it is of great necessity to accurately monitor and simulate the properties of SOA to facilitate future climate assessment.

5.1.2 Challenges in measuring and simulating SOA

Existing measurements have great difficulty in capturing SOA formation and estimating their subsequent evolution in the atmosphere. SOA consist of hundreds of individual species, and each of them may contain a lot more isomers (Goldstein and Galbally, 2007). Therefore, it is impossible to explicitly characterize the SOA composition using existing experimental instruments. Instead, current approaches tried to measure the bulk SOA concentration using indirect methods, or characterize the composition information by functional groups in SOA (Hallquist et al., 2009). The start-of-the-art techniques include both offline and online methods. Offline methods (e.g., gas chromatography/mass spectrometry, liquid chromatography/MS) provide detailed information on SOA chemical composition but with low time and size resolution (Forstner et al., 1997; Kourtchev et al., 2015). On the other hand, online methods (e.g., aerosol mass spectrometry) provide less detailed composition information but have high size resolution and real-time data (Jayne et al., 2000; Nash et al., 2006). Moreover, the formation of SOA involves complex reactions, or series of reactions including thousands of precursors and products, and the formation mechanism is also sensitive to atmospheric
conditions, such as temperature, humidity and OH/O₃/NOₓ levels (Kroll and Seinfeld, 2008; Kroll et al., 2009; Carlton et al., 2009). Figure 5.1 (taken from McMurry et al. (2004, Chap. 3)) shows the speciation results for organic aerosol in Southern California (Rogge et al., 1993b). It is a clear demonstration that even we can identify hundreds of individual organic compounds, these only represent around 15% of the total organic mass.

Figure 5.1: Speciation results for organic aerosol in Southern California (Rogge et al., 1993b). Figure taken from (McMurry et al., 2004, Chap. 3).

Due to the limitations in measurement techniques and knowledge of SOA formation mechanisms, and the cost involved in the analytical methods required for complex reactions (even if we knew the exact reaction mechanisms), the estimation of SOA production in existing numerical models is largely simplified. Existing models use surrogate species to represent SOA instead of explicitly resolving individual species. Pankow (1994) proposed thermodynamic partitioning theory for SOA formation, where SOA consisted of a mixture of semi-volatile organic compounds that can partition between aerosol and gas phases. The partitioning was defined by using an equilibrium partitioning coefficient which was inversely proportional to the saturation vapor pressure of the pure semi-volatile compound. Odum et al. (1996) extended the framework by Pankow (1994) and determined the volatility distribution of the oxidation products as a function of the semi-volatile product yields and partition coefficients of each product. Two surrogate products, including a more volatile

![Figure 5.1](image-url)
product and a less volatile product, were used due to good fit to the yields obtained from the chamber studies. This “two-product” model was then used as a standard in representing SOA formation mechanism and widely applied in later atmospheric models (Seinfeld and Pankow, 2003; Dechapanya et al., 2004; Lack et al., 2004; Henze and Seinfeld, 2006; Parikh et al., 2012) and is currently used in PartMC-MOSAIC.

Recent studies have shown that existing models using simplified SOA formation representations may lead to underestimation of SOA production in the atmosphere (Griffin et al., 2005; Heald et al., 2005; Morris et al., 2006; Johnson et al., 2006; Hodzic et al., 2009). Although the underlying mechanisms responsible for this underestimation are still under investigation, evidence has shown that there are three major reasons for this issue. First, SOA span a wide range of volatilities thus require a larger number of surrogate species for representation (Donahue et al., 2006; Presto and Donahue, 2006; Pathak et al., 2007). Second, the oxidation reactions of SOA precursor VOCs are usually assumed to be one-stage, i.e., no further reaction will take place after the generation of oxidation products. However, it has been discovered that the products of first generation of reactions can undergo further oxidation to produce less volatile products (Chan et al., 2007; Ng et al., 2008; Kessler et al., 2011; Donahue et al., 2012a). Third, traditionally POA were treated as non-volatile and non-reactive in aerosol models. However, recent studies have shown that POA consist of a dynamic system which contains multi-component mixture of semi-volatile species that can evolve in the atmosphere by chemical reactions and gas-particle partitioning (Robinson et al., 2007). Therefore, a more comprehensive framework needs to be developed to more accurately represent the complex SOA production pathway.

5.1.3 Volatility basis set and scope of this work

Donahue et al. (2006) developed the so-called volatility basis set (VBS) framework to treat both semi-volatile primary emissions and SOA production. The VBS framework was established based on chamber measurements on SOA oxidation reactions. This framework does not resolve the chemical identity of OA. Instead, the organic precursors were lumped into nine surrogate volatility species with the effective saturation concentrations \( C^* \) ranging from \( 10^{-2} \) to \( 10^6 \) \( \mu g m^{-3} \). The volatility species were classified by a factor of 10 of \( C^* \) values at 298 K. During the aging, semi-volatile VOCs will undergo gas-phase photochemical oxidation reactions and the products will condense onto existing particles to form SOA. Each oxidation reaction will reduce the volatility of VOCs by one decade of \( C^* \). The VBS framework takes into account the semi-volatile nature of primary emissions and additional pathways for SOA production, and has been confirmed to provide improved predictions of SOA concentration in numerous studies (Lane et al., 2008; Farina et al., 2010; Tsimpidi et al., 2010; Shrivastava et al., 2011; Jathar et al., 2011; Bergström et al., 2012;
In this study, we applied the volatility basis set approach to model the formation of SOA in air mass trajectories during CARES 2010 field campaign. We implemented the VBS framework in the particle-resolved box model PartMC-MOSAIC, which currently uses a traditional two-product SOA module SORGAM (Schell et al., 2001) to simulate SOA production. Importantly, POA are assumed non-volatile and non-reactive in the current PartMC-MOSAIC model. The implementation of the VBS framework allows POA to be semi-volatile and the organic vapors can undergo further oxidations to produce additional SOA. The detailed description of the VBS approach will be discussed in Section 5.2.1. The contribution of this work is to extend the capability of PartMC-MOSAIC on simulating aging of organic aerosols, thus uniquely provide particle-level information and mixing state of SOA-containing particles, while most previous studies only focused on the bulk concentration of SOA production.

This chapter is organized as follows. Section 5.2 introduces the numerical implementation of VBS framework in the governing equation of PartMC-MOSAIC, and the model setup for simulations of air trajectories from CARES campaign. Section 5.3 provides the simulation results and discussions. Section 5.4 summarizes the major findings and proposes future work.

5.2 Numerical implementation

5.2.1 Volatility basis set framework

The equations governing the evolution of aerosol and gas species in this study are exactly the same as Eqs. 2.2 and 2.3 except for one modification. The gas-particle transfer mechanism for POA species was replaced by volatility basis set scheme that took into account the semi-volatile nature of POA emissions.

