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Size Distribution Dynamics of SOA Formation

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SECONDARY ORGANIC AEROSOL BREAKOUT SESSION, ASR FALL WORKING GROUP MEETING, ROCKVILLE, MD
NOVEMBER 4, 2013

Importance of SOA Size Distribution

- Particles in the range 0.03 to 0.1 µm and larger (dry diameter) may serve as CCN.
- Particles > 0.1 µm (wet diameter) are optically active.
- A majority of these climatically active particles are produced by growth of smaller particles via SOA formation.
- Climate models must therefore be able to capture evolution of **size distribution** as well as the **total mass of SOA**.

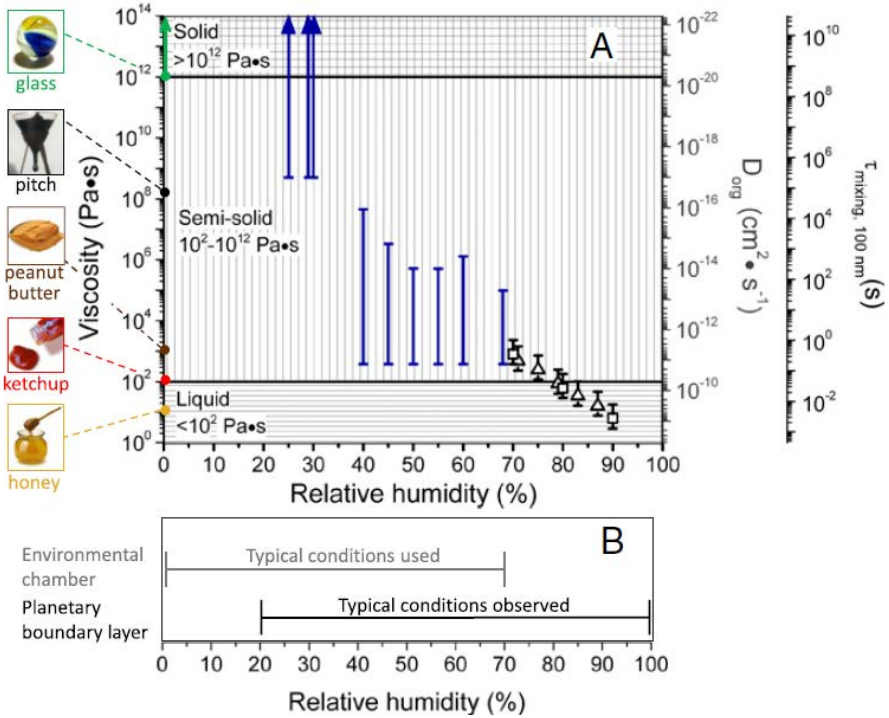
Mechanisms of SOA Formation

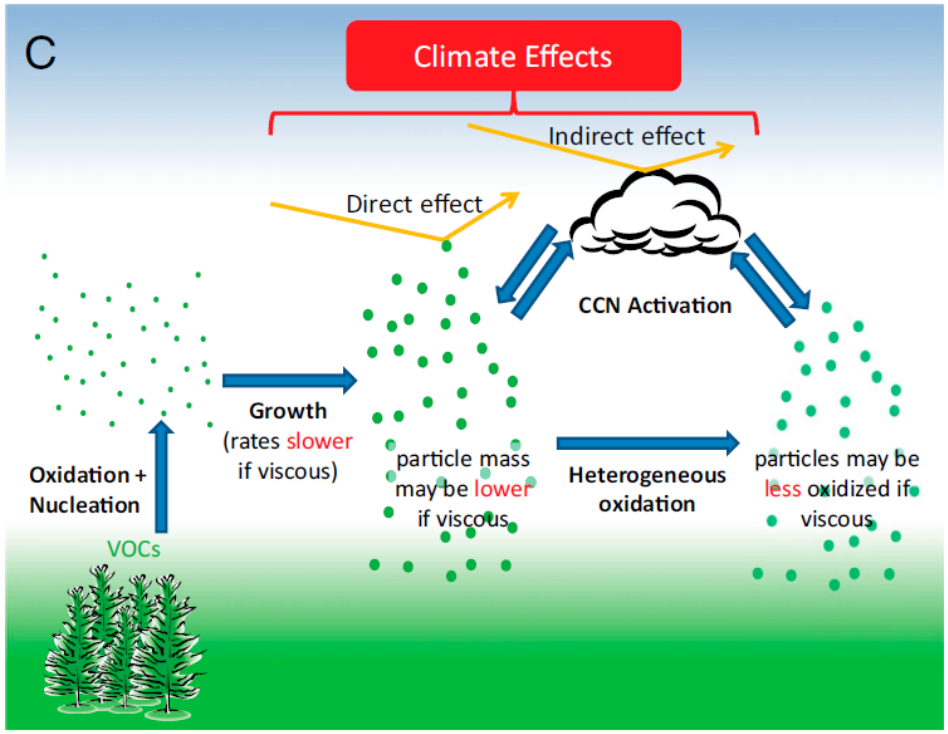
No.	Mechanism	Parameters Controlling Growth Dynamics
#1	Gas-phase diffusion limited condensation of effectively non-volatile organics	Aerosol surface area
#2	Absorption of semi-volatile organic vapors according to Raoult's law or Henry's law	Aerosol volume (& composition), Solute volatility, Phase state (viscosity, diffusivity)
#3	Mechanism #2 followed by particle-phase chemical reactions to form effectively non-volatile oligomers, organic salts, organosulfates, organic acids, etc.	Particle size (& composition), Solute Volatility, Phase state (viscosity, diffusivity), Particle-phase reactivity

Viscosity of α-pinene secondary organic material and implications for particle growth and reactivity

