Kinetic modelling of secondary organic aerosol (SOA) formation: connecting the data points

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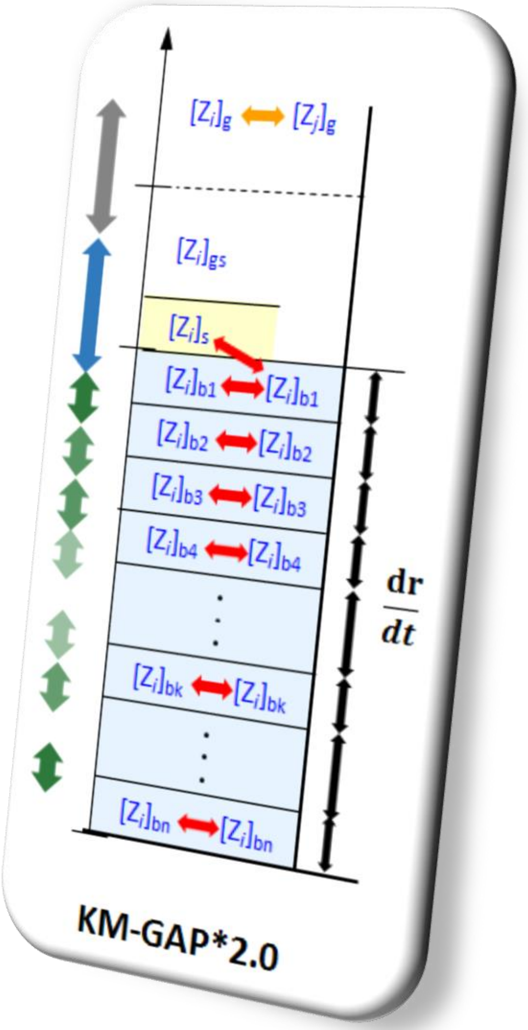
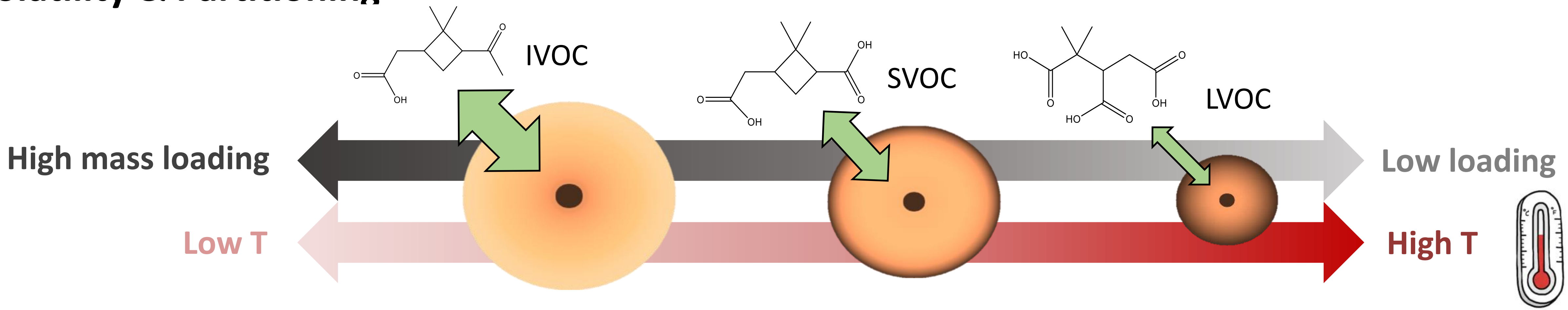