Considering $C_{OA} \,(\mu g \, m^{-3})$ as the total condensed-phase organic mass concentration, we can define a partition coefficient $\xi_i$ for compound $i$ as

$$\xi_i = \left( 1 + \frac{C^*_{i}}{C_{OA}} \right)^{-1}; \quad C_{OA} = \sum_i C_i \xi_i \quad (5.1)$$

where $C^*_{i} \,(\mu g \, m^{-3})$ is effective saturation concentration for compound $i$, $C_i \,(\mu g \, m^{-3})$ is the organic compounds concentration in gas and aerosol phases. Note that $C^*_{i}$ is the inverse of partitioning coefficient $K_p$ which was used in traditional gas-particle partition theory (Pankow, 1994). Eq. 5.1 must be solved iteratively for $C_{OA}$ in numerical models.
In the atmosphere, to cover the wide range of volatilities of OA species, typically we use the following basis set defined at 298 K:

$$C_i^* = 10^{-2}, 10^{-1}, 10^0, 10^1, 10^2, 10^3, 10^4, 10^5, 10^6 \mu g \text{ m}^{-3}$$  \hspace{2cm} (5.2)

which is referred as volatility basis set, to lump the organic species into a set of $C_i^*$ bins which differ by an order of magnitude from bin to bin. The lower the $C_i^*$ is, the larger the fraction in the condensed phase. For example, for the lowest volatility bin with $C_i^* = 10^{-2} \mu g \text{ m}^{-3}$ at remote areas with $C_{OA} = 0.1 \mu g \text{ m}^{-3}$, based on Eq. 5.1 around 90% of the organic material will be in the condensed phase. For the highest volatility bin with $C_i^* = 10^5 \mu g \text{ m}^{-3}$, under polluted urban area typically with $C_{OA} = 100 \mu g \text{ m}^{-3}$, only 0.1% of the materials will be in the condensed phase. Figure 5.2 from Donahue et al. (2006) shows an example of ambient volatility distribution of semi-volatile compounds. Total loadings of organic species are represented as full bar (plotted as $\log_{10} C^*$). Green shadings represent the condensed organic mass in each volatility bin, and the green arrow shows the total OA mass in this case. The bin with $C^*$ value close to $C_{OA}$ is evenly split between two phases, while lower volatility materials are mostly condensed. The volatility spectrum of $C^*$ is conventionally divided into semi-volatile (SVOC, $0.01 - 10^3 \mu g \text{ m}^{-3}$) and intermediate volatile (IVOC, $10^4 - 10^6 \mu g \text{ m}^{-3}$) organic compounds. A substantial fraction of SVOC will partition to POA in the atmosphere, while IVOC will mostly remain in the gas phase in the absence of photochemistry.

Some studies only used two surrogate volatility species in their VBS framework, including one with low $C^*$ value and one in the higher volatility bin (Shrivastava et al., 2011; Mahmud and Barsanti, 2013). However, this configuration is too simplified since it does not represent the full spectrum of volatility distribution of ambient OA. Therefore, we implemented 9-species VBS framework in this study which is most widely used in the current research community.

The VBS framework described here is referred as one-dimensional (1-D) VBS, which means it lumps organic species by only saturation concentration $C_i^*$. Recently, a two-dimensional (2-D) VBS framework was developed to add the extent of oxygenation as second dimension (Donahue et al., 2011, 2012b). The extended framework tries to improve its capability of predicting the thermodynamics, including organic mixing and polarity, and ultimately to coherently describe oxidation chemistry. Although the 2-D VBS framework has been deployed in several studies to produce encouraging results on SOA estimation, the addition of a second dimension can also cause more uncertainties as it introduces more parameters that are not well-constrained (Murphy et al., 2011). Zhao et al. (2015) evaluated the performance of both 1-D and 2-D VBS on simulating
Figure 5.2: A schematic showing ambient volatility distribution fit to the volatility basis set. The full bars show the total loadings of semi-volatile compounds, while the green shading represent the mass in the condensed phase. Figure taken from Donahue et al. (2006).

Gas-particle partitioning in each volatility bin is shifted due to the change in temperature. This shift is represented using the Clausius-Clapeyron equation (Donahue et al., 2006)

\[
C_i^*(T) = C_i^*(T_{ref}) \exp \left[ \frac{\Delta H_{vap}}{R} \left( \frac{1}{T_{ref}} - \frac{1}{T} \right) \right] \frac{T_{ref}}{T} \tag{5.3}
\]

where \(T_{ref}\) (K) is the reference temperature (298 K), \(\Delta H_{vap}\) (kJ mol\(^{-1}\)) is the enthalpy of vaporization and \(R\) (JK\(^{-1}\)mol\(^{-1}\)) is the universal gas constant.

The concentrations distributions shown here, and they are also consistent with recovery (compound-by-compound basis. However, unspecific, carbon-mass of the emissions have been characterized on a distribution in the example because less than half of organic gasoline (19) engine exhaust. We must use an assumed distribution in the example because less than half of organic mass by a factor of 4000 because of repartitioning into the vapor phase. (d) The effect of dilution, as depicted in panel b above but now depicted above. The dilution factor of 1000 is indicated with a horizontal black arrow. Dilution by a factor of 1000 reduces the aerosol concentration (\(y_\mu g\ m^{-3}\)) in Figure 1b are very high (the condensed-phase portion with filled (green) bars. Compounds are distributed according to their mass-equivalent effective saturation also presented as a logarithmically distributed basis set.

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5.2.2 SOA formation

Gas-phase SVOC and IVOC will undergo photochemical oxidations with OH radical to produce lower volatility species, which may then condense to form SOA. SOA formed from photochemical oxidation of S/IVOC species are named “SI-SOA”. In addition, SOA can also be formed through gas-phase oxidation of VOCs which have $C^*$ greater than $10^6 \text{ µg m}^{-3}$. These VOCs contain both of anthropogenic (e.g., aromatics, olefins) and biogenic components (e.g., isoprene, terpene). SOA produced from oxidation of VOCs are named “V-SOA”. The terminology of various classes of organic species is tabulated in Table 5.1. In general, SI-SOA formation is thought to be more efficient compared to V-SOA formation, since S/IVOC species have lower volatility favoring partitioning to the particle phase after oxidation (Donahue et al., 2006). A schematic showing the formation paths of SI-SOA and V-SOA from semi-volatile primary emission is presented in Figure 5.3 which is taken from Jathar et al. (2011). In this diagram it uses the term POC as the sum of all the emissions that have a $C^*$ lower than $10^6 \text{ µg m}^{-3}$, in both aerosol and gas phases.

<table>
<thead>
<tr>
<th>OA</th>
<th>Organic aerosols: include both POA and SOA (defined below)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POA</td>
<td>Primary organic aerosols: defined as organic aerosols directly emitted into the atmosphere</td>
</tr>
<tr>
<td>SOA</td>
<td>Secondary organic aerosols: defined as organic aerosols formed after photochemical oxidation and condensation of organic vapors, including SI-SOA and V-SOA</td>
</tr>
<tr>
<td>SI-SOA</td>
<td>Component of SOA formed due to photochemical oxidation of all S/IVOC precursors</td>
</tr>
<tr>
<td>V-SOA</td>
<td>Component of SOA formed due to photochemical oxidation of all VOC precursors</td>
</tr>
<tr>
<td>aV-SOA</td>
<td>Anthropogenic component of V-SOA</td>
</tr>
<tr>
<td>bV-SOA</td>
<td>Biogenic component of V-SOA</td>
</tr>
<tr>
<td>SVOC</td>
<td>Semi-Volatile Organic Compounds with $C^*$ between $10^{-2} \text{ µg m}^{-3}$ and $10^3 \text{ µg m}^{-3}$ at 298 K</td>
</tr>
<tr>
<td>IVOC</td>
<td>Intermediate-Volatile Organic Compounds with $C^*$ between $10^3 \text{ µg m}^{-3}$ and $10^5 \text{ µg m}^{-3}$ at 298 K</td>
</tr>
<tr>
<td>S/IVOC</td>
<td>SVOC + IVOC</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compounds: gas-phase organic species with $C^* \geq 10^7 \text{ µg m}^{-3}$</td>
</tr>
</tbody>
</table>

Table 5.1: Terminology used in this chapter for different organic species.