Lindsay Renbaum-Wolff[a], James W. Grayson[a], Adam P. Bateman[b], Mikinori Kuwata[b], Mathieu Sellier[c], Benjamin J. Murray[d], John E. Shilling[e], Scot T. Martin[b,f,1], and Allan K. Bertram[a,1]

PNAS 2013

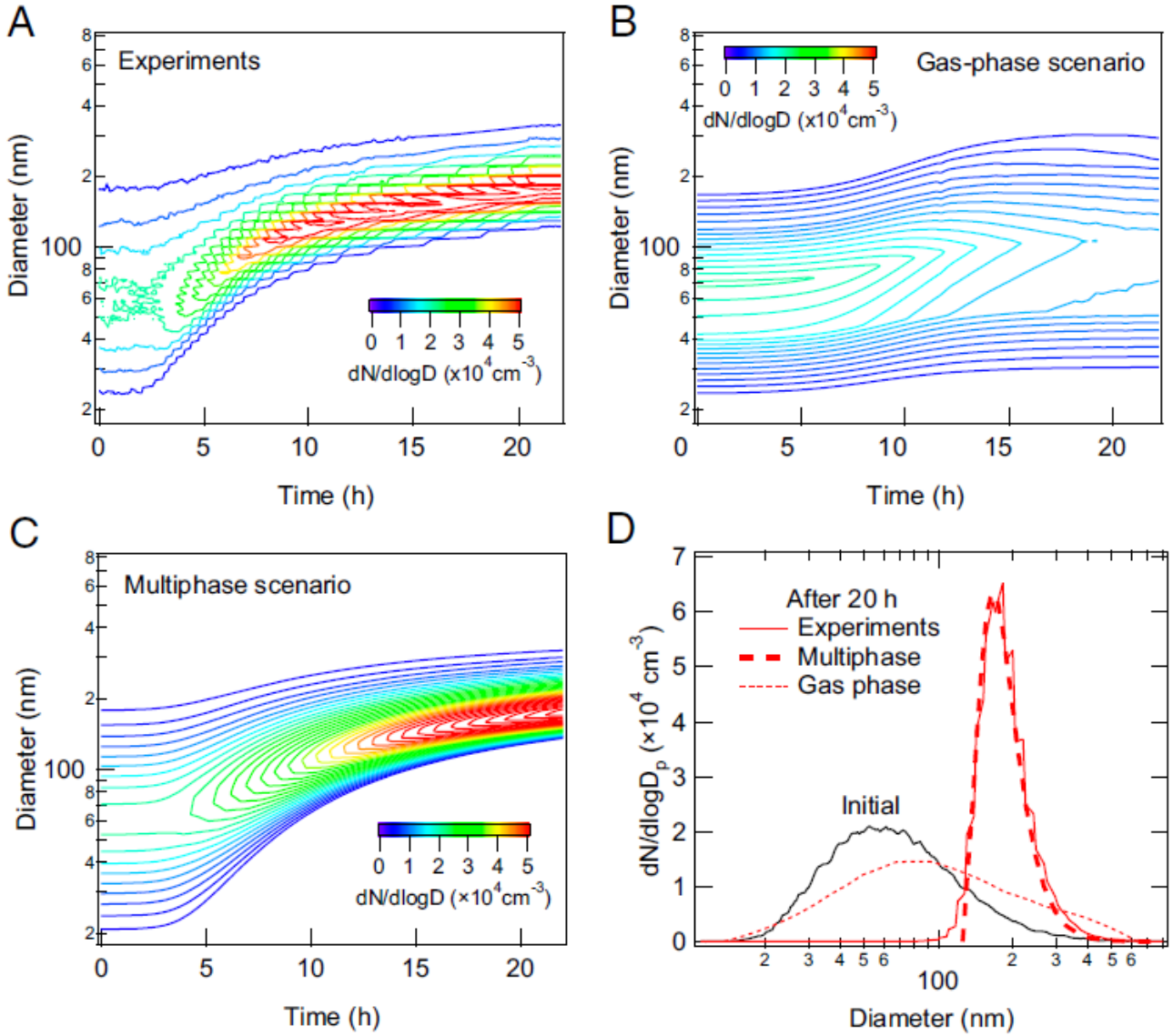




Size distribution dynamics reveal particle-phase chemistry in organic aerosol formation

PNAS, 2013

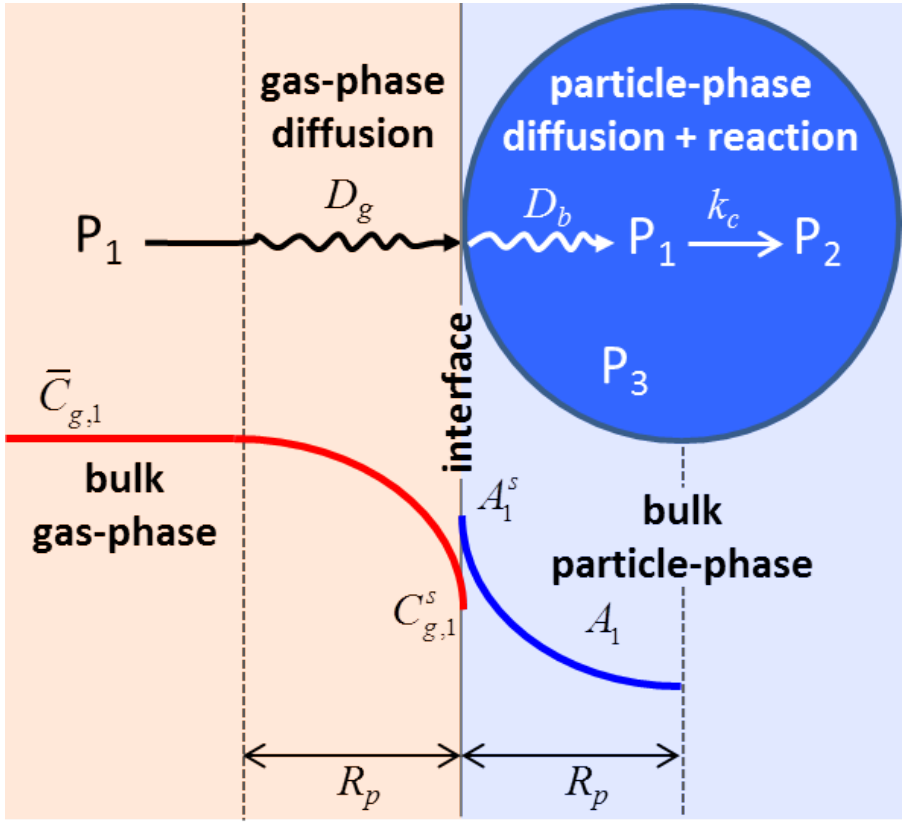
Manabu Shiraiwa[a,b], Lindsay D. Yee[c], Katherine A. Schilling[a], Christine L. Loza[a], Jill S. Craven[a], Andreas Zuend[a,d], Paul J. Ziemann[e], and John H. Seinfeld[a,c,1]



