Modeling Effects of Phase State and Particle-phase Chemical Reactions on SOA Partitioning Dynamics

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1. Introduction

Recent studies suggest particle phase state and particle-phase reactions control the number-diameter distribution of the resulting SOA. A proper representation of these physicochemical processes are therefore needed in the next generation models to reliably predict not only the total SOA mass, but also its composition and number size distribution, all of which together determine the optical and cloud-nucleating properties.

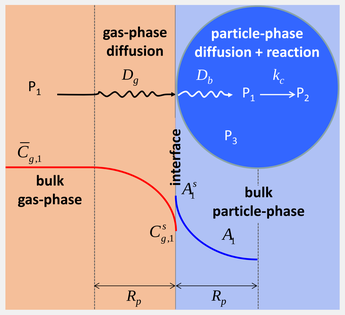
This poster describes a new framework within **MOSAIC** (Zaveri et al., 2008, JGR) for modeling kinetic gas-particle partitioning of SOA that takes into account diffusion and chemical reaction within the particle phase (Zaveri et al., 2013, ACPD). The framework is amenable for use in large-scale atmospheric models, although it currently awaits specification of the various gas- and particle-phase chemical reactions and the related physicochemical properties that are important for SOA formation.

2. New SOA Modeling Framework

The model framework uses a combination of:

(a) Analytical quasi-steady-state treatment for the diffusion-reaction process within the particle for fast-reacting species
(b) Two-film theory approach for slow- and non-reacting solutes.

Approximation 1: $k_c \geq 0.01$ s^{-1}
Quasi-Steady-State Solution



$$\frac{d\bar{C}_{a,i,m}}{dt} = 4\pi R_{p,m}^2 N_m k_{g,i,m}\left(\bar{C}_{g,i} - \frac{\bar{C}_{a,i,m}}{\sum_j \bar{C}_{a,j,m}}\frac{C_{g,i}^*}{Q_i}\right) - k_{c,i}\bar{C}_{a,i,m}$$

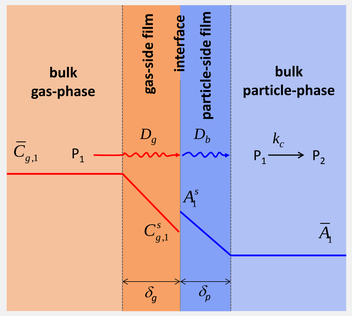
Gas-side mass transfer coefficient

$$k_{g,i} = \frac{D_{g,i}}{R_p} f(Kn_i, \alpha_i)$$

Where quasi-steady-state concentration parameter

$$Q_i = 3\left(\frac{q_i \coth q_i - 1}{q_i^2}\right) \qquad q_i = R_p\sqrt{\frac{k_{c,i}}{D_{b,i}}}$$

Approximation 2: $k_c < 0.01$ s^{-1}
Two-Film Theory



$$\frac{d\bar{C}_{a,i,m}}{dt} = 4\pi R_{p,m}^2 N_m K_{g,i,m}\left(\bar{C}_{g,i} - \bar{C}_{a,i,m} S_{i,m}\right) - k_{c,i}\bar{C}_{a,i,m}$$

Overall gas-side mass transfer coefficient

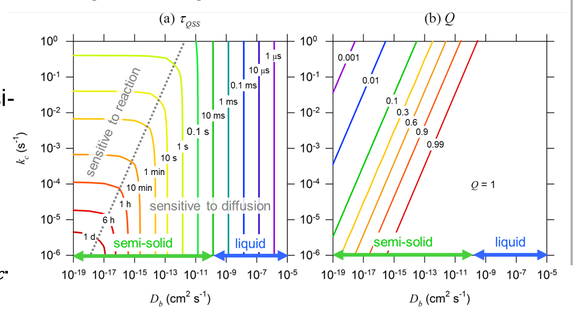
$$\frac{1}{K_{g,i}} = \frac{1}{k_{g,i}} + \frac{1}{k_{b,i}}\frac{C_{g,i}^*}{\sum_j \bar{A}_j}$$