SI-SOA formation

SI-SOA formation reactions are based on the framework described by Shrivastava et al. (2011). We consider a multi-generational gas-phase oxidation of S/IVOC precursors with OH radical. S/IVOC come from partial evaporation of POA emission due to the semi-volatile nature of POA. During each oxidation reaction, the mass of parent SVOC or IVOC species is assumed to increase by 15% for each generation of oxidation
to account for added oxygen mass or functionalization. This 15% increase rate doubles the value used in Robinson et al. (2007), which was observed to significantly underpredict the O:C ratio in the atmosphere (Hodzic et al., 2010). For all reactions an OH reaction rate of $4 \times 10^{-11} \text{ cm}^3\text{molecules}^{-1}\text{s}^{-1}$ is assumed. Each reaction will move the S/IVOC species at volatility bin $i$ to successively lower volatility bin $i - 1$.

Figure 5.4 from Shrivastava et al. (2008) shows the general process of SI-SOA production in VBS framework. Semi-volatile POA undergo gas-particle partitioning instantaneously after emission to the atmosphere. The gaseous component will then react with OH to produce less-volatile and more oxidized gas-phase products, which will then either condense onto existing particles to form SI-SOA, or undergo further oxidation reactions to produce even less volatile species.

**V-SOA formation**

V-SOA formed from VOC precursors are currently represented by the SORGAM scheme (Schell et al., 2001), which is based on traditional dynamic gas-particle partitioning theory (Pankow, 1994; Odum et al., 1996). Eight SOA model species with four anthropogenic species and four biogenic species are taken into account in SORGAM model. The anthropogenic classes include two from aromatic precursors, one from higher alkanes and one from higher alkenes. The biogenic species contain two classes from $\alpha$-pinene and two from limonene degradation. The detailed gas-phase reactions can be referred to Table 2 in Schell et al. (2001).

Due to the fact that original SORGAM scheme produced much lower SOA levels compared to ambient
levels in urban areas (Volkamer et al., 2006; Kleinman et al., 2007), some SORGAM model parameters have been adjusted (increased gas phase yields by a factor of 2 and reduced saturation vapor pressures by a factor of 2) to increase SOA concentration to match observations (Zaveri et al., 2010). We need to note that V-SOA formation could also be extended to VBS framework. We did not include it in this study since our focus was the semi-volatile nature of POA emissions and its impact on SI-SOA formation.

**Verification of the implementation of VBS**

The implementation of VBS framework has been verified with two test cases, including one test for gas-particle partition and one for chemical reaction. To test the gas-partition partition, we initialized two gas-phase VBS species, PCG1_B_C and PCG2_B_C which represented the carbon component (“C”) from biomass burning (“B”) of surrogate primary organic compounds (PCG). We started a gas concentration of 0.04 ppb for the two species and let them partition under certain temperature profile. The simulation results exactly match the analytical solutions derived from Eq. 5.1 as shown in Figure 5.5.

To test the gas oxidation reactions under VBS framework, we consider the following reaction
Figure 5.5: Comparison of analytical and simulated gas and aerosol concentrations of two VBS species under gas-particle partitioning.

PCG2_B_C + OH $\rightarrow$ OPCG1_B_C + 0.5 OPCG1_B_O

This reaction accounts for the gas phase oxidation to convert high volatile species (PCG2_B_C) to low volatile, oxidized species (OPCG1_B_C for carbon component, OPCG1_B_O for oxygen component). We initialized PCG2_B_C gas mixing ratio to be 0.04 ppb, and assigned a constant OH mixing ratio of $2 \times 10^{-6}$ ppb and a constant temperature $T = 298$ K during the simulation. No other gas or aerosol species were initialized. Our analytical solution is obtained by solving a system of initial value problems, with ODEs specified as

\[
\frac{d[PCG2_B_C]}{dt} = -k[PCG2_B_C][OH] \quad (5.4)
\]
\[
\frac{d[OPCG1_B_C]}{dt} = k[PCG2_B_C][OH] \quad (5.5)
\]
\[
\frac{d[OPCG2_B_O]}{dt} = 0.5k[PCG2_B_C][OH] \quad (5.6)
\]

The comparison result of analytical solution and PartMC-MOSAIC prediction is shown in Fig. 5.6.
Perfect match was obtained between modeled and analytical results for all the three species, confirming the successful implementation of VBS framework in PartMC-MOSAIC.

![Figure 5.6: Comparison of analytical and modeled evolution of gas mixing ratios.](image)

5.2.3 Mixing state quantification

To investigate the effect of using VBS scheme on the chemical composition, we used the concepts developed by Riemer and West (2013) to quantify the particle mixing state. Inspired by the information-theoretic entropy measures, the authors introduced two parameters associated with the "diversity" of an aerosol population: the average per-particle species diversity $D_\alpha$ and the bulk population diversity $D_\gamma$. $D_\alpha$ is a measure of the average effective number of chemical species in each particle, and $D_\gamma$ is the effective number of species in the population. Suppose we have $A$ species in an aerosol population, the values of $D_\alpha$ and $D_\gamma$ are between 1 and $A$. The mixing state parameter $\chi$ is defined as $(D_\alpha - 1)/(D_\gamma - 1)$ which indicates the degree to which a population is internally mixed. The value of $\chi$ is between 0 and 1, with $\chi = 1$ indicating the particles are completely internally mixed, and $\chi = 0$ indicating completely externally mixed. The formulations to calculate the three quantities are listed in Tables B.1 and B.2 in Appendix B.

Figure 5.7 illustrates the concepts of these three diversity measures in a phase space spanned by $D_\alpha$ and $D_\gamma$. There are seven examples of aerosol population in Figure 5.7, denoted by $\Pi^i$, where $i$ is from 1 to 7. These populations are described by unique pairs of $D_\alpha$ and $D_\gamma$.

For the simplest case $\Pi^1$, all the particles contain only one species, and there is only one species in the entire population, thus both $D_\alpha$ and $D_\gamma$ equal to 1. It then has $\chi = 0$, meaning it is completely externally mixed. For $\Pi^3$, each particle only contains one species, so $D_\alpha = 1$. However, there are three species in the population, so $D_\gamma = 3$. As a result, the population has $\chi = 0$, so it is also completely externally mixed. Same behavior can be observed for $\Pi^4$ as well.
Populations $\Pi^2$, $\Pi^3$ and $\Pi^5$ are along the $D_\gamma = 3$ line, since there are three species in equal bulk amounts. Their individual $D_\alpha$ values vary due to the difference in the average per-particle species number. Each particle in $\Pi^2$ contain 3 species, hence $D_\alpha = 3$. The $D_\alpha$ value for $\Pi^5$ is between 2 and 3 since the number of species in each particle is either 2 or 3.