Photooxidation of dodecane in the presence of ammonium sulfate seed aerosol.

KM-GAP Model: Kinetic Multilayer Model of Gas-Particle Interactions in Aerosols and Clouds

Dynamics of Diffusion and Reaction



$$C_{g,i}^s = \frac{A_i^s}{\sum_j A_j^s} C_{g,i}^*$$

Mathematical Representation

$$\frac{\partial A(r,t)}{\partial t} = D_b \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial A(r,t)}{\partial r}\right) - k_c A(r,t)$$

Initial Condition: $A(R_p, 0) = 0,$

Boundary Condition 1: $A(R_p, t) = A^s$

Boundary Condition 2: $\frac{\partial A(0,t)}{\partial r} = 0$

Analytical Solution

$$\frac{A(r,t)}{A^s} = \frac{R_p}{r}\frac{\sinh(qr/R_p)}{\sinh(q)} + \frac{2R_p}{\pi r}\sum_{n=1}^{\infty}\frac{(-1)^n n \sin(n\pi r/R_p)}{(q/\pi)^2 + n^2}\exp\left\{-\left(k_c + \frac{n^2\pi^2 D_b}{R_p^2}\right)t\right\}$$

where $q_i = R_p\sqrt{\frac{k_{c,i}}{D_{b,i}}}$ Diffuso-Reaction Parameter

(Schwartz and Freiberg, 1981)

Volume Average Concentration

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Volume average concentration

$$\frac{\bar{A}(t)}{A^s} = \frac{\int_0^{R_p} 4\pi r^2 \frac{A(r,t)}{A^s}\, dr}{\frac{4}{3}\pi R_p^3} = Q - U(t)$$