Where particle-side mass transfer coefficient

$$k_{p,i} = \frac{D_{b,i}}{R_p}\left(\frac{q_i \coth q_i - 1}{1 - Q_i}\right)$$

Quasi-Steady State System Behavior

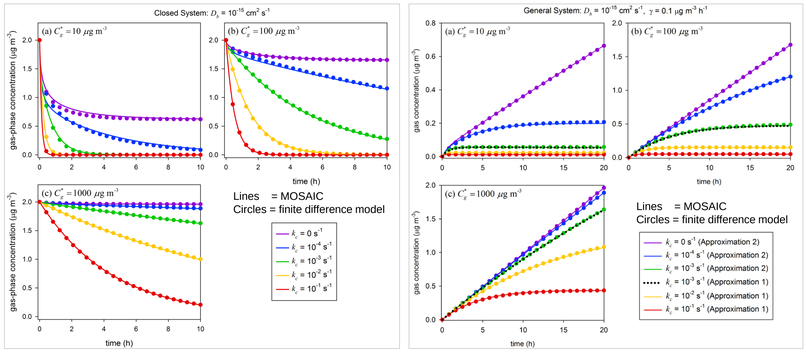
Timescale (τ_{QSS}) for the concentration profile to reach quasi-steady state within the particle and the parameter Q are shown for a particle of D_p = 0.1 µm as a function of D_b and k_c.



2. Model Validation

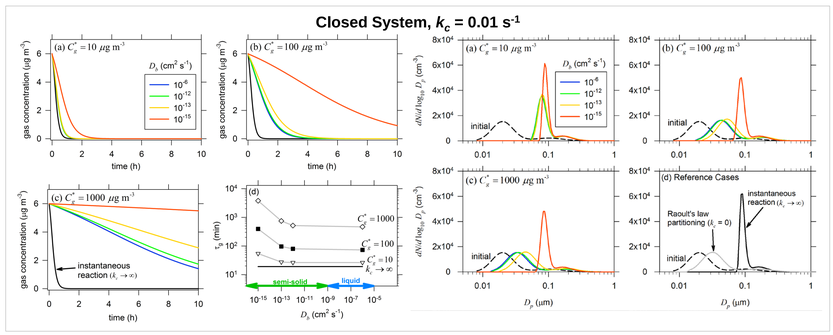
The new framework in MOSAIC was successfully validated against a "fully numerical" finite difference solution to the diffusion-reaction problem for both closed and general systems.

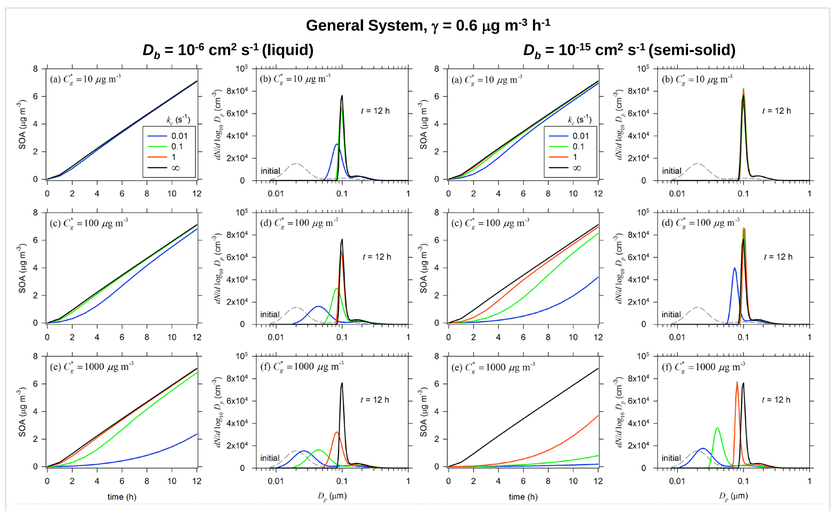
Initial Particle Diameter, D_p = 0.2 µm, Number Concentration, N = 5000 cm^{-3}



3. Model Evaluation for Test Cases

Competitive growth dynamics of the Aitken and accumulation modes due to SOA formation are illustrated below for several test cases consisting of different values of C^*, D_b, and k_c for both closed and general systems.