Populations $\Pi^1$, $\Pi^2$ and $\Pi^6$ are all composed of identical particles, so they will have $\chi = 1$, meaning they are completely internally mixed. The completely externally mixed line ($\chi = 0$ line) and completely internally mixed line ($\chi = 1$ line) converges at where $\Pi^1$ is. Population $\Pi^7$ is the intermediate case when particles are between completely internally mixed and completely externally mixed.

Figure 5.7: Mixing state diagram illustrating the concepts of average per-particle diversity $D_\alpha$, bulk population diversity $D_\gamma$, and the mixing state parameter $\chi$. Figure taken from Riemer and West (2013).

5.2.4 Model setup for trajectory simulations

In this study, we conducted PartMC-MOSAIC model simulation on air mass trajectories obtained from Carbonaceous Aerosols and Radiative Effects Study (CARES). The CARES field campaign took place in the central California region, to the northeast of Sacramento, from June 2-28, 2010. The campaign consisted of measurements from a Gulfstream-1 (G-1) research aircraft and two instrumented ground stations in California (T0 and T1). Measurements on trace gases, aerosols and meteorology around Sacramento area were conducted to obtain new process-level knowledge on aerosols and the evolution of their climate effects.
during transport and aging process. Detailed information on CARES field campaign is provided in Zaveri et al. (2012).

Figure 5.8 shows the measurements conducted during CARES field campaign, with the locations of T0 and T1 ground sites. T0 site was located at American River College which is approximately 14 km northeast of downtown Sacramento, while T1 site was located at Northside School which is approximately 52 km northeast of downtown Sacramento. At each site, aerosol, gas and meteorological instruments were deployed to measure emissions originating in Sacramento and transported via airflow toward the Sierras. Gulfstream-1 (G-1) aircraft conducted regular flights through and around the Sacramento plume. The aircraft measurement consisted of two flight patterns. Morning flight patterns were designed to sample either morning emissions from Sacramento as they flew northwest, or San Francisco Bay Area emissions if the airflow was moving toward Sacramento. Afternoon flight patterns sampled the aged emissions based on the morning flight patterns during the day. During the campaign, the G-1 was based out of McClellan Airport which is located around 12 km northeast of downtown Sacramento (ARM, 2010).

Figure 5.8: Measurements during CARES field campaign. Two ground sites (T0 and T1) and the G-1 aircraft will measure air as it flows northeast from Sacramento to the Blodgett Forest area. Figure taken from https://www.arm.gov/campaigns/cares.

In this study, we will focus on five air mass trajectories that were obtained from a combined flight measurement and model simulation during CARES campaign on June 15, 2010, when the trajectories were observed to move to T1 site. The starting times of these trajectories range from 10 am to 2 pm on a hourly basis. By investigating the aerosol aging in these trajectories we can obtain a comprehensive diurnal pattern
of the evolution of aerosols from urban/manmade and biogenic sources, which can then be integrated into regional and global aerosol models used to estimate the direct and indirect radiative effects on climate. The model input and observational data processing was done by Dr. Jerome Fast and Dr. Joseph Ching from Pacific Northwest National Laboratory (PNNL), who were supported by the US DOE’s Atmospheric Science Research (ASR) Program under Contract DE-AC06-76RLO 1830 at PNNL.

**Initial conditions**

The aerosol initial distributions of the trajectories were obtained from Single Particle Mass Spectrometer (SPLAT II, Zelenyuk et al. (2009)) for biomass burning, sea salt and 4 classes of SOA-sulfate internal mixture with different mass fractions. Scanning Mobility Particle Sizer (SMPS) provided compositions of additional two classes of SOA-sulfate mixtures with particle sizes between 12 nm and 90 nm. Biogenic aerosols (assumed to be α-pinene) dominate the SOA-sulfate mixtures. In addition, 151 classes of BC-containing particles that were obtained from Single Particle Soot Photometer (SP2, Subramanian et al. (2010)) were derived from core-coating two-dimensional distribution assuming coating contains ammonium sulfate, OC and SOA. The chemical compositions of the initial aerosol classes used in initial conditions are list in Table 5.2. Particle size distributions were obtained from SMPS, which span a size range between 12 nm to 800 nm.

The gas phase initial conditions came from Weather Research and Forecasting (WRF) model. Meteorological conditions, including temperature, pressure, mixing height and initial relative humidity, were also obtained from WRF simulations. The relative humidity along the trajectories were adjusted according to temperature, assuming that the moisture content of the parcel was conserved.

**Background conditions**

Aerosol background size distributions and compositions were obtained from smoothed 8-bin WRF-output along trajectories. Background aerosols are comprised of varying fractions of OC, BC, sulfate, nitrate, ammonium, sea salt and other inorganic species among the eight bins. Background gas species concentrations were also obtained from WRF-output. A constant dilution rate of 1.5 s$^{-1}$ was used during the entire course of the simulation. The values of background aerosol and gas concentrations were obtained from the layer above the boundary layer.

**Emissions**

Aerosol emission distributions consisted of two modes including one primary organic carbon (POC) mode and one diesel mode. The POC mode could be meat cooking, biomass burning, etc., and was assumed to
be comprised of 100% OC. The diesel mode contained 30% OC and 70% BC (Table 5.2). A log-normal size distribution was used for both of the two emission modes. The emission profiles of OC components for the five trajectories we analyzed are shown in Fig. 5.9. The POA emissions are generally highest close to the trajectory starting point (T0) and decrease downwind of T0, as the distance from Sacramento increases.

Figure 5.9: Emission profiles of primary organic aerosols for the five trajectories described in this study.

One key uncertainty of modeling OA is whether the POA in the emissions inventory is assumed to be the aerosol fraction before or after the evaporation of SVOC has occurred. Existing studies have discussed in detail about this issue and usually assumed POA reported in emission inventory corresponded to the aerosol mass after evaporation of semi-volatile compounds (Hodzic et al., 2010; Shrivastava et al., 2011). In our approach we adopted the same assumption, and adjusted the POA emission by multiplying 7.5 to account for the semi-volatile behavior. Total SVOC was assumed to be 3 times aerosol-phase POA emission,
Table 5.2: Chemical compositions of aerosol initial and emission conditions.

<table>
<thead>
<tr>
<th>Initial Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass burning</td>
</tr>
<tr>
<td>Sea salt</td>
</tr>
<tr>
<td>SOA-sulfate mixture 1</td>
</tr>
<tr>
<td>SOA-sulfate mixture 2</td>
</tr>
<tr>
<td>SOA-sulfate mixture 3</td>
</tr>
<tr>
<td>SOA-sulfate mixture 4</td>
</tr>
<tr>
<td>SOA-sulfate mixture 5 (SMPS)</td>
</tr>
<tr>
<td>SOA-sulfate mixture 6 (SMPS)</td>
</tr>
<tr>
<td>BC-containing mixtures</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Emission Composition</td>
</tr>
<tr>
<td>POC</td>
</tr>
<tr>
<td>Diesel</td>
</tr>
</tbody>
</table>

Table 5.3: Mass factors $f_i$ used to calculate S/IVOC emissions from POA based on Shrivastava et al. (2011).

