Soot Aging With Particle-Resolved Simulations

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Aerosol Aging: A Poorly-Defined Concept

Freshly emitted particles, or particles just after formation via homogeneous nucleation, are initially externally mixed but can be transferred into an internal mixture by coagulation, condensation or photochemical processes, collectively known as aging. The understanding of this aging process is of crucial importance to assess the chemical reactivity, cloud condensation nuclei (CCN) activity, radiative properties and health impacts of aerosol particles. However, the definition of when a particle is considered "aged" depends on the application and is currently poorly defined. In this study we investigate different measures of the aging process for soot aerosol with a new approach, the particle-resolved aerosol model PartMC.

PartMC: Particle-resolved Aerosol Model

Particle-resolved aerosol model. Modal and sectional aerosol representations cannot resolve the internal mixing state of the aerosol without storage that is exponential in the number of species. As an alternative we use a particle-resolved model that stores the composition of many individual aerosol particles, representing a certain computational volume. Particle positions within the volume are not tracked so a well-mixed box model is assumed. The simulation results shown here use 100,000 particles. PartMC accurately predicts both number and mass size distributions and is therefore suited for applications where either quantity is required.

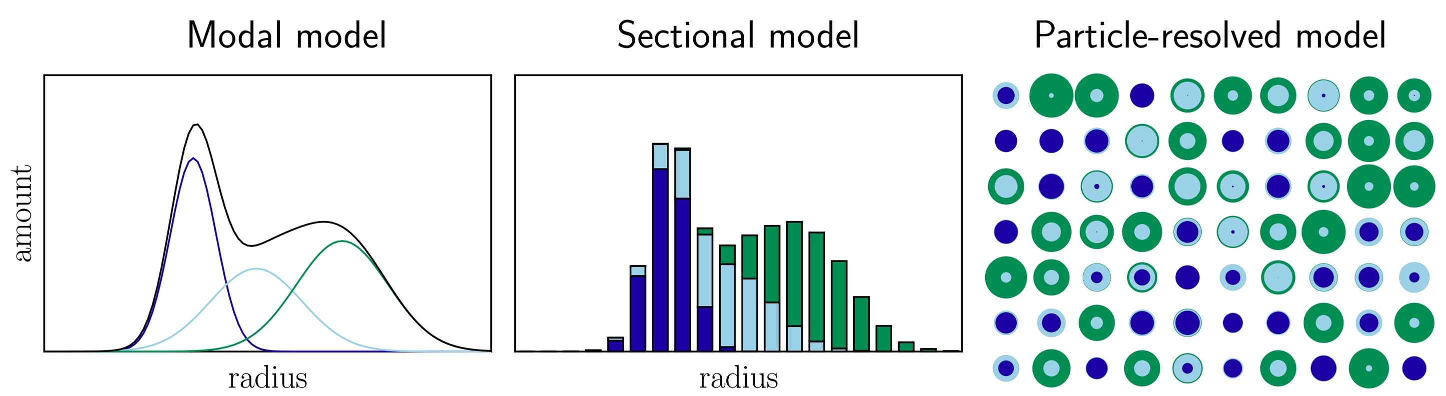

Figure 1: Modal aerosol models (left) represent the aerosol size distribution as a sum of modes, typically log-normal functions defined by mean radius, standard deviation and magnitude. Sectional models (center) store the number or mass of aerosol per bin. Both modal and sectional representations cannot accurately resolve the internal mixing state without storage that is exponential in the number of species. In contrast, a particle-resolved model (right) such as PartMC has storage that scales with particle number and can easily store complex internal mixing states. Efficient simulation techniques make particle-resolved methods feasible.

Stochastic particle coagulation. Coagulation between aerosol particles is simulated by generating a realization of a Poisson process with a Brownian kernel. For the large number of particles used here it is necessary to use an efficient approximate simulation method, as described in Riemer and West [2007]. This uses a hierarchical sampling method to efficiently sample from the highly multi-scale coagulation kernel in the presence of a very non-uniform particle size distribution.