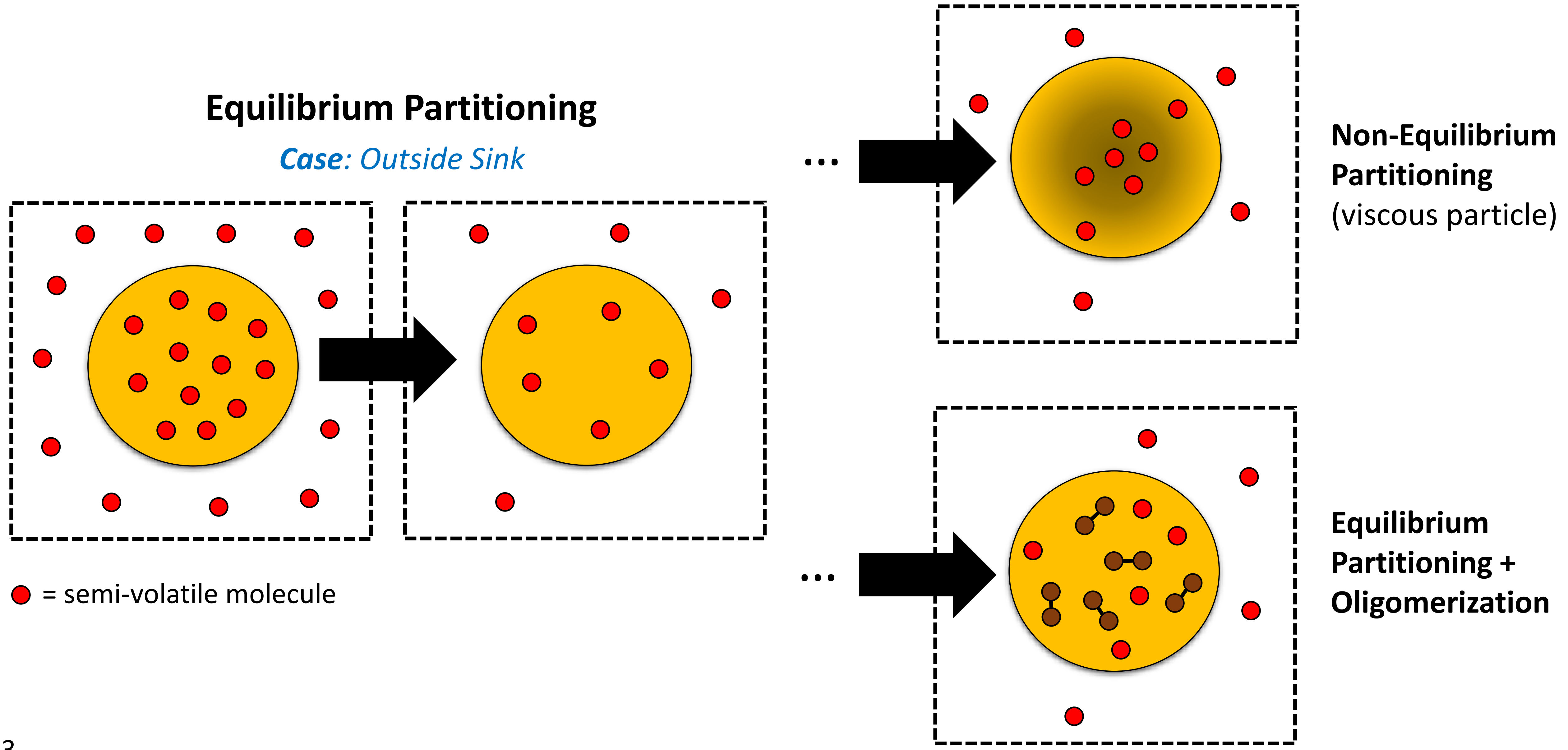
Volatility & Partitioning



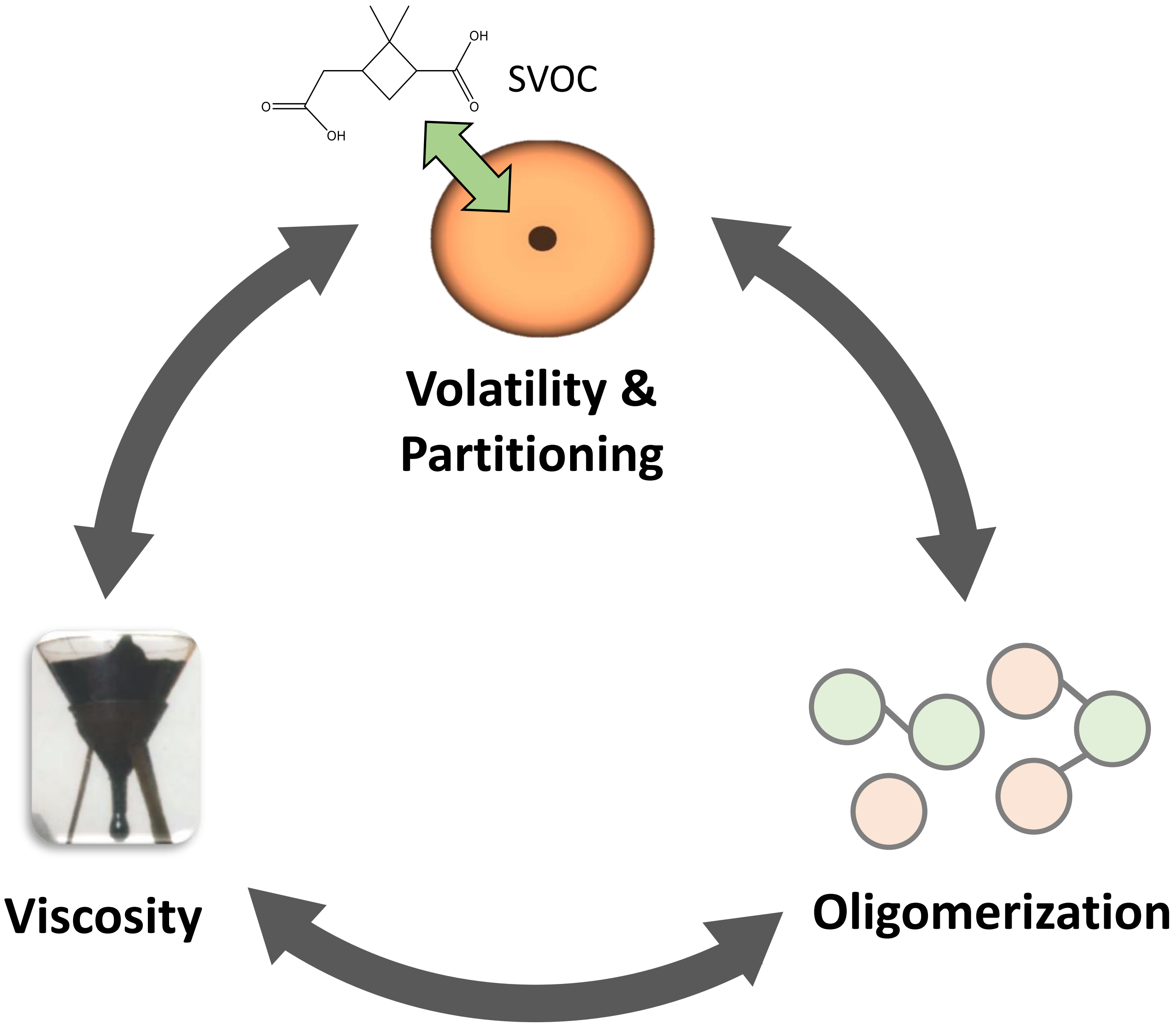
Viscosity

Koop *et al*. PCCP (2011)

Consequences of SOA Properties



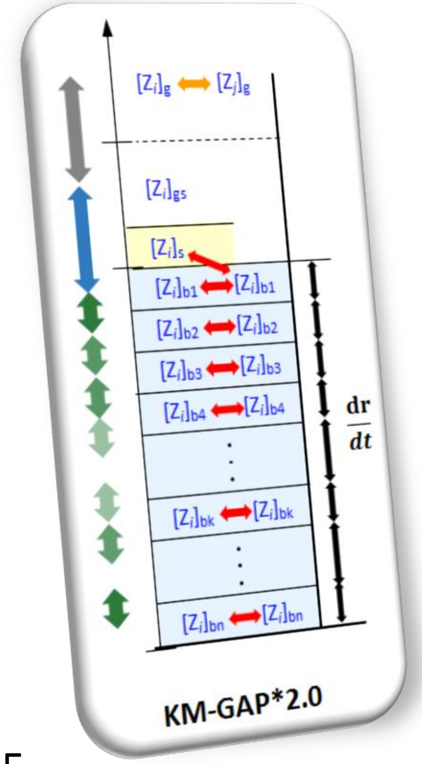
Feedback & Interaction Between SOA Properties