<table>
<thead>
<tr>
<th>$C^*$ at 298 K ($\mu g m^{-3}$)</th>
<th>Cooking ($f_i$)</th>
<th>Diesel ($f_i$)</th>
<th>$\Delta H_{vap}$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.09</td>
<td>0.23</td>
<td>112</td>
</tr>
<tr>
<td>0.1</td>
<td>0.18</td>
<td>0.17</td>
<td>106</td>
</tr>
<tr>
<td>1</td>
<td>0.27</td>
<td>0.26</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>0.42</td>
<td>0.40</td>
<td>94</td>
</tr>
<tr>
<td>100</td>
<td>0.54</td>
<td>0.51</td>
<td>88</td>
</tr>
<tr>
<td>1000</td>
<td>0.90</td>
<td>0.86</td>
<td>82</td>
</tr>
<tr>
<td>$10^4$</td>
<td>1.20</td>
<td>1.17</td>
<td>76</td>
</tr>
<tr>
<td>$10^5$</td>
<td>1.50</td>
<td>1.50</td>
<td>70</td>
</tr>
<tr>
<td>$10^6$</td>
<td>2.40</td>
<td>2.40</td>
<td>64</td>
</tr>
</tbody>
</table>

and IVOC was assumed to be 1.5 times SVOC emission. These treatments are consistent with those used in Shrivastava et al. (2011). Table 5.3 shows the mass factors $f_i$ used to calculate S/IVOC emissions from POA emissions in each volatility bin which are based on Shrivastava et al. (2011). Note that Shrivastava et al. (2011) provided the mass factors for biomass and anthropogenic emissions only. In our approach, we assume that the factors of meat cooking is the same as those of biomass, and diesel emission represents the anthropogenic emission.

To adjust the total POA emission, the total mass concentration from aerosol normal distribution is given by

$$M = Nd_{pg}^3 \exp \left(\frac{9}{2} \ln^2 \sigma_g\right)$$  \hspace{1cm} (5.7)
where \( M \) is total mass concentration (kg m\(^{-3}\)), \( N \) is number concentration (m\(^{-3}\)), \( d_{pg} \) is geometric mean diameter (m), and \( \sigma_g \) is geometric standard deviation of diameter. For the POC emission mode comprised of 100% OC, to increase \( M \) by 7.5 times we increase the \( d_{pg} \) value by multiplying \( \sqrt[3]{7.5} \approx 1.9574 \). In this way we make the total mass 7.5 times larger, while keeping the originally emitted particle number flux and the geometric standard deviation \( \sigma_g \). For the diesel mode which contains 30% OC and 70% BC, we increase the \( d_{pg} \) value by multiplying 1.4342 and adjust the OC and BC fractions to be 76.3% and 23.7%, respectively. This will scale up the emitted OC by a factor of 7.5 while the BC emissions are not changed.

**Setup of case study**

We initialized our model with \( 10^4 \) computational particles and followed the air parcel as it evolved for 7 hours to predict the evolution of SOA and mixing state along the trajectories for the CARES campaign. For comparison we also conducted a simulation where the VBS scheme was disabled, and POA was assumed to be non-volatile and non-reactive. The simulation runs with and without VBS are referred to “With VBS” and “No VBS” in this context, respectively. PartMC-MOSAIC version 2.3.0 was used for these simulations.

### 5.3 Results and discussion

In this section we present the results from simulations including the new VBS treatment and using the old formulation where POA was non-volatile. To provide context, we first show the evolution of gas mixing ratios, bulk aerosol mass concentrations and total number concentration with comparison to observational data. We then show the two-dimensional particle number distributions and quantify the aerosol mixing state during the aerosol evolution along the trajectories. In this section, we show the trajectory starting at 10 am local time as representative case. The results of other trajectories are provided in Appendix B.

**5.3.1 Evolution of gas and bulk aerosol species**

Figure 5.10 shows the evolution of gas species NO, NO\(_2\), O\(_3\) and SO\(_2\) along the trajectory. The black and red lines represent the simulation result of the run without and with VBS, respectively. The blue circles represent the observation data obtained from G1-aircraft measurement when the trajectory and the G1 aircraft were close enough (within 5 km horizontally) at around 4 pm local time (6 hours after simulation started). Both PartMC-MOSAIC runs have the same gas mixing ratios for these species, which is expected. The predicted gas species mixing ratios are comparable with the observation data, except some extent of overestimation of NO and NO\(_2\), as well as underestimation of O\(_3\).
Figure 5.10: Evolution of gaseous species along the trajectory starting at 10 am local time.

Figure 5.11 shows the evolution of bulk aerosol species including BC, SO$_4$, NO$_3$, NH$_4$, SOA and total OA along the trajectory as it evolves for 7 hours. For the two PartMC-MOSAIC simulations, the time evolutions of BC and inorganic species are similar except for minor differences due to the stochastic noise in PartMC-MOSAIC. The comparison to the observation data shows that the model tends to overestimate the BC, SO$_4$ and NH$_4$ concentration, while the prediction of NO$_3$ matches the observation well. Note that there is no NO$_3$ initialized for simulation, we suspect the overestimation of BC, SO$_4$ and NH$_4$ is due to the high initial mass concentrations which were obtained from reconstructed SPLAT measurements.

When VBS was enabled, the production of SOA mass concentration was increased. The enhancement of SOA level was from the daytime chemical oxidation of semi-volatile organic vapors from POA emissions and the subsequent condensation to form SI-SOA based on the VBS framework. After 6 hours of simulation when VBS was enabled, the model predicted around 4 $\mu$g m$^{-3}$ of V-SOA and 2 $\mu$g m$^{-3}$ of SI-SOA, with a total OA concentration of 6 $\mu$g m$^{-3}$ which is comparable to the observed values obtained from AMS measurements. The “No VBS” run underestimated the total OA by around 2 $\mu$g m$^{-3}$ since the SOA produced was purely V-SOA, while the “With VBS” run filled this gap by resolving the unidentified SI-SOA species.

In addition, we show the evolution of individual SOA species including V-SOA and SI-SOA when VBS was enabled (right bottom panel of Figure 5.11). V-SOA is further divided into two categories of anthropogenic V-SOA (aV-SOA) and biogenic V-SOA (bV-SOA). The bV-SOA dominates the total SOA mass loading, which represents an intensified biogenic background in the environment of CARES campaign.
Figure 5.11: Evolution of bulk aerosol species along the trajectory starting at 10 am local time.

Similar evolution patterns of gas and aerosol species (inorganics and BC) were obtained in simulations of other trajectories (Appendix B). Using VBS leads consistently to more OA mass which sometimes improves the comparison to observations, while for some trajectories it overestimates the total OA mass loading (e.g., Fig. B.7) since a large fraction of OA has already been captured by biogenic SOA. Overall, these comparison results demonstrate that PartMC-MOSAIC is able to reproduce the aerosol and gas concentrations in an aged air plume, although it can not resolve the spatial resolution over the measurement domain, which is a general limitation of box models.

5.3.2 Evolution of total number concentration

Figure 5.12 compares the predicted aerosol number concentrations to those measured in the G-1 aircraft during the trajectory that started at 10 am. The measured data were obtained from condensation particle
counter (TSI CPC-3010) equipped in the G-1 aircraft. The modeled time series of aerosol number concentration shows a rapid decrease at the beginning due to dilution and coagulation. The inclusion of VBS framework does not influence the evolution of aerosol number concentration since it only affects the particle mass concentration. The modeled number concentration after 6 hours of simulation is around $8 \times 10^4$ cm$^{-3}$, which is less than the CPC measurement data of around $1 \times 10^5$ cm$^{-3}$. However, for other four trajectories, the modeled aerosol concentrations are much closer to the observation values. Therefore, the underestimation of aerosol number concentration of the trajectory starting at 10 am might be due to the error from the initial condition for this specific trajectory, which was based on SMPS measurements.