where

$$Q_i = 3\left(\frac{q_i \coth q_i - 1}{q_i^2}\right)$$

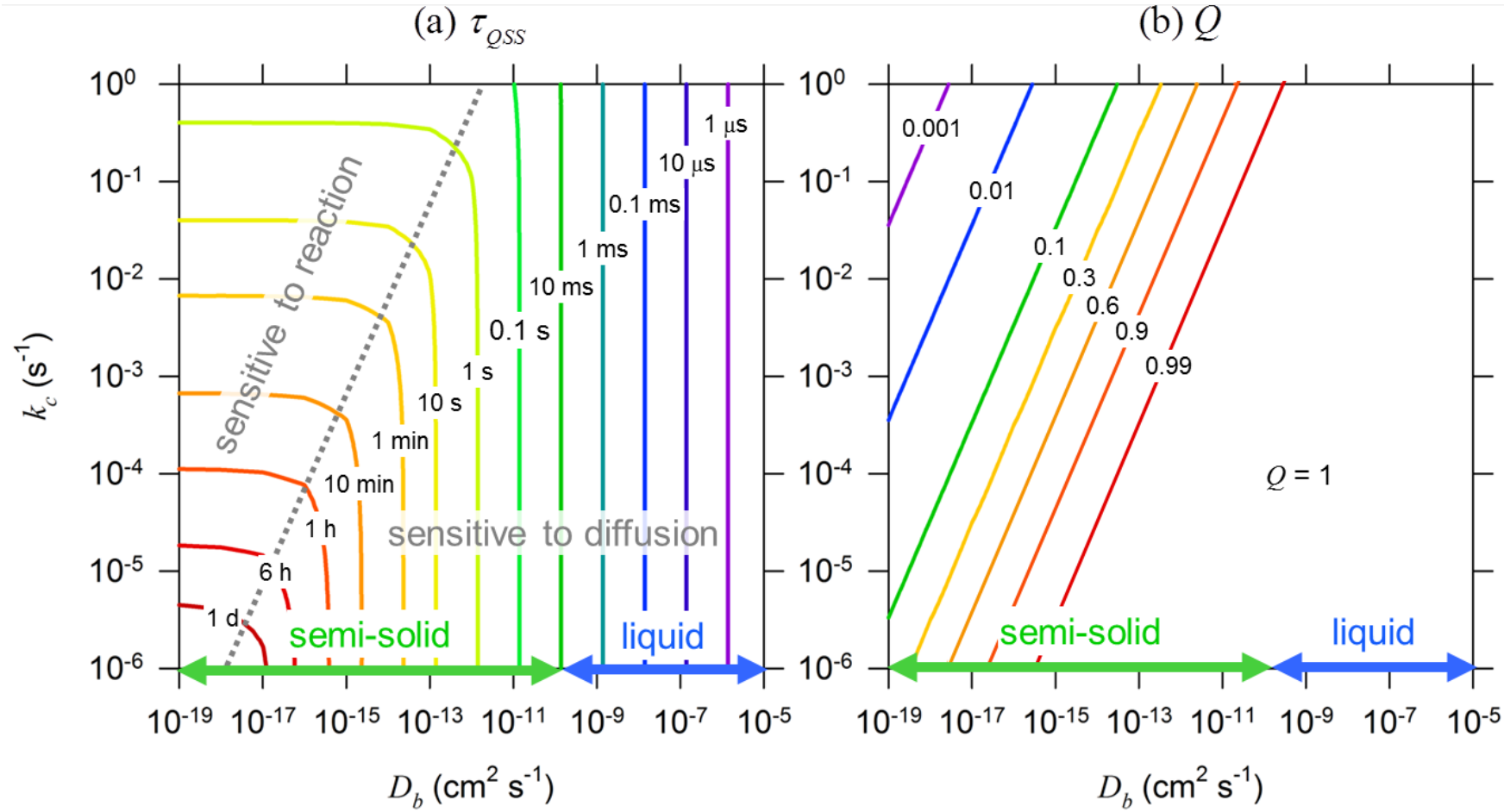
Steady-State Term

$$U_i(t) = \frac{6}{\pi^2}\sum_{n=1}^{\infty} \frac{\exp\left\{-\left(k_{c,i} + \frac{n^2\pi^2 D_{b,i}}{R_p^2}\right)t\right\}}{(q_i/\pi)^2 + n^2}$$