Approach

Interactions of Physical-Chemical Properties of SOA

Inverse Modelling

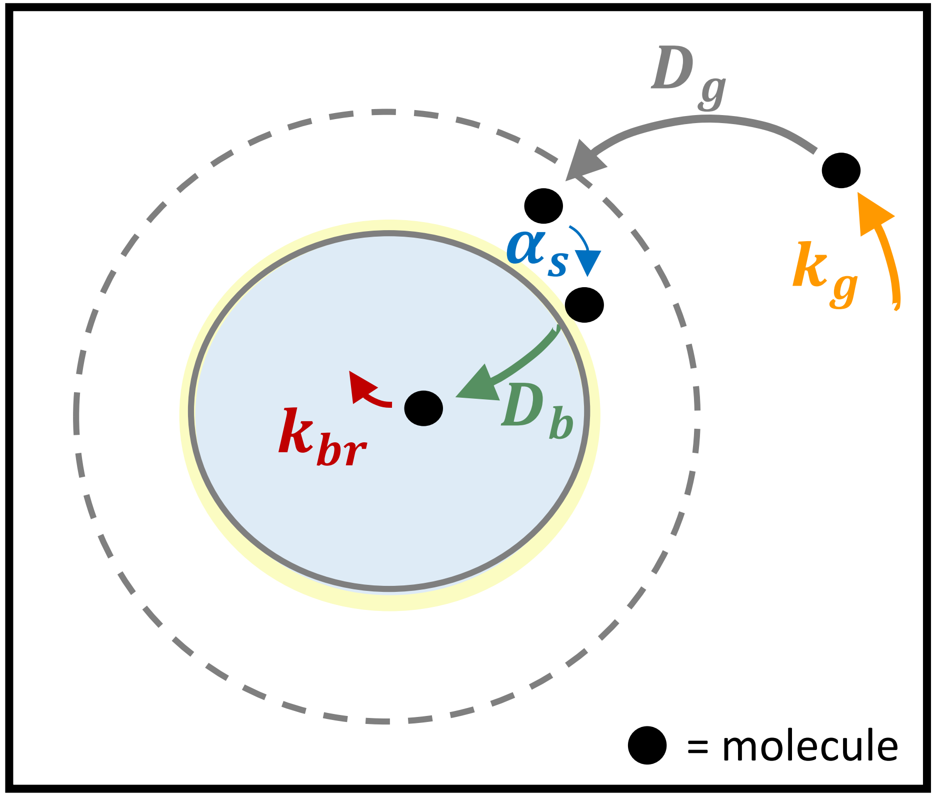


Kinetic Model

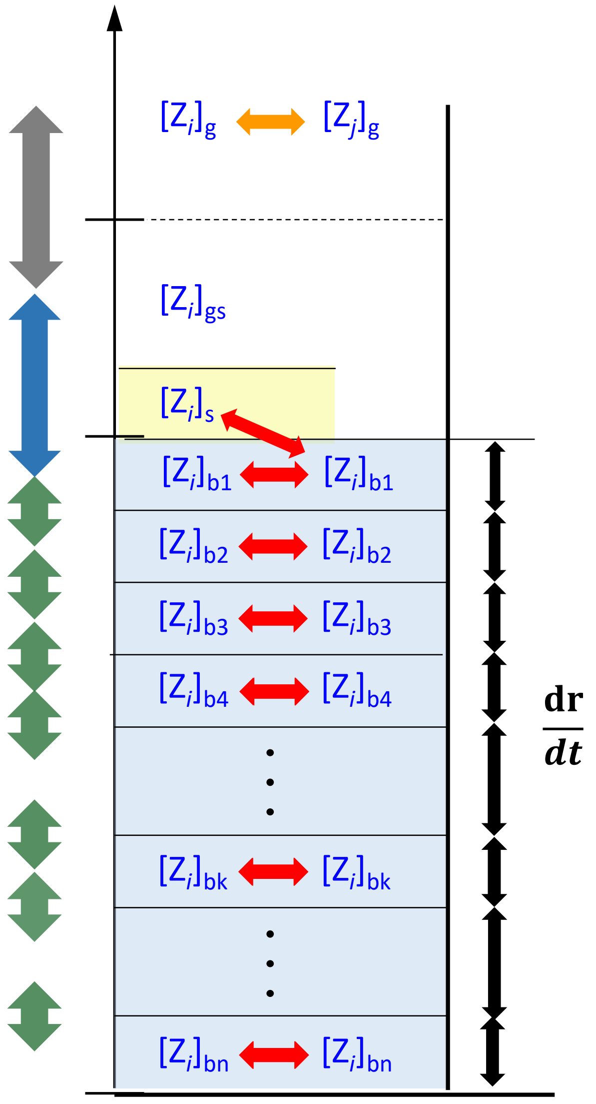
microscopic properties

Chamber Experiments

macroscopic observables



Aerosol Particle:
Multiphase Chemical System

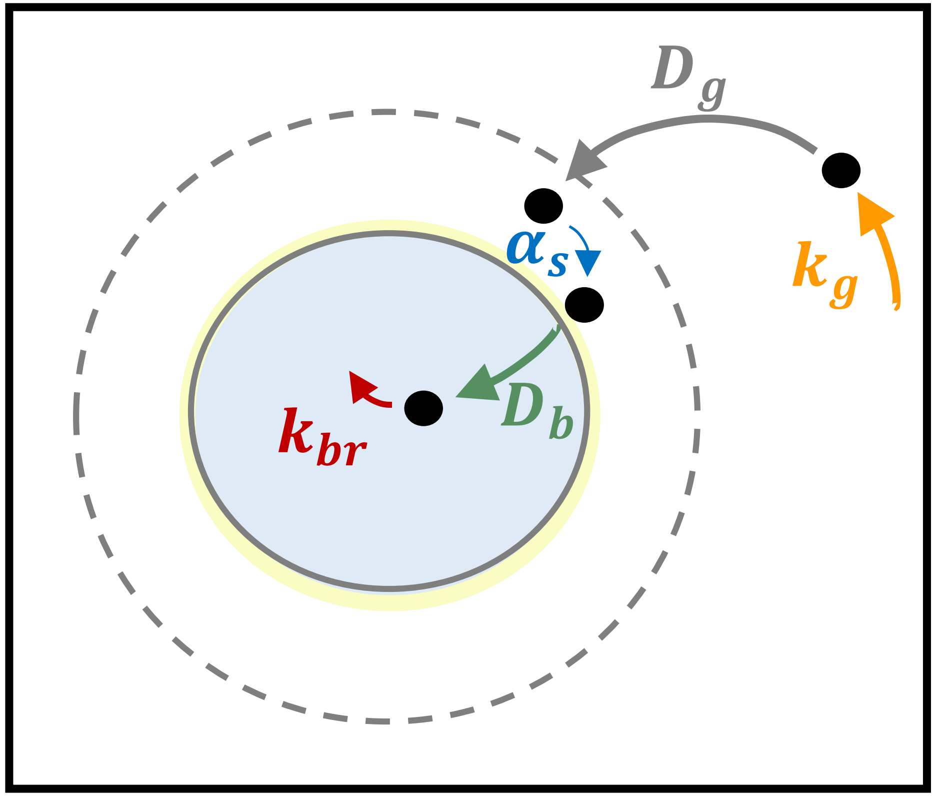


KM-GAP
(Shiraiwa ACP 2012)

Complications for treatment of SOA formation:

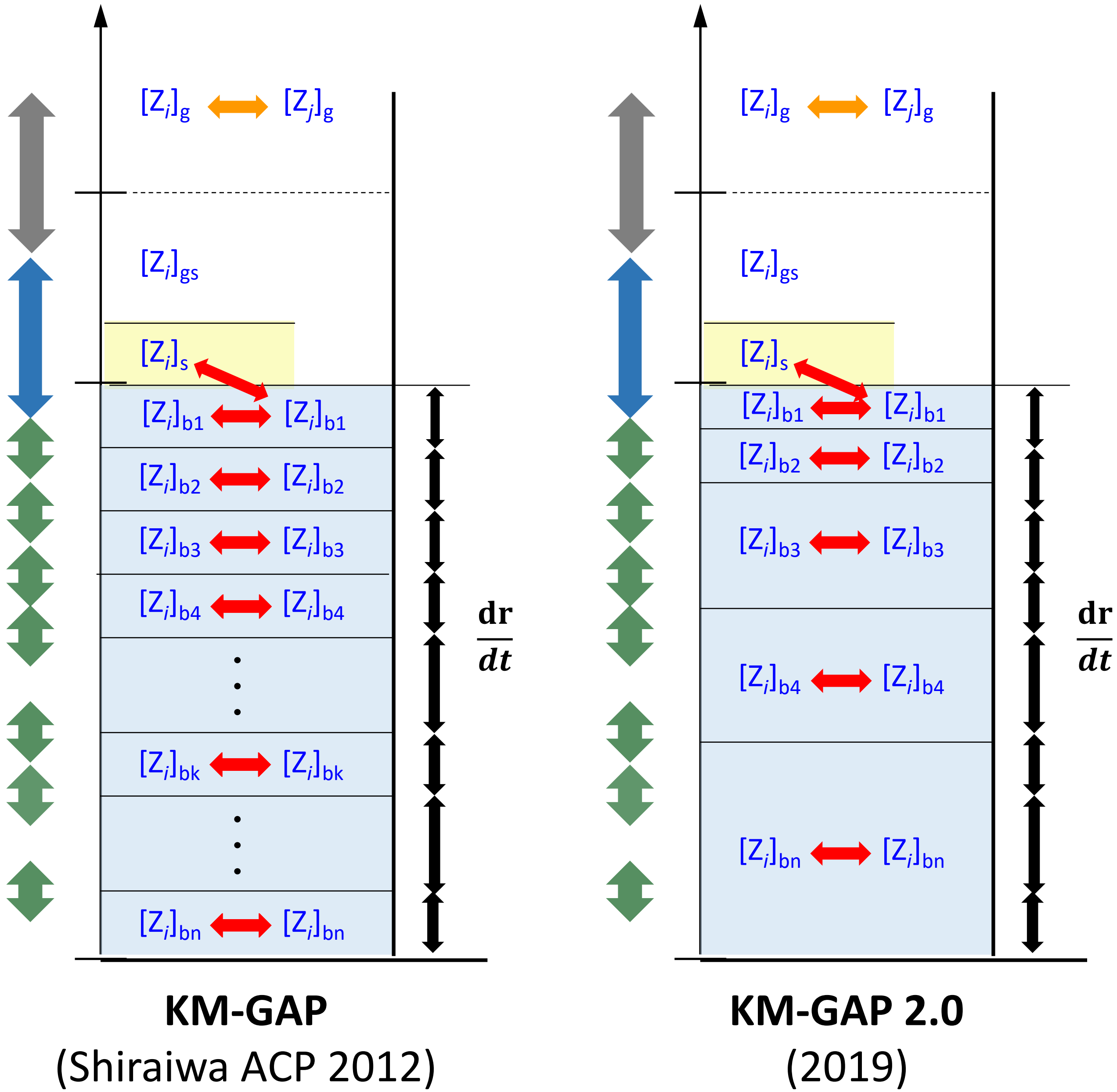
- Particle growth leads to imbalance in layer sizes.
- Evolving concentration gradients require high initial layer count.
- Low computational efficiency.

Kinetic Multi-Layer Model **KM-GAP 2.0**



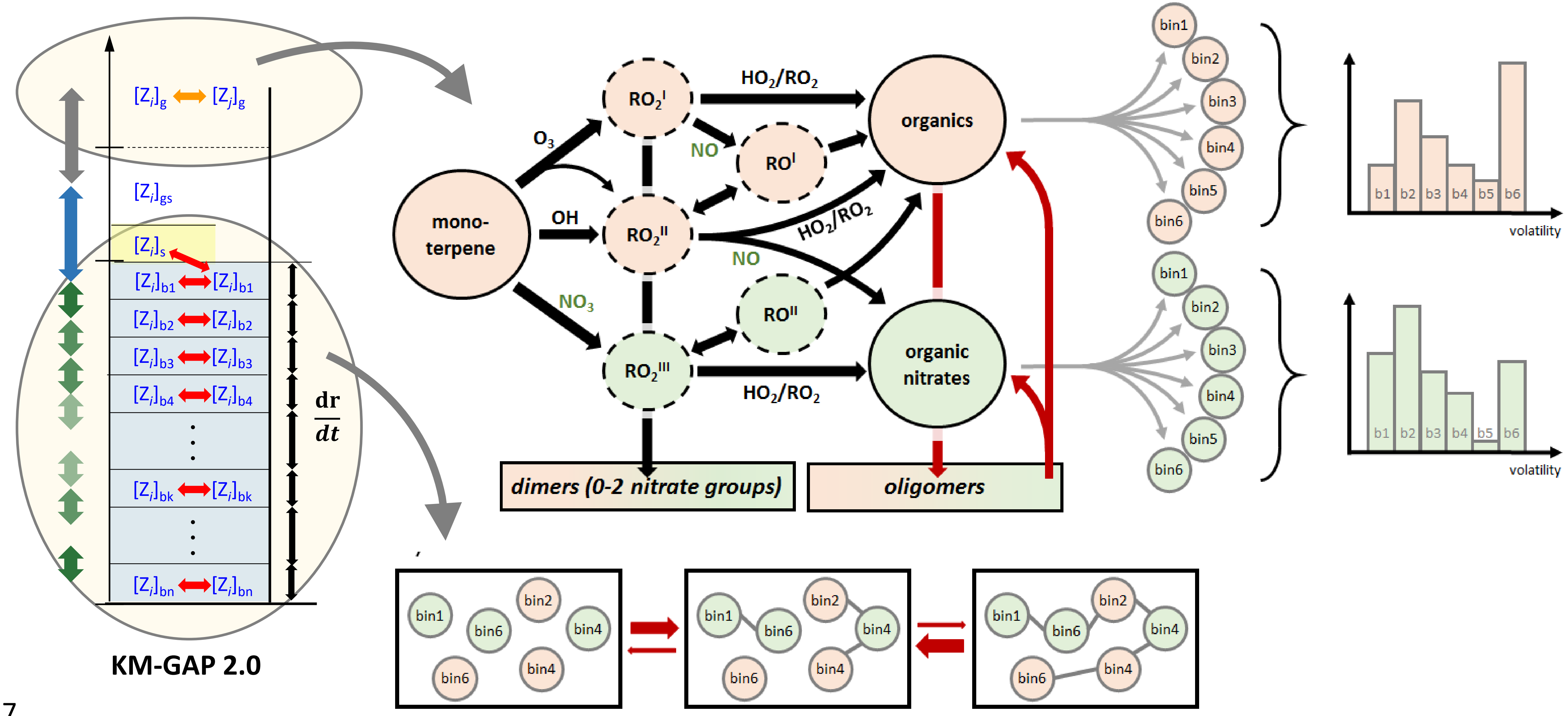
Aerosol Particle:
Multiphase Chemical System

New: Adaptive Layer Splitting and Merging Scheme (size and gradient)



Modelling Strategy for SOA Chamber Experiments

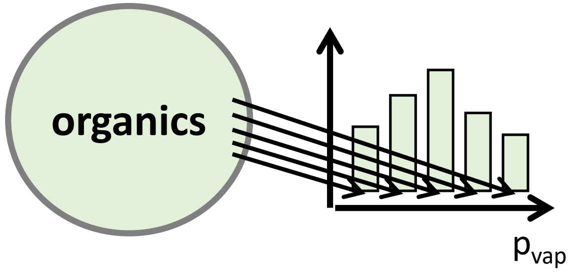
Kinetic Model | **Chemical Mechanism** (semi-explicit) | **Volatility**



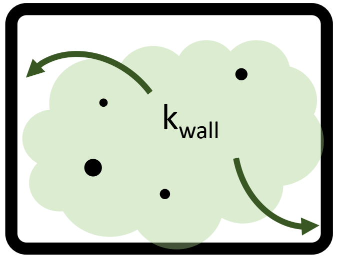
Key Model Parameters and Global Optimization Algorithm