![Figure 5.12: Evolution of total aerosol number concentration along the trajectory starting at 10 am local time.](image)

5.3.3 Evolution of aerosol number distribution and mixing state

To illustrate the evolution of aerosol number distribution and mixing state over the course of the simulation, we show the two-dimensional number distribution as a function of dry diameter and BC mass fraction at 20:00 UTC (3 hours after simulation, Figure 5.13) and 23:00 UTC (6 hours after simulation, Figure 5.14). The two-dimensional number distribution is defined in Eq. (3.12). BC came from various sources, including the initial biomass burning and 151 classes of BC-containing mixtures, the emitted diesel particles, as well as the background BC mixture. For the “No VBS” run at 20:00 UTC, the two-dimensional number distribution represents a continuum of internal mixing states with BC dry-mass fraction ranging from 0 to 92%. At 23:00 UTC it still presents an internal mixture, but with the highest BC fraction slightly dropped to 88%. We observe a dramatic decrease of BC fraction for the set of particles between 40 and 100 nm with original BC
dry-mass fraction between 40% and 70% at 20:00 UTC. At 23:00 UTC the BC fractions of these particles drop to as low as 20%. This is due to the photochemical oxidation processes during the daytime along the trajectories to convert gaseous species to condensed phases, hence reduce the BC fractions.

The similar evolution pattern can be observed for the “With VBS” run. For this simulation the photochemical aging is more intensified due to extra amount of semi-volatile organic vapors. The gaseous S/IVOCs underwent oxidation reactions and the products condensed on existing particles to form SI-SOA, which further reduced the BC dry mass fraction. As a result, the BC fraction for particles in all size ranges was observed to decrease significantly compared to the “No VBS” run. In addition, the two-dimensional distributions for particles between 200 and 400 nm represent separated “stripes” when VBS was enabled, compared to the continuous distribution pattern observed in the “No VBS” run. These “stripes” were formed due to the co-effect of the evaporation of POA which increased the BC dry mass fraction, and condensation of SOA which lowered the BC fraction. Similar patterns can be observed in the two-dimensional distributions of all other four trajectories (shown in Appendix B).

Figure 5.13: Two-dimensional number distributions after 3 hr of simulation for trajectory starting at 10 am local time.

We further quantify the particle mixing state by using mixing state parameter $\chi$ as described in Section 5.2.3. This parameter determines the extent to which the particles are mixed. The value of $\chi$ is between 0 and 1 with 0 indicating completely externally mixed while 1 indicating completely internally mixed. The evolution of the $\chi$ value for simulations with and without VBS is shown in Figure 5.15. In both cases, the $\chi$ values decreased for the first three hours due to the addition of freshly emitted particles, and increased thereafter. When VBS was enabled, the $\chi$ values were slightly larger compared to the run without VBS. For example, at 3 h after simulation started the $\chi$ values were 0.36 and 0.37 for “No VBS” and “With VBS”
Figure 5.14: Two-dimensional number distributions after 6 hr of simulation for trajectory starting at 10 am local time.

The other four trajectories also showed a decrease of $\chi$ during the first few hours, followed by an increase of $\chi$ leading to an internal mixture. However, the $\chi$ values of the “No VBS” and “With VBS” simulations for the trajectories starting at 1 pm and 2 pm did not vary much compared to the other three trajectories. In addition, for the trajectory from 2 pm the $\chi$ values for the “With VBS” run became smaller compared to those from “No VBS” run after 5 hours of simulation. This is probably due to the reduced daylight exposure as the simulation has entered the nighttime.
5.4 Conclusion

We implemented the volatility basis set (VBS) framework in the particle-resolved model PartMC-MOSAIC based on Shrivastava et al. (2011) to investigate the chemical aging of organic aerosols in the atmosphere. Instead of treating primary organic aerosols (POA) as non-volatile and non-reactive, we now classify POA into nine volatility bins by assuming that they are semi-volatile and the evaporated gas phase species can undergo further oxidation to form secondary organic aerosols (SOA). This approach can increase the level of SOA concentration, which is usually underestimated in existing aerosol models.

The updated PartMC-MOSAIC model with VBS framework was then applied to the simulations of air trajectories obtained from CARES field campaign conducted in California in June 2010. A blend of measurement and model data were used as input to setup the case studies. We also adjusted the POA emissions to consider the semi-volatile nature of POA. We then conducted model simulations on five air trajectories from CARES campaign on June 15, 2010.

We presented the model results from two simulations, with and without VBS framework, respectively. The results were compared to the aircraft measurement for gas and aerosol mass concentrations and aerosol number concentrations. For our representative trajectory starting at 10 am local time, PartMC-MOSAIC was able to produce gas and aerosol concentrations at similar levels compared to the observational data. Moreover, the simulation with VBS enabled produced additional $2 \mu g m^{-3}$ of SI-SOA which made the total OA concentration much closer to the observed values.

We also investigated the particle mixing state along this trajectory. The two-dimensional number distribution showed a reduction of BC dry-mass fraction when VBS was enabled, which was due to the additional condensed SI-SOA mass. The time evolution of mixing state parameter $\chi$ showed that, overall, the particle mixing state did not change much when using the VBS framework.

We observed similar evolution patterns of gas and aerosol concentrations for the other four trajectories we analyzed. For some trajectories the model over-predicted total OA mass loading due to the dominance of biogenic VOC in the environment of the campaign. The evolution of particle mixing state indicated that including the VBS framework did not lead to a more internal mixture in those cases, especially as the trajectories extended to the nighttime when photochemical oxidations were largely limited.
Chapter 6

Conclusions

6.1 Overview

This dissertation focuses on the development and application of particle-resolved model PartMC-MOSAIC. The overall research question is: is PartMC-MOSAIC able to capture the evolution of aerosol particles in different environments, and what is the dominant process governing the particle evolution? To answer the research question, this work contributes to the following two areas. First, the validation of PartMC-MOSAIC model requires the comparison with experimental data, during which explicit representations of main aerosol processes in the atmosphere need to be established. Therefore, PartMC-MOSAIC model was extended to include additional modules on particle physical and chemical aging processes. This includes two major implementations: 1) wall loss and fractal particle dynamics to account for the coagulational growth of particles in chamber environment, and 2) volatility basis set (VBS) framework for the chemical aging of organic aerosols. Second, PartMC-MOSAIC was applied to three distinct real-world scenarios to study the evolution of particles in an evolving ship plume, a closed aerosol chamber, and an ambient air trajectory. Process-level analyses have been performed for the three scenarios to investigate the evolution of aerosol properties due to coagulation, condensation, nucleation and chemical processes. This is the first time PartMC-MOSAIC was integrated with real-world measurement to validate its capability of reproducing experimental data, hence provide information of aerosol properties at particle level, which can not be obtained from existing models.