Coupling with MOSAIC gas/aerosol chemistry. Gas- and aerosol-phase chemistry is implemented deterministically by coupling with the MOSAIC chemistry code [Zaveri et al., 2007]. MOSAIC treats all the globally important aerosol species including sulfate, nitrate, chloride, carbonate, ammonium, sodium, calcium, primary organic mass, secondary organic mass, soot, and inert organic mass. It consists of accurate yet computationally efficient modules for thermodynamics, internal solid-liquid equilibrium, dynamic gas-particle mass transfer, and the gas-phase photochemical mechanism CBM-Z.

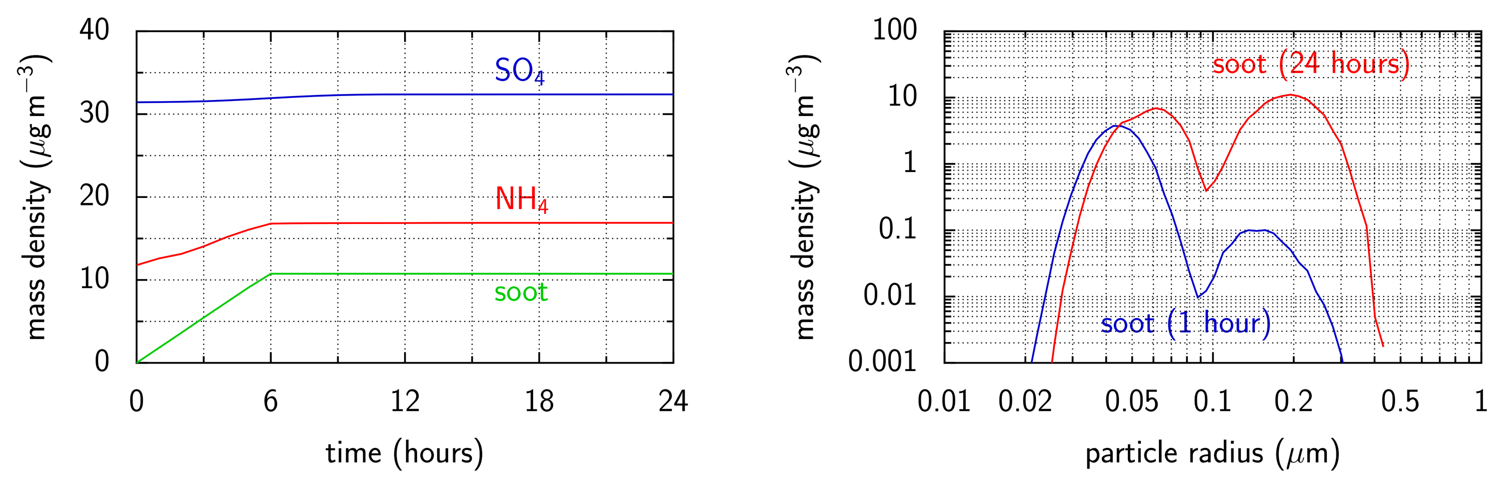

Figure 2: Left: Evolution of the total mass of various species in the aerosol phase, summed over all particles. Right: Evolution of the mass size distribution of soot.

For the case presented here the initial particle size distribution consists of NH_4SO_4 and organic carbon, with emissions of gas phase species and aerosol particles (90% soot, 10% organic carbon). After 6 hours emissions are switched off. Chemical reactions and gas-particle exchanges continue for 18 more hours of simulation time. **Figure 2** shows the evolution of aerosol particles in the traditional way: total mass versus time and the mass size distribution of soot versus particle size. This does not tell us what the mixing state of individual particles looks like. PartMC provides this information and we can relate the mixing state information to various measures of aging.

Aerosol Aging Measures

Depending on the application we can define several different measures of aging. For example, if we are interested in optical properties, we can use the composition (core and shell) as an aging measure. **Figure 3** shows that after one hour of simulation, two externally mixed distributions exist, small primary particles containing mainly soot, and larger particles containing mainly ammonium nitrate and ammonium sulfate. After 24 hours, the primary particles have grown due to condensation. They also have undergone mixing with the larger particles through coagulation, increasing the amount of soot in the initially soot-free particles.