Model Parameters

Volatility basis set

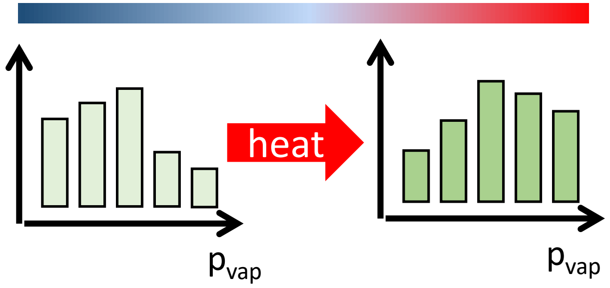


Gas-phase wall loss rate

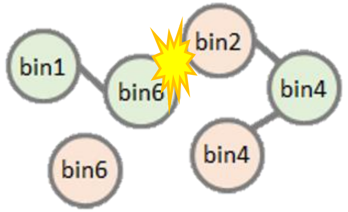


~ 0.25 h^{-1}

Enthalpy of vaporization



Oligomerization rate

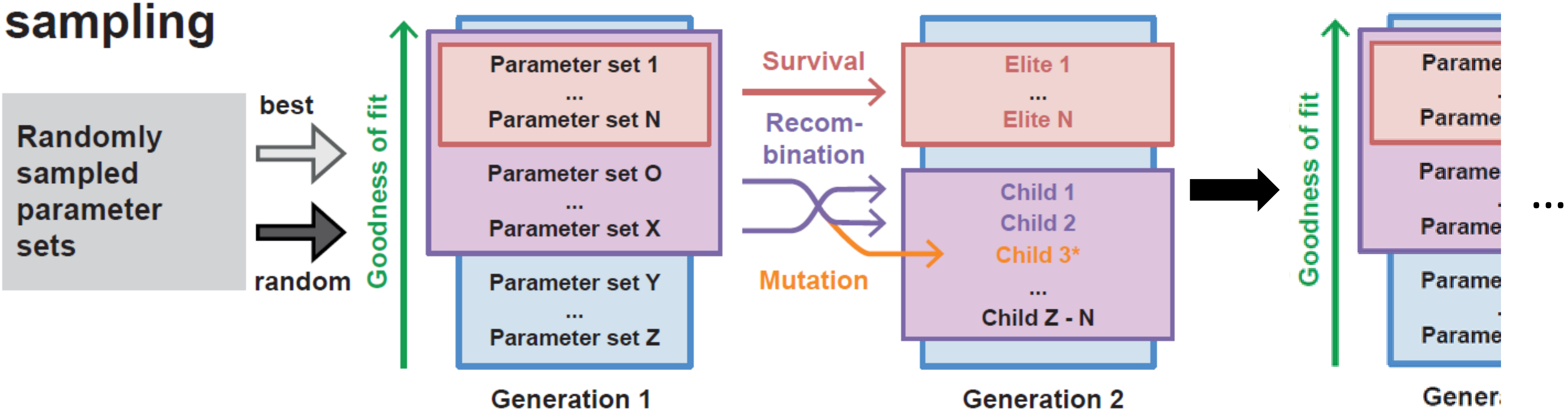


Viscosity

MCGA - Global Optimization Algorithm (Inverse Modelling Approach)

Monte Carlo sampling

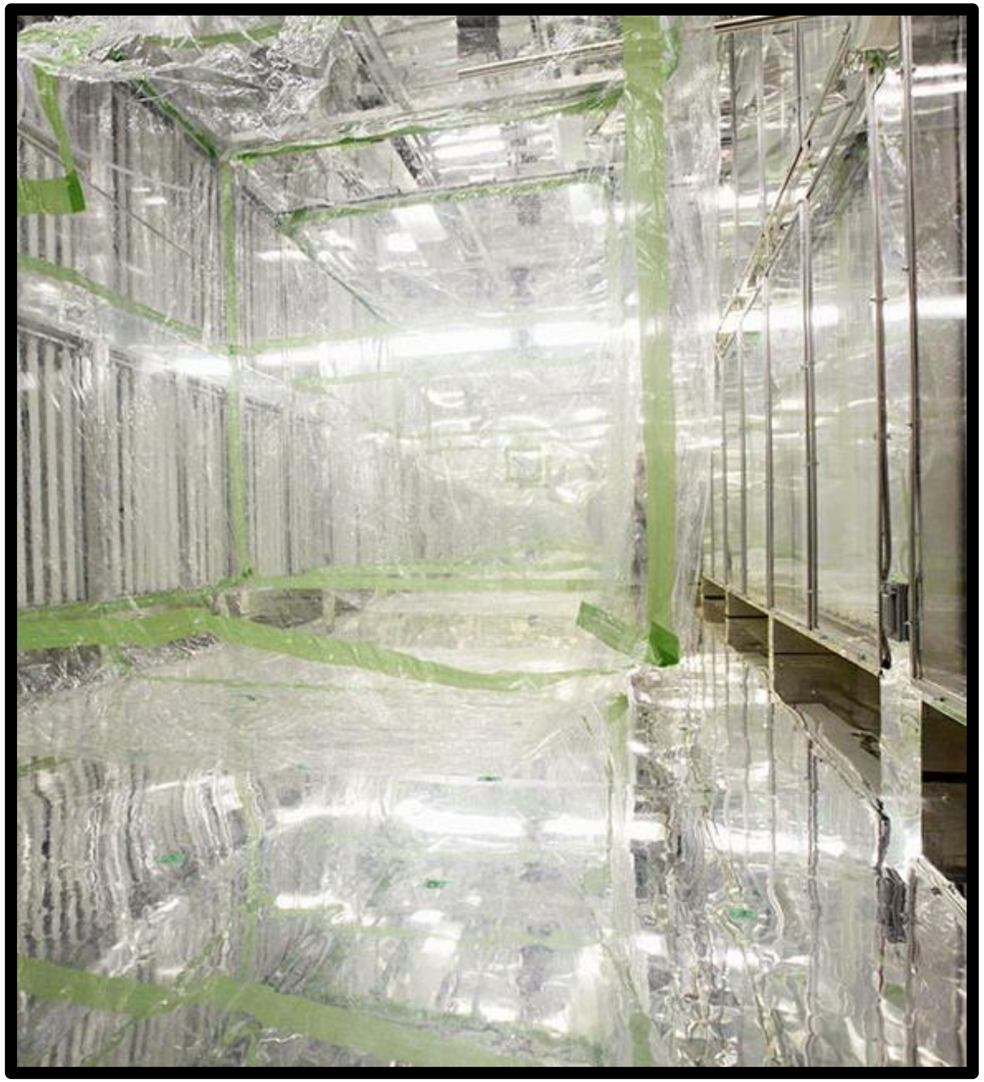
Genetic Algorithm

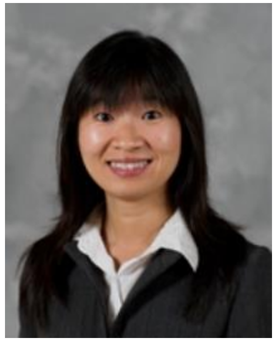


T. Berkemeier, M. Ammann, U. K. Krieger, T. Peter, P. Spichtinger, U. Pöschl, M. Shiraiwa and A. J. Huisman, *Atmos. Chem. Phys.*, **2017**