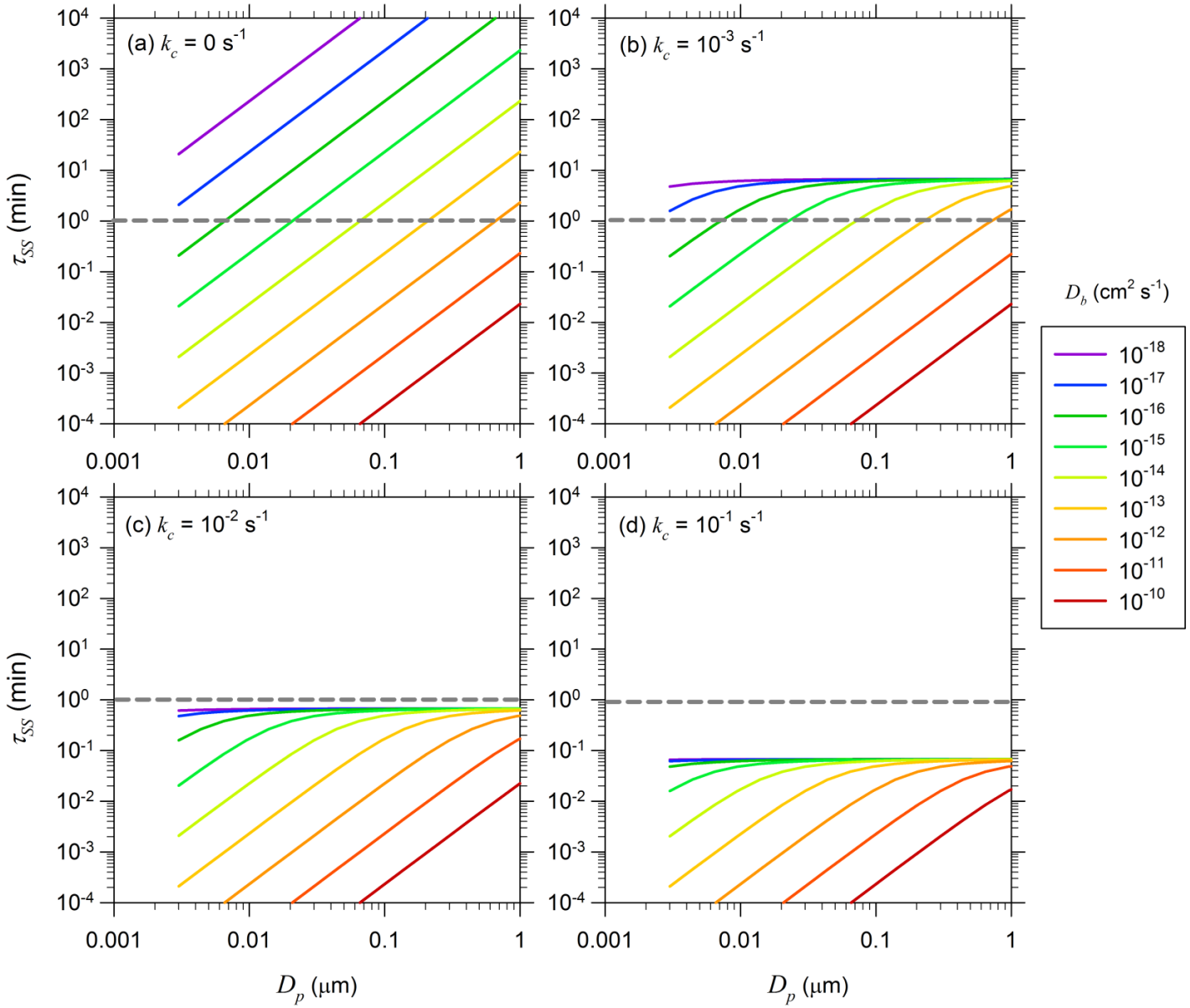
Transient Term

Timescale to Reach Steady-State

D_p = 0.1 µm



Timescale to Reach Steady-State



New Kinetic SOA Partitioning Model

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

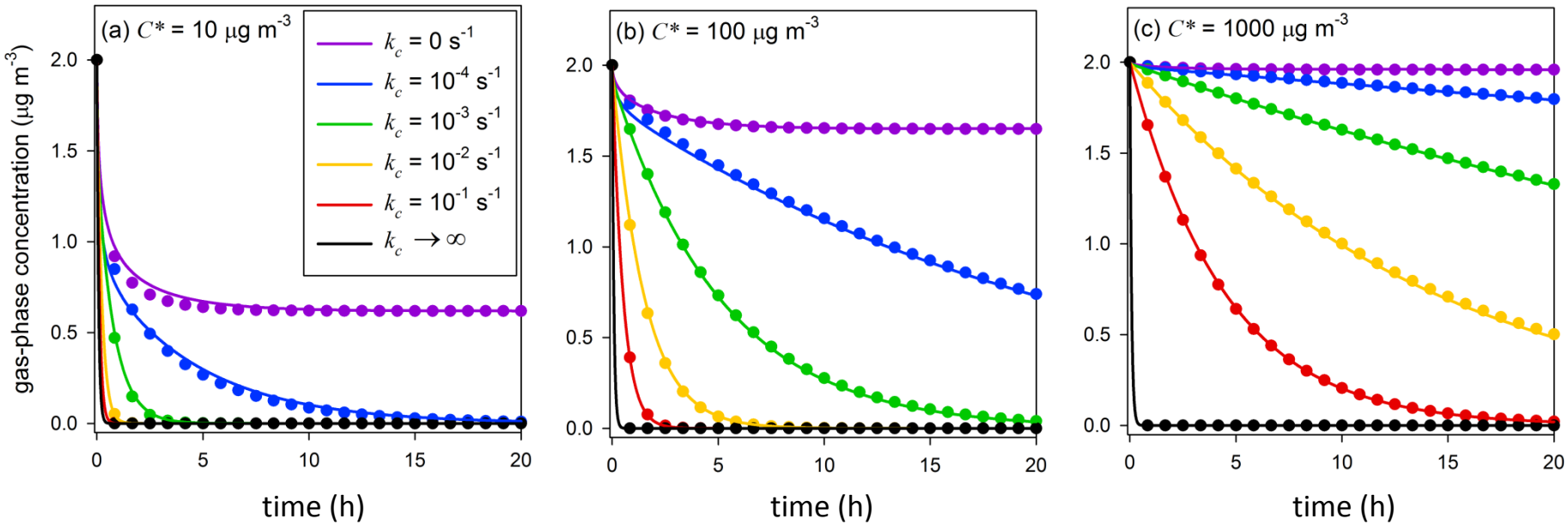
Implemented in the sectional aerosol model MOSAIC. Efficiently accounts for effects of:

- Volatility
- Phase state and viscosity (in terms of diffusivity)
- Particle-phase chemical reactivity

Zaveri, R. A., Easter, R. C., Shilling, J. E., and Seinfeld, J. H.: Modeling kinetic partitioning of secondary organic aerosol and size distribution dynamics: representing effects of volatility, phase state, and particle-phase reaction, Atmos. Chem. Phys. Discuss., 13, 28631-28694, doi:10.5194/acpd-13-28631-2013, 2013.

Model Validation

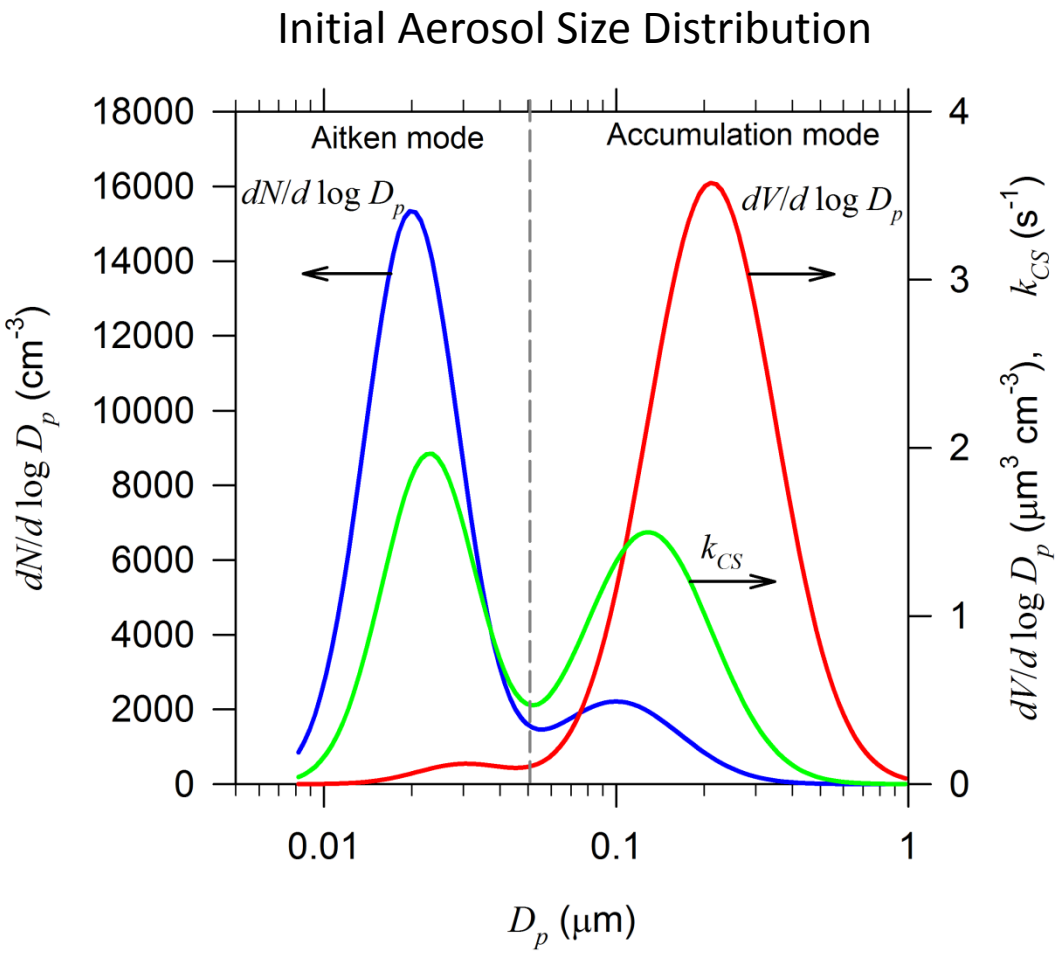
Viscous Particle: $D_b = 10^{-15}$ cm^2 s^{-1}