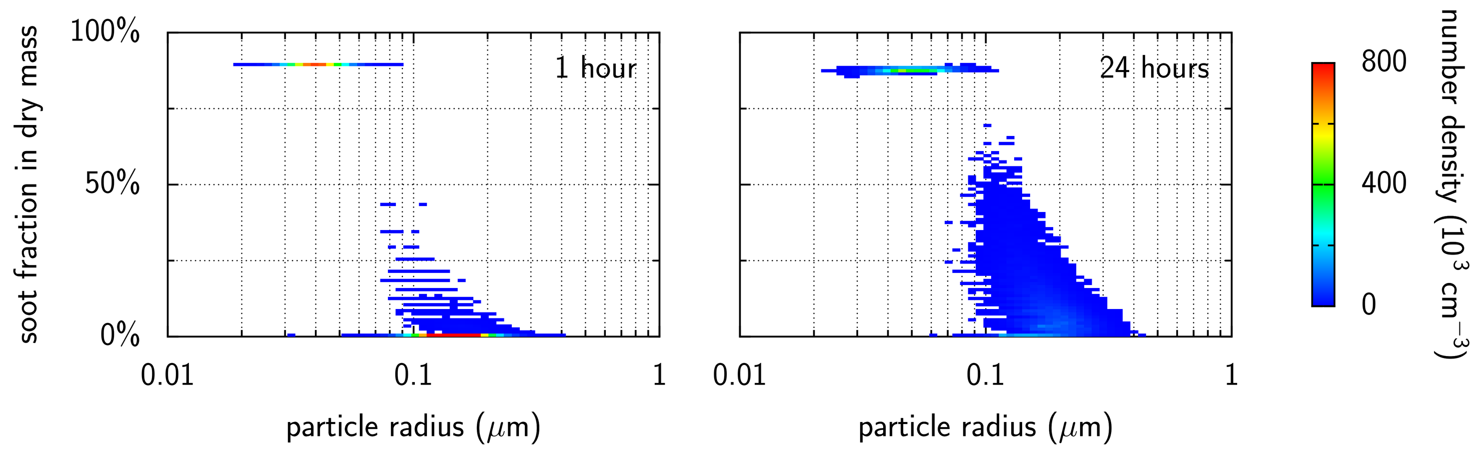

Figure 3: Size resolved distribution of soot mixing state.

Another way of defining aging is by means of the critical supersaturation necessary to activate the particle. This is appropriate if one is interested in aerosol-cloud interactions. **Figure 4** shows how this changes over the course of the simulation. At the beginning the primary particles require a large supersaturation to activate, while condensation of soluble substances lowers the critical supersaturation of these particles by the end of the simulation.