Georgia Tech Environmental Chamber

12 m^3 Teflon bag

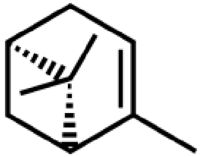




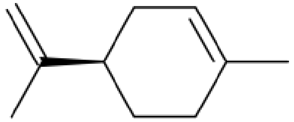
Sally Ng

Reaction System

NO_3 oxidation via injection of N_2O_5



(+)-α-pinene



limonene

Conditions

< 5 % RH

$(NH_4)_2SO_4$ seed

Instruments

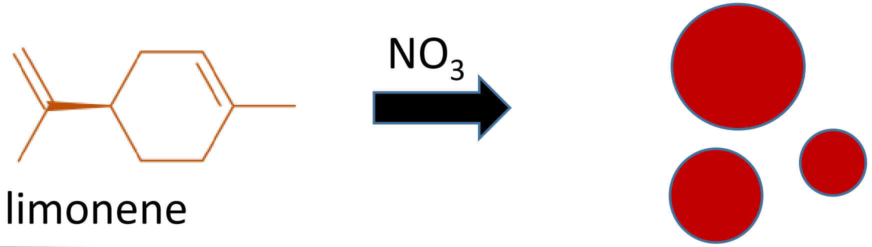
HR-ToF-AMS

HR-FIGAERO-CIMS

SMPS

Formation

1



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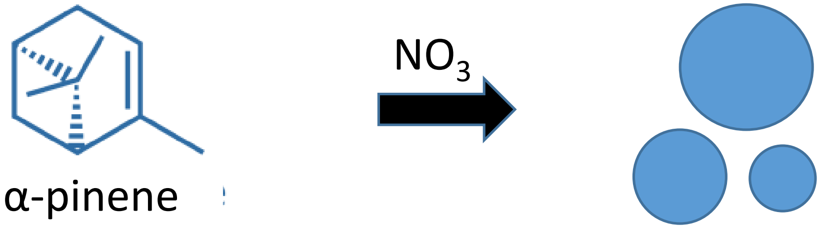

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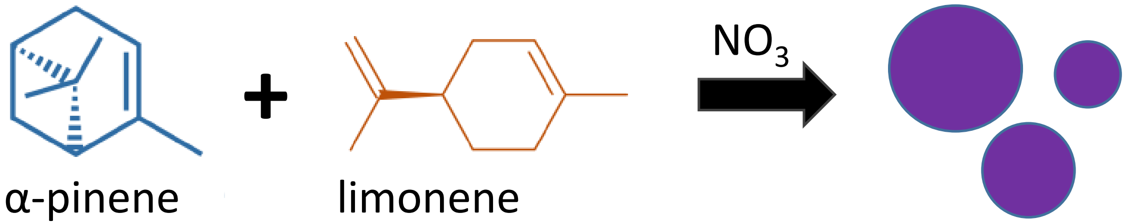
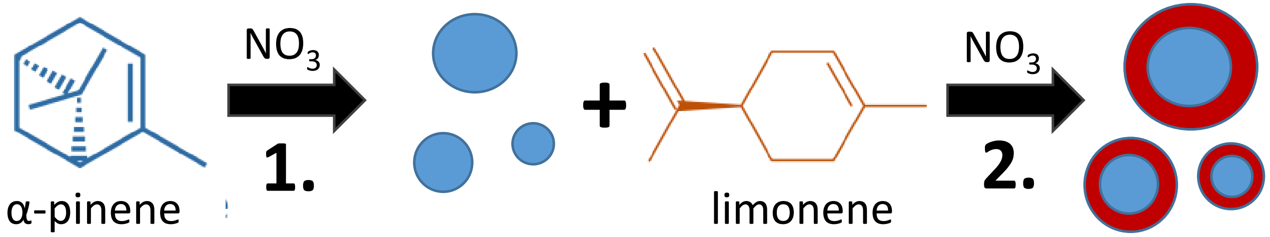
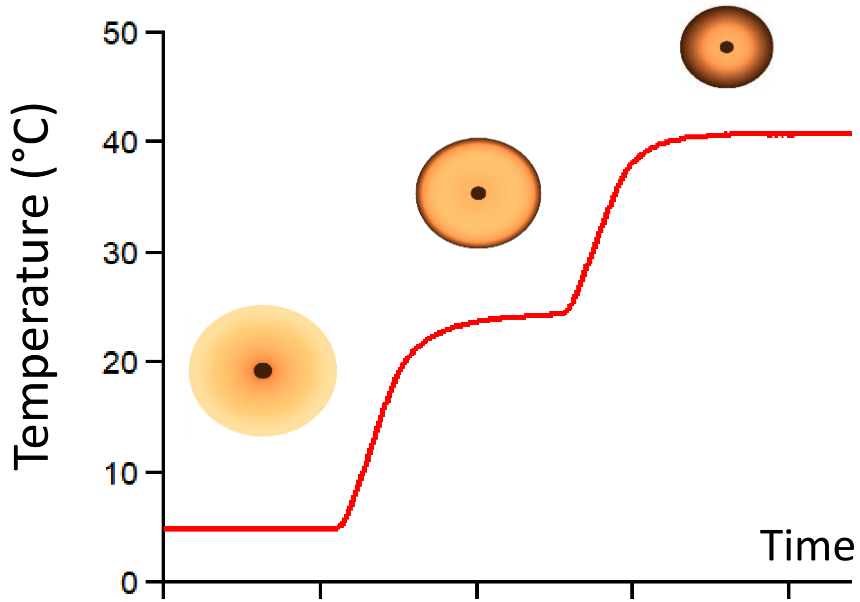