The comparison results between PartMC-MOSAIC and the three measurement scenarios are promising. This demonstrates the robustness of the model under different atmospheric environments. The main findings of the individual components of the work are summarized below, followed by a discussion of future directions at the end of this chapter.
6.2 Summary of findings

6.2.1 The evolution of particle mixing state and CCN properties in a ship plume

Chapter 3 presents the application of PartMC-MOSAC to investigate the evolution of aerosol mixing state and the associated changes of CCN properties in a ship plume. The measurement was conducted during QUANTIFY SHIPS campaign in 2007. This work provides the first validation study of PartMC-MOSAIC by showing good agreement of model results with observed particle number concentrations. The process analyses include the investigation of importance of dilution, coagulation, condensation and nucleation on influencing the particle distribution and the resulting CCN activation properties. Dilution and coagulation are found to dominate evolution of particle number concentration in the ship plume. Dilution reduces the in-plume total particle number concentration by about four orders of magnitude within 15 min from simulation start. Coagulation further reduces the particle number concentration by another order of magnitude and preferentially depletes small sulfuric acid particles.

The two major processes dominating the particle mixing state and CCN properties are coagulation and condensation, leading to internally mixed aerosols containing BC and sulfate. Their relative contributions on CCN properties are sensitive to ambient supersaturation threshold and the daylight exposure time, which is proved by conducting a set of sensitivity simulations with different supersaturation thresholds and model starting times. Nucleation is not found to be a big contributor to CCN concentration due to limited condensable material available to grow the particles formed by nucleation to CCN-relevant sizes.

6.2.2 The evolution of particle population and size distributions in chamber environment

In Chapter 4 we present the extension of PartMC to allow for the representation of fractal particle structure and for wall loss to simulate the evolution of coagulating particle populations in a chamber environment. The implementation of wall loss and fractal dynamics is based on Naumann (2003). We use theoretical self-preserving size distributions to verify the implementation of fractal particle dynamics under both free molecular and continuum regimes.

The wall loss and fractal dynamics framework introduces five unknown parameters. Based on the three chamber experiments conducted in Department of Civil and Environmental Engineering in University of Illinois at Urbana-Champaign, we use Scanning Electron Microscope (SEM) images of the particle samples to constrain two of them (radius of the primary particles $R_0$ and volume filling factor $f$) while develop a
global optimization procedure to determine the remaining three parameters including wall loss parameters $k_D$ and $a$, and fractal dimension $d_f$. Excellent agreement between modeled and measured size distributions can be achieved if the optimization procedure is applied to each experiment individually. Further, we can successfully simulate the measured size distributions by using the same set of parameters for all three experiments obtained from applying the optimization procedure to all three experiments combined.

### 6.2.3 Secondary organic aerosol formation in ambient air trajectories

Chapter 5 presents the work of implementation of volatility basis set (VBS) framework in PartMC-MOSAIC based on Shrivastava et al. (2011) to investigate the chemical aging of organic aerosols in the atmosphere. Under this framework, primary organic aerosols (POA) are assumed to be semi-volatile and the primary organic vapors can undergo atmospheric oxidation to form secondary organic aerosols (SOA). The semi-volatile nature of POA has been proved in several previous studies, and using the VBS approach can increase the level of simulated SOA concentration, which is usually underestimated in existing aerosol models.

The updated PartMC-MOSAIC model was integrated with air trajectories obtained from CARES field campaign conducted in California in June 2010 and the results were compared with aircraft measurement data during the campaign. For our representative trajectory starting at 10 am local time, PartMC-MOSAIC is able to produce gas and aerosol concentrations at similar levels compared to the observational data. Moreover, the simulation with VBS produced additional $2 \mu g m^{-3}$ of SOA which made the total OA concentration much closer to the observed values.

Similar evolution patterns of gas and aerosol concentrations were observed for the other four trajectories, which started at 11 am, 12 pm, 1 pm and 2 pm local time, respectively. For some trajectories the model over-predicted total OA mass loading due to the dominance of biogenic VOC in the environment of the campaign. Including VBS framework did not lead to a more internally mixture in trajectories starting from 1 pm and 2 pm, since both trajectories were extended to nighttime.

### 6.3 Discussion of future direction

#### 6.3.1 Future development for chamber simulations

Currently the model with chamber process and fractal dynamics included uses a constant value of fractal dimension $d_f$ throughout the simulation period. From the comparison of the model results to the experimental data we conclude that using a constant $d_f$ value is a good approximation for simulating coagulating particle populations in these experiments. For future work it will be beneficial to implement a time- and size-
dependent fractal dimension to better quantify particle restructuring during more complex mixing and coating processes. This can be easily achieved by adding fractal dimension as an additional entry in particle-resolved representation using PartMC model. At the same time, this would necessitate more detailed particle size measurements to constrain the rate of change of $d_f$ during the evolution of particles in the chamber.

Moreover, the model framework developed in this work is only used for particle growth under coagulation. In the future, this framework can be further applied to more complex experiments, for example to investigate the evolution of aerosol mixing state when secondary aerosol material is coating the particles, and model-measurement comparison of optical properties with particle morphology taken into account.

6.3.2 Sensitivity studies on VBS framework

Although VBS has been widely used in current research community, it still suffers from many uncertainties due to the simplified assumptions it makes to represent a complex system of SOA formation. Currently we implemented a one-dimensional VBS, which means it groups the organic aerosols only based on their volatilities. In the future we will also implement more complex two-dimensional VBS framework (with additional dimension of oxygenation level), and conduct more sensitivity studies on the uncertain parameters including the number of surrogate species and oxygen to carbon ratio. These parameters have been shown to play important roles in VBS framework on predicting SOA formation.

Another large uncertainty of our current VBS integration with PartMC-MOSAIC is the treatment of POA emission. For the simulations of CARES trajectories we followed the approach proposed by Shrivastava et al. (2011) to scale up the POA emission by a factor of 7.5 to account for the semi-volatile properties of POA. However, this factor is poorly constrained. Ideally it should be determined from measurement and the value should vary among different ambient scenarios. Under the situation that the semi-volatile organics are not currently included in emission inventory, we will need to investigate the sensitivity of this scaling parameter and the fraction distribution of volatility species used in our model to estimate their impacts on the production of SOA.
References


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Appendix A

Appendix to Chapter 4: Supplementary figures

Figure A.1: Experimental and simulated time evolutions of number distributions from experiments 1–3 (top to bottom) at 7 min, 70 min and 210 min (left to right). Shaded areas represent $3 \times \sigma$ as described in Eq. (4.22). The optimization procedure to determine the parameters $k_d$, $a$, and $d_t$ was applied separately to the individual experiments.
Figure A.2: Time evolution of experimental and simulated mean diameter, standard deviation and skewness of size distribution (left to right) from experiments 1, 2 and 3. The optimization procedure to determine the parameters $k_d$, $a$, and $d_f$ was applied separately to the individual experiments.

Figure A.3: Sensitivity of free parameters $k_d$, $a$ and $d_f$ on model-measurement comparison results (experiments 1–3, from top to bottom), described by the value of root mean square error.
Figure A.4: Evolution of particle number concentration of experiment 1 from measurement (red line) and three sensitivity simulations with: 1) only coagulation (green line); 2) only wall loss (blue line); and 3) coagulation and wall loss (black line).