4. Application to Chamber Experiments

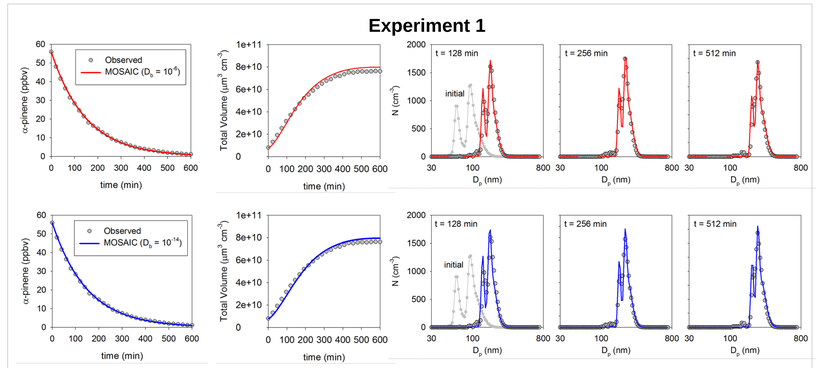
The model was applied to interpret chamber experiments of SOA formation from photolysis of a-pinene in the presence of two types of seed aerosols.

$$\alpha\text{-pinene} + OH \longrightarrow \alpha_1 P_1 + \alpha_2 P_2 + \alpha_3 P_3 + \alpha_4 P_4$$

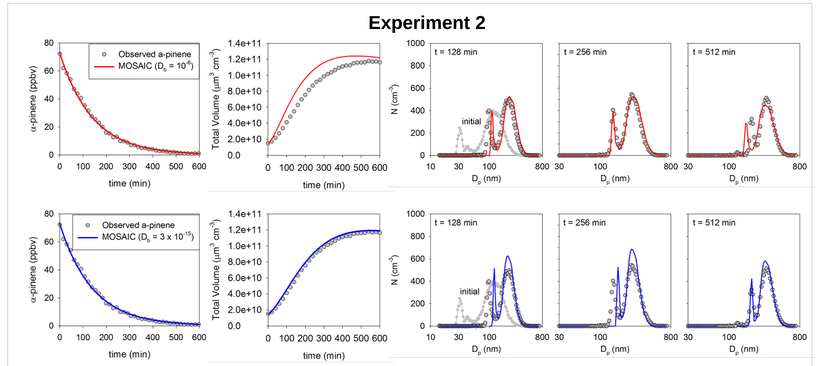
Experiment	Small Mode Seed	Large Mode Seed
1	ammonium sulfate	ammonium sulfate
2	ammonium sulfate	oxidized oleic acid

Product	C* (mg m^{-3})	Gas-phase Yields, a_i
P1	0	0.07
P2	10	0.01
P3	100	0.26
P4	1000	0.55

Experiment 1



Experiment 2



Evolutions of total SOA mass and size distribution appear to be insensitive to phase state in Experiment #1. In contrast, both total mass and size distribution evolutions are sensitive to whether the assumed phase state is liquid or semi-solid, although neither yield "perfect" agreement with the observations. Measurements of SOA volatility and size-dependent composition are needed to fully constrain and evaluate the new model.

5. Conclusions & Future Work

- Results show that the timescale of SOA partitioning and the associated size distribution dynamics depend on the complex interplay between SOA volatility, phase state, and particle-phase reactivity.
- Implement multigenerational gas-phase VOC oxidation chemistry and particle-phase reactions that produce oligomers and other products.
- Apply the model to interpret laboratory chamber and field observations (e.g., CARES, GoAmazon) of aerosol growth.

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