4



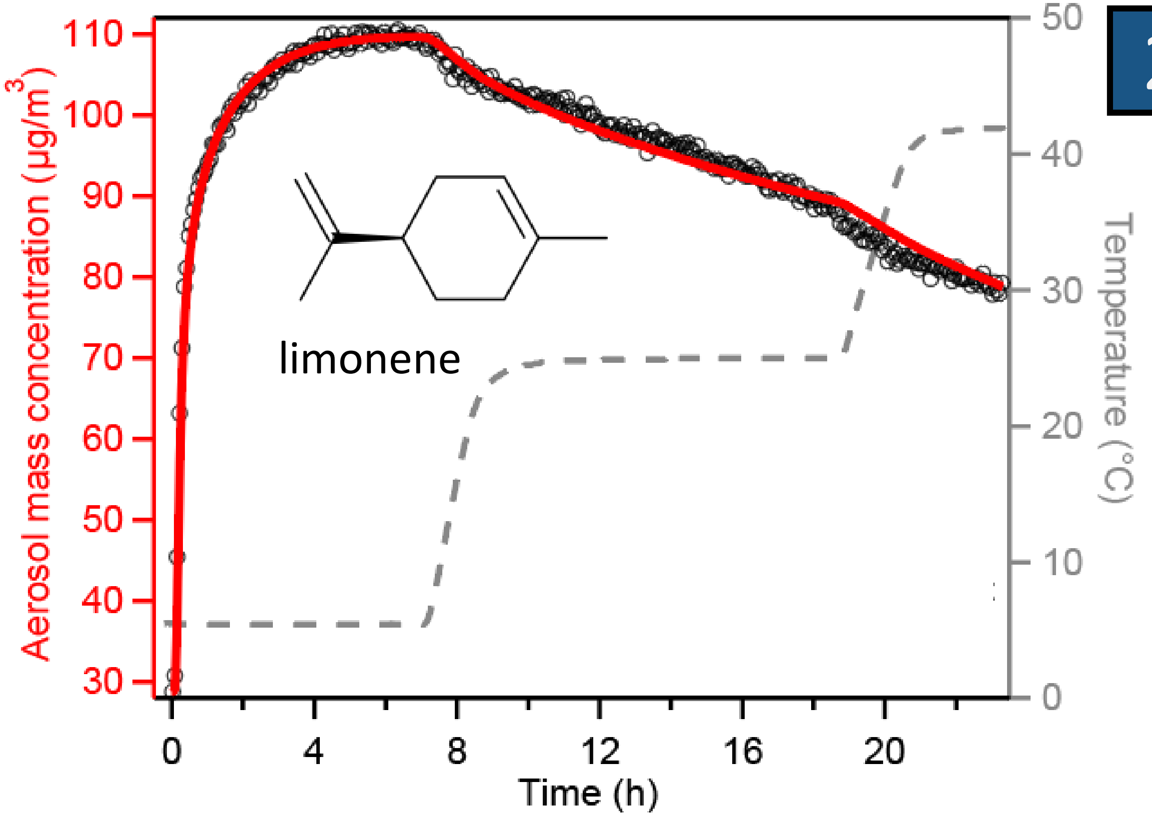
Evaporation

Temperature Profile



Pure Precursor Experiments – Well-mixed Particle Phase

1



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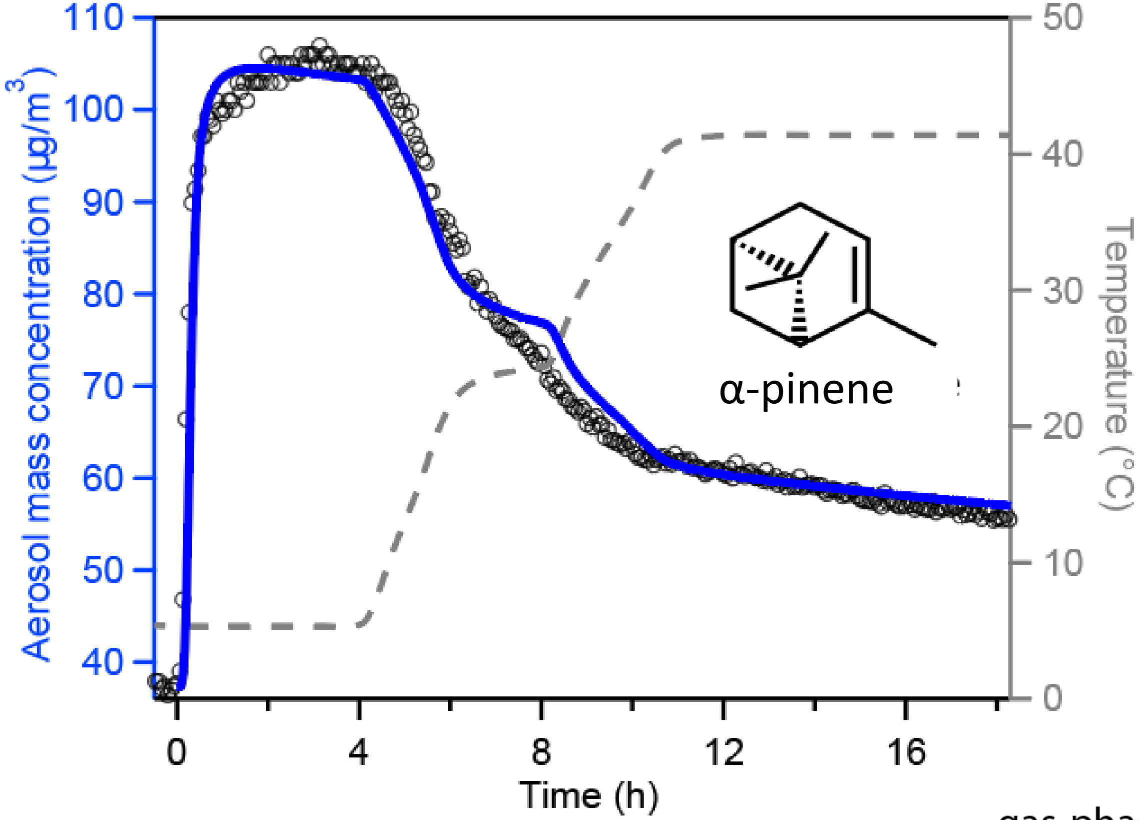
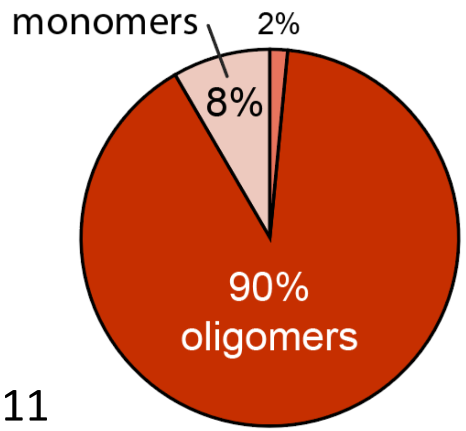
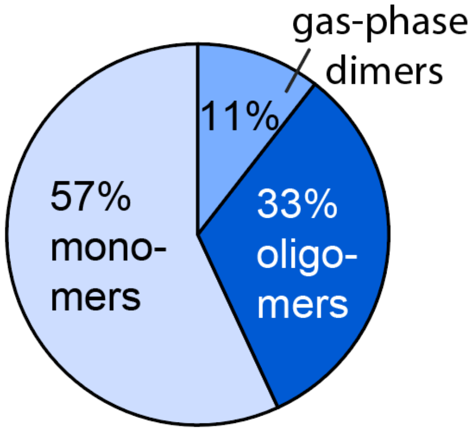