Lines = MOSAIC

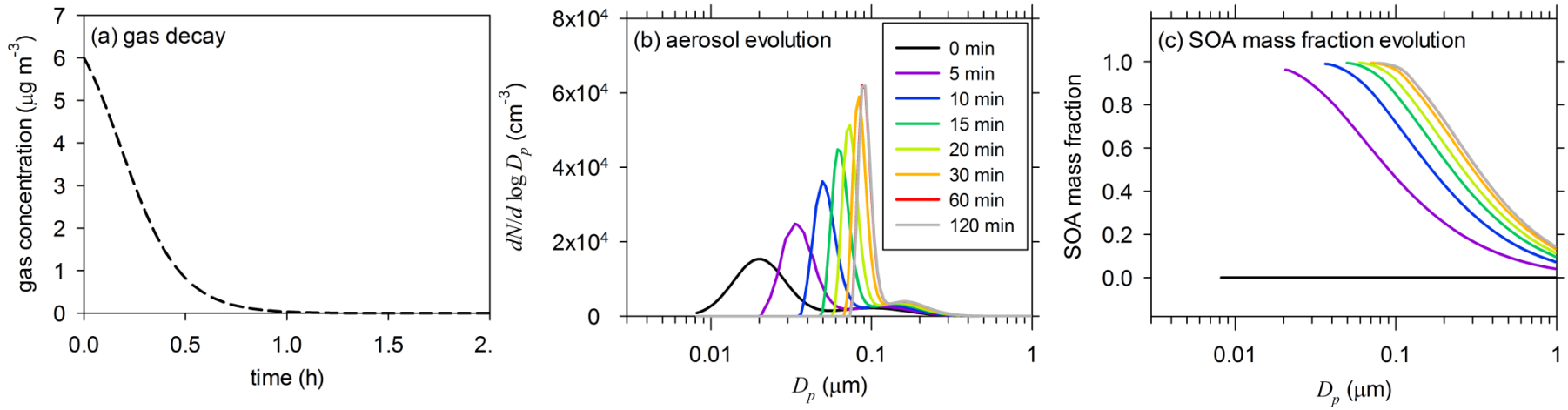
Filled circles = finite difference model (similar to KM-GAP model)