Figure A.5: Experimental and simulated time evolutions of number distributions from experiments 1–3 (top to bottom) at 7 min, 70 min and 210 min (left to right). Shaded areas represent $3 \times \sigma$ as described in Eq. (4.22). The optimization procedure to determine the parameters $k_d$, $a$, and $d_f$ was applied to all three experiments combined.
Figure A.6: Time evolution of experimental and simulated mean diameter, standard deviation of size and skewness of size distribution (left to right) from experiments 1, 2 and 3. The optimization procedure to determine the parameters $k_d$, $a$, and $d_f$ was applied to all three experiments combined.

Figure A.7: Sensitivity of free parameters $k_D$, $a$ and $d_f$ on model-measurement comparison results described by the value of root mean square error for the combined optimization procedure.
Appendix B

Appendix to Chapter 5: Supplementary tables and figures

Table B.1: Aerosol mass and mass fraction definitions and notations. The number of particles in the population is $N$, and the number of species is $A$. (Adapted from Riemer and West (2013))

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_i^a$</td>
<td>mass of species $a$ in particle $i$</td>
</tr>
<tr>
<td>$\mu_i = \sum_{a=1}^{A} \mu_i^a$</td>
<td>total mass of particle $i$</td>
</tr>
<tr>
<td>$\mu^a = \sum_{i=1}^{N} \mu_i^a$</td>
<td>total mass of species $a$ in population</td>
</tr>
<tr>
<td>$\mu = \sum_{i=1}^{N} \mu_i$</td>
<td>total mass of population</td>
</tr>
<tr>
<td>$p_i^a = \frac{\mu_i^a}{\mu_i}$</td>
<td>mass fraction of species $a$ in particle $i$</td>
</tr>
<tr>
<td>$p_i = \frac{\mu_i}{\mu}$</td>
<td>mass fraction of particle $i$ in population</td>
</tr>
<tr>
<td>$p^a = \frac{\mu^a}{\mu}$</td>
<td>mass fraction of species $a$ in population</td>
</tr>
</tbody>
</table>
Table B.2: Definitions of aerosol mixing entropies, particle diversities, and mixing state index. In these definitions we take $0 \ln 0 = 0$ and $0^0 = 1$. (Adapted from Riemer and West (2013))

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Name</th>
<th>Units</th>
<th>Range</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_i = \sum_{a=1}^{A} -p_{a}^i \ln p_{a}^i$</td>
<td>mixing entropy of particle $i$</td>
<td>—</td>
<td>0 to $\ln A$</td>
<td>Shannon entropy of species distribution within particle $i$</td>
</tr>
<tr>
<td>$H_\alpha = \sum_{i=1}^{N} p_i H_i$</td>
<td>average particle mixing entropy</td>
<td>—</td>
<td>0 to $\ln A$</td>
<td>average Shannon entropy per particle</td>
</tr>
<tr>
<td>$H_\gamma = \sum_{a=1}^{A} -p^\alpha \ln p^\alpha$</td>
<td>population bulk mixing entropy</td>
<td>—</td>
<td>0 to $\ln A$</td>
<td>Shannon entropy of species distribution within population</td>
</tr>
<tr>
<td>$D_i = e^{H_i} = \prod_{a=1}^{A} (p_{a}^i)^{-p_{a}^i}$</td>
<td>particle diversity of particle $i$</td>
<td>effective species</td>
<td>1 to $A$</td>
<td>effective number of species in particle $i$</td>
</tr>
<tr>
<td>$D_\alpha = e^{H_\alpha} = \prod_{i=1}^{N} (D_i)^{p_i}$</td>
<td>average particle (alpha) species diversity</td>
<td>effective species</td>
<td>1 to $A$</td>
<td>average effective number of species in each particle</td>
</tr>
<tr>
<td>$D_\gamma = e^{H_\gamma} = \prod_{a=1}^{A} (p_a)^{-p_a}$</td>
<td>bulk population (gamma) species diversity</td>
<td>effective species</td>
<td>1 to $A$</td>
<td>effective number of species in the population</td>
</tr>
<tr>
<td>$D_\beta = \frac{D_\alpha}{D_\gamma}$</td>
<td>inter-particle (beta) diversity</td>
<td>—</td>
<td>1 to $A$</td>
<td>amount of population species diversity due to inter-particle diversity</td>
</tr>
<tr>
<td>$\chi = \frac{D_\alpha - 1}{D_\gamma - 1}$</td>
<td>mixing state index</td>
<td>—</td>
<td>0 to 100%</td>
<td>degree to which population is externally mixed ($\chi = 0$) versus internally mixed ($\chi = 100%$)</td>
</tr>
</tbody>
</table>
B.1 Simulation results for trajectory starting at 11 am local time (18:00 UTC)

Figure B.1: Evolution of bulk aerosol species along the trajectory starting at 11 am local time.
Figure B.2: Evolution of gaseous species along the trajectory starting at 11 am local time.

Figure B.3: Evolution of total aerosol number concentration along the trajectory starting at 11 am local time.
Figure B.4: Two-dimensional number distributions after 3 hr of simulation for trajectory starting at 11 am local time.

Figure B.5: Two-dimensional number distributions after 6 hr of simulation for trajectory starting at 11 am local time.
Figure B.6: Evolution of mixing state index $\chi$ along the trajectory starting at 11 am.
B.2 Simulation results for trajectory starting at 12 pm local time (19:00 UTC)

Figure B.7: Evolution of bulk aerosol species along the trajectory starting at 12 pm local time.
Figure B.8: Evolution of gaseous species along the trajectory starting at 12 pm local time.

Figure B.9: Evolution of total aerosol number concentration along the trajectory starting at 12 pm local time.
Figure B.10: Two-dimensional number distributions after 3 hr of simulation for trajectory starting at 12 pm local time.

Figure B.11: Two-dimensional number distributions after 6 hr of simulation for trajectory starting at 12 pm local time.
Figure B.12: Evolution of mixing state index $\chi$ along the trajectory starting at 12 pm.
B.3 Simulation results for trajectory starting at 1 pm local time (20:00 UTC)

Figure B.13: Evolution of bulk aerosol species along the trajectory starting at 1 pm local time.
Figure B.14: Evolution of gaseous species along the trajectory starting at 1 pm local time.

Figure B.15: Evolution of total aerosol number concentration along the trajectory starting at 1 pm local time.
Figure B.16: Two-dimensional number distributions after 3 hr of simulation for trajectory starting at 1 pm local time.

Figure B.17: Two-dimensional number distributions after 6 hr of simulation for trajectory starting at 1 pm local time.
Figure B.18: Evolution of mixing state index $\chi$ along the trajectory starting at 1 pm.
B.4 Simulation results for trajectory starting at 2 pm local time (21:00 UTC)

Figure B.19: Evolution of bulk aerosol species along the trajectory starting at 2 pm local time.
Figure B.20: Evolution of gaseous species along the trajectory starting at 2 pm local time.

Figure B.21: Evolution of total aerosol number concentration along the trajectory starting at 2 pm local time.
Figure B.22: Two-dimensional number distributions after 3 hr of simulation for trajectory starting at 2 pm local time.

Figure B.23: Two-dimensional number distributions after 6 hr of simulation for trajectory starting at 2 pm local time.
Figure B.24: Evolution of mixing state index $\chi$ along the trajectory starting at 2 pm.