LIMONENE + NO_3

A-PINENE + NO_3



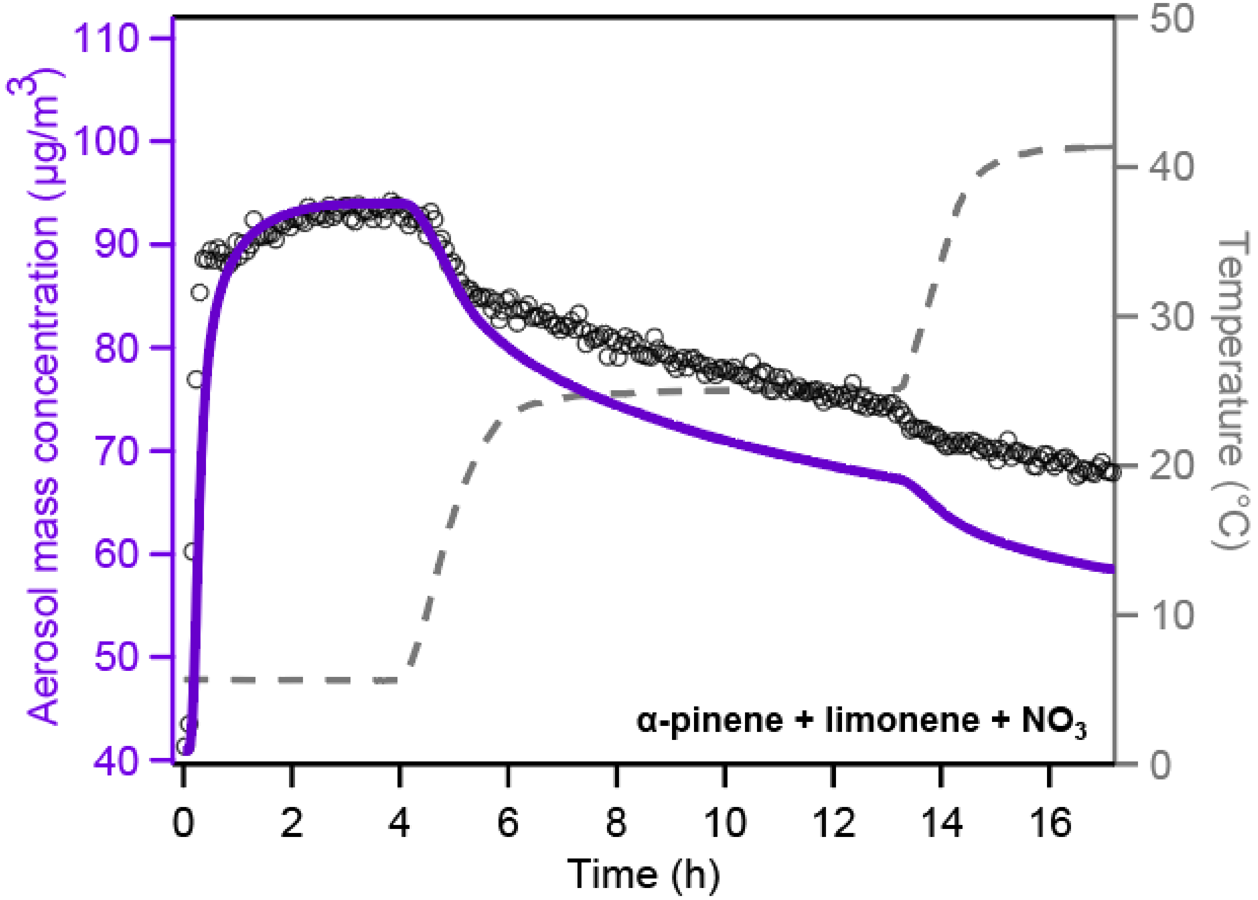
<u>Model simulations with well-mixed particle phase:</u>

Reversible oligomerization can explain differences.

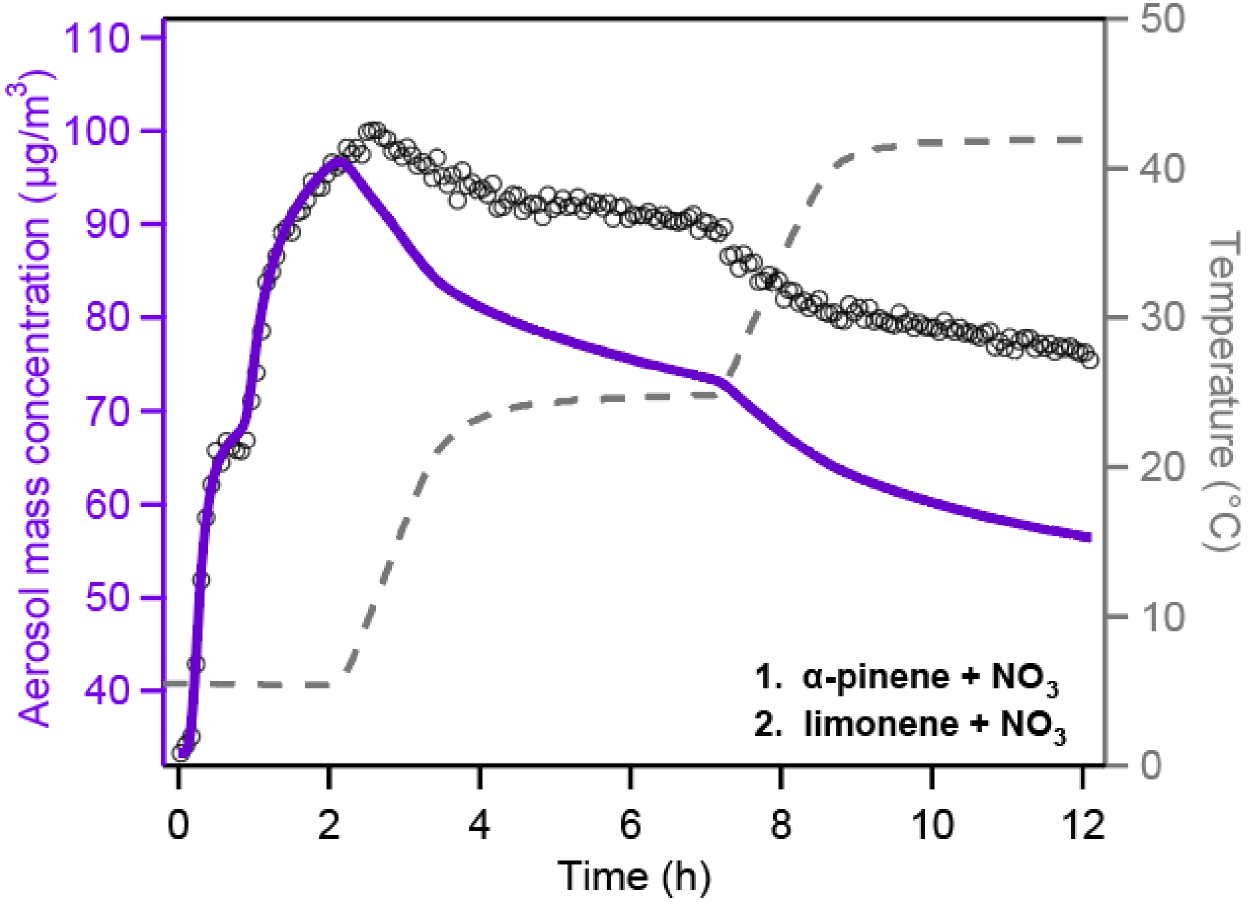
Limonene SOA more oligomerized than α-pinene SOA.

Mixed Precursor Experiments – Well-mixed Particle Phase

3 SIMULTANEOUS OXIDATION



4 SEQUENTIAL OXIDATION