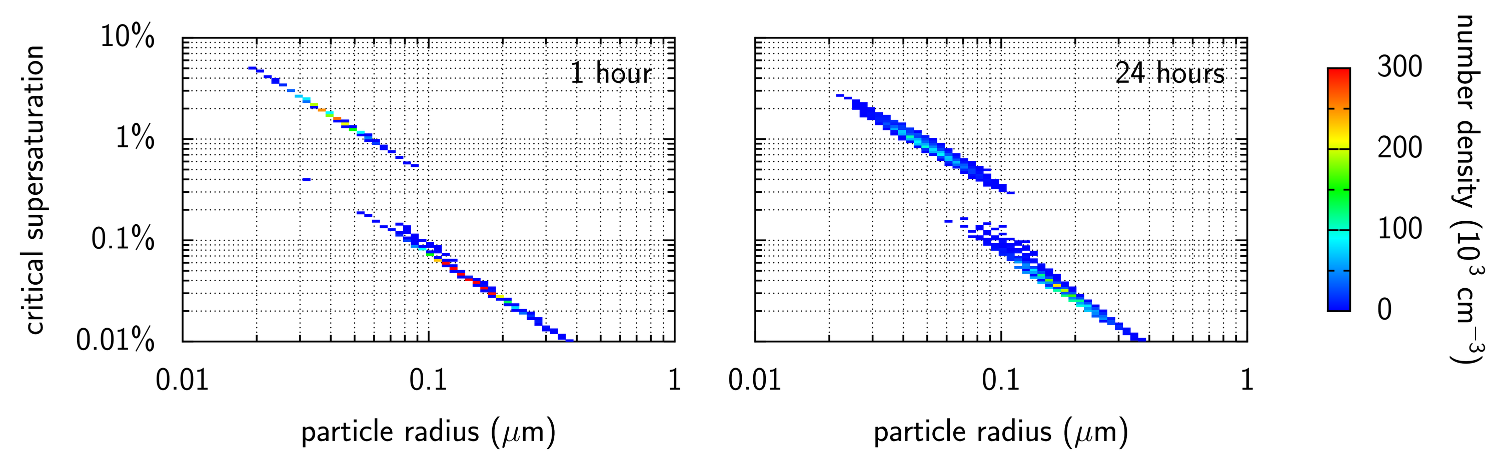

Figure 4: Size resolved distribution of critical supersaturation, based on Petters and Kreidenweis [2007].

Figure 5 shows that depending on how we define "aging", the "aged" fraction evolves differently in time. A composition-oriented definition will find that after 24 hours 40% of the particles are at least 80%-pure soot, down from a peak of 70% of the particles at 6 hours. A CCN-oriented definition will find that after 24 hours, 25% of the particles would activate at 0.03% supersaturation, half the particles at 0.05% and 90% at 1%. The CCN spectrum reflects how the particle population becomes more hygroscopic over the 24 hours of simulation.

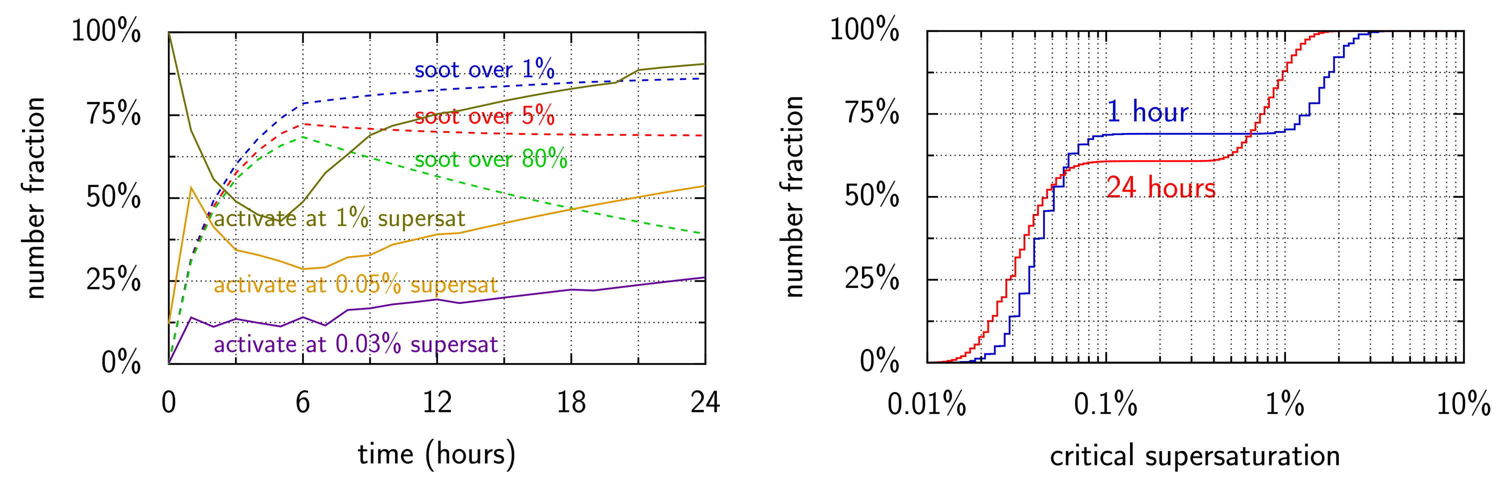

Figure 5: Left: Time evolution of the particle distribution assuming different measures of aging. Right: CCN spectrum on the basis of this case study.

Conclusion

This study introduces the particle-resolved model PartMC for improving the current treatment of the aerosol mixing state. We present a composition-based and a CCN-based aging definition and show that they give different estimates of aerosol aging. This highlights that there is no single aging criterion, and that application-dependent measures of aging must be used.

References

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