Competitive Growth Dynamics



C_{OA} = 2 μg m^{-3}

Mechanism #1: $C^* = 0$

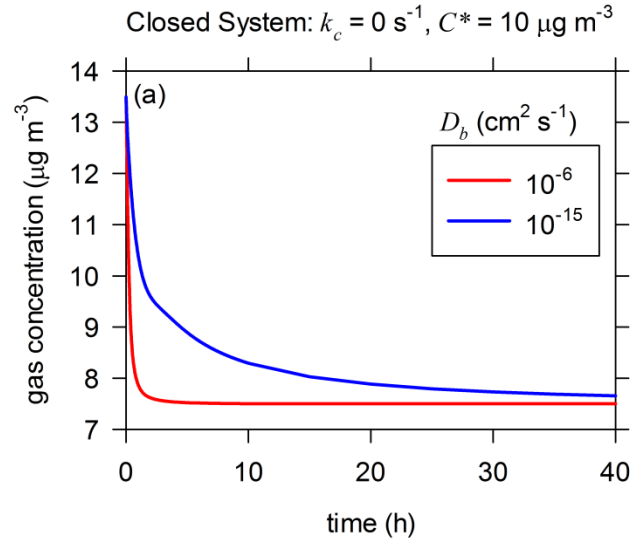


Final C_{SOA} = 6 μg m^{-3}

Final bulk SOA mass fraction = 0.75

Final C_{OA} = 8 μg m^{-3}

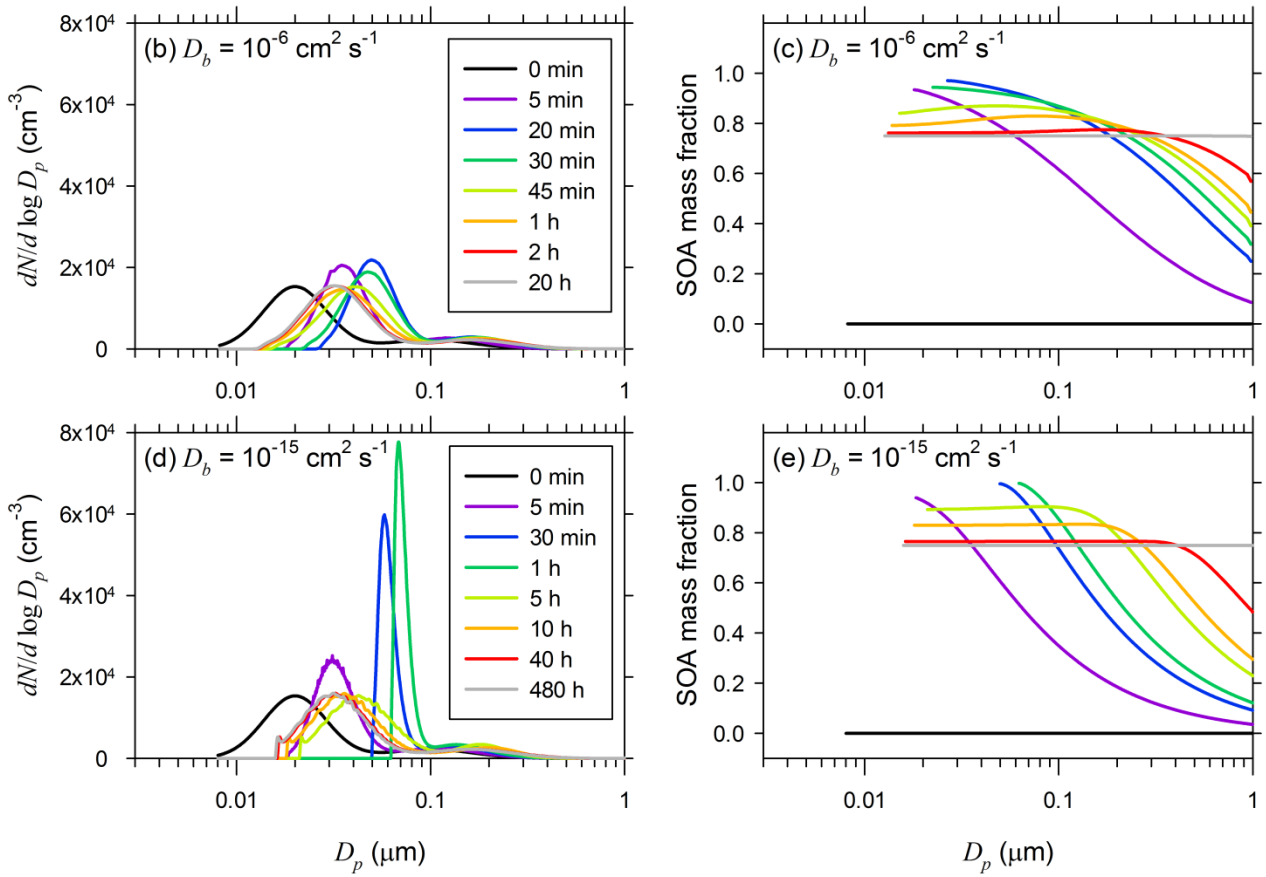
Mechanism 2:
k_c = 0, C^* = 10 µg m^{-3}



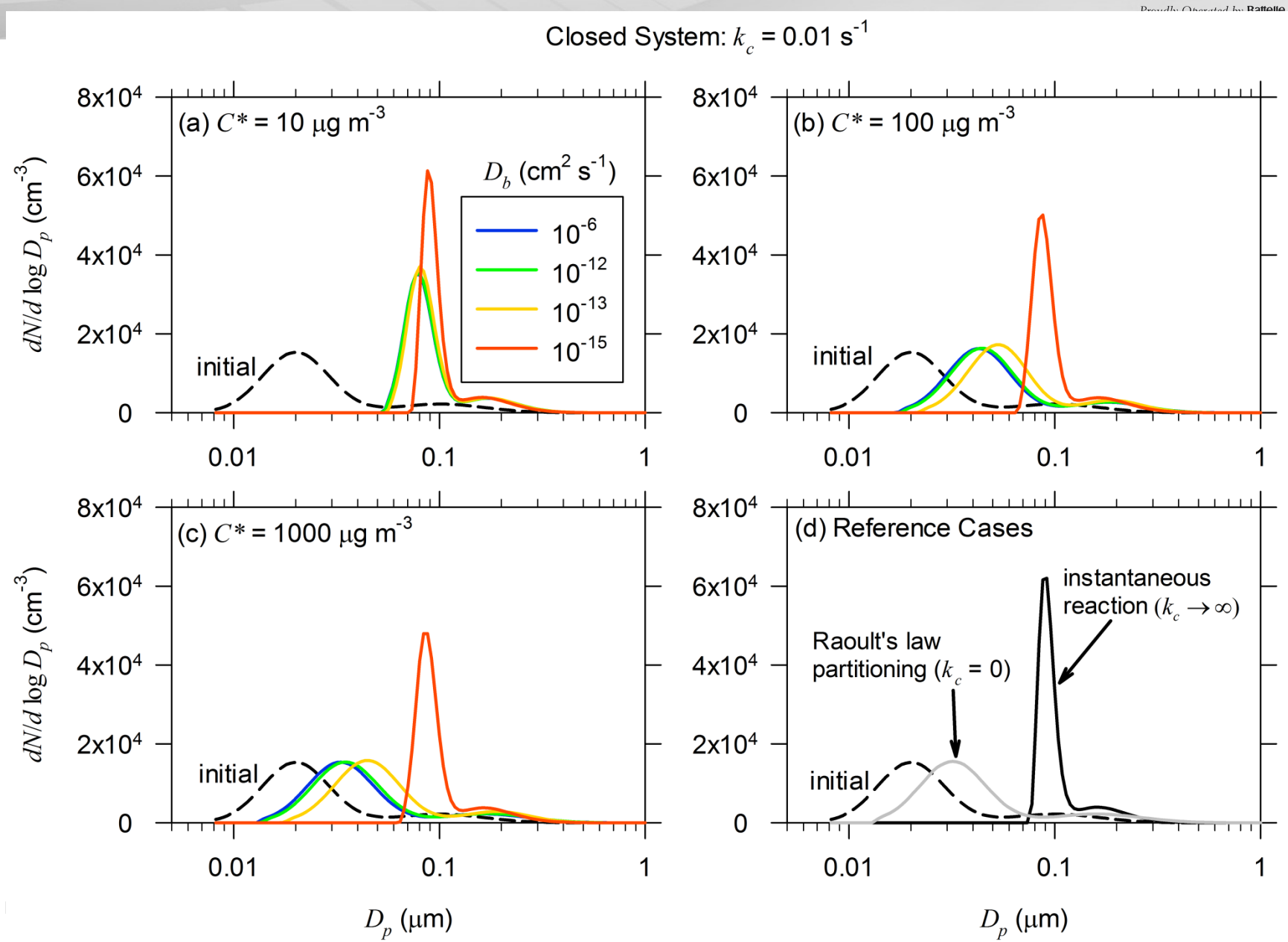
Final C_{SOA} = 6 µg m^{-3}

Final C_{OA} = 8 µg m^{-3}

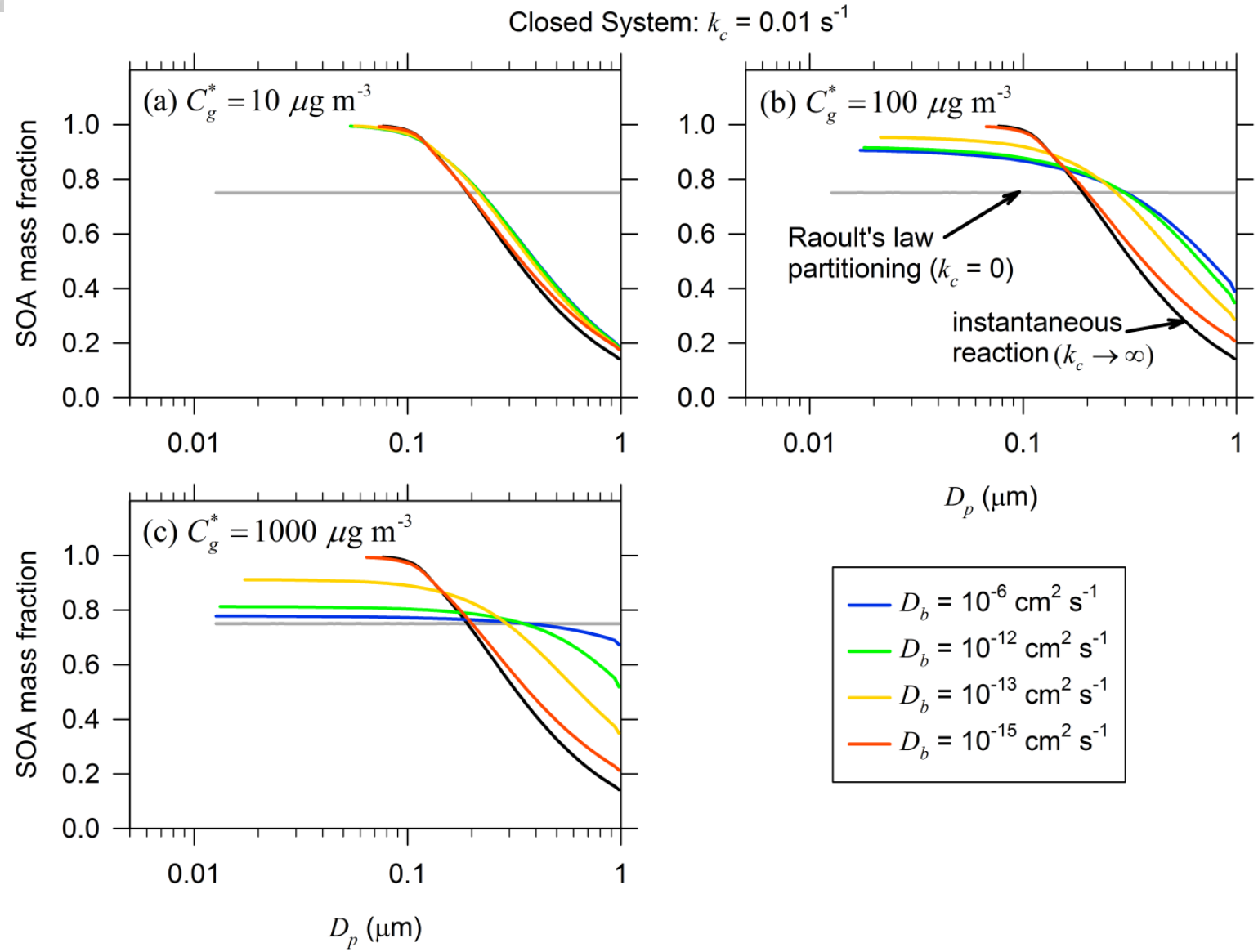
Final SOA m.f. = 0.75



Mechanism #3: dN/dlogDp



Mechanism #3: SOA Mass Fraction



Summary

- SOA partitioning and number – diameter distribution evolution depend on **volatility**, **diffusivity**, and **particle-phase reactivity**, each of which can vary over several orders of magnitude.
- In general, viscous particles will favor growth of smaller particles due to severe diffusion limitation in accumulation mode particles.
- The new mathematical formulation can be implemented in regional and global model, but presently awaits specification of the actual species, reactions, and phase state properties.

Future Directions and Needs

- Couple MOSAIC with GECKO (in collaboration with Sasha Madronich & Julia Lee-Taylor)
- Implement known particle-phase reactions
- Interface with other focus groups (NPF, Absorbing Aerosol, Mixing State)
- Apply model to investigate A-B interactions, with special attention to size distribution dynamics

Need specific laboratory and field observations to:

- Constrain and evaluate gas and particle-phase reactions and products, role of inorganic-organic interactions
- Parameterize phase state as a function of composition, RH, T (in collaboration with Scot Martin, Allan Bertram, Alla Zelenyuk)
- Evaluate number-diameter and composition-diameter distributions evolution under different atmospherically relevant conditions (in collaboration with John Shilling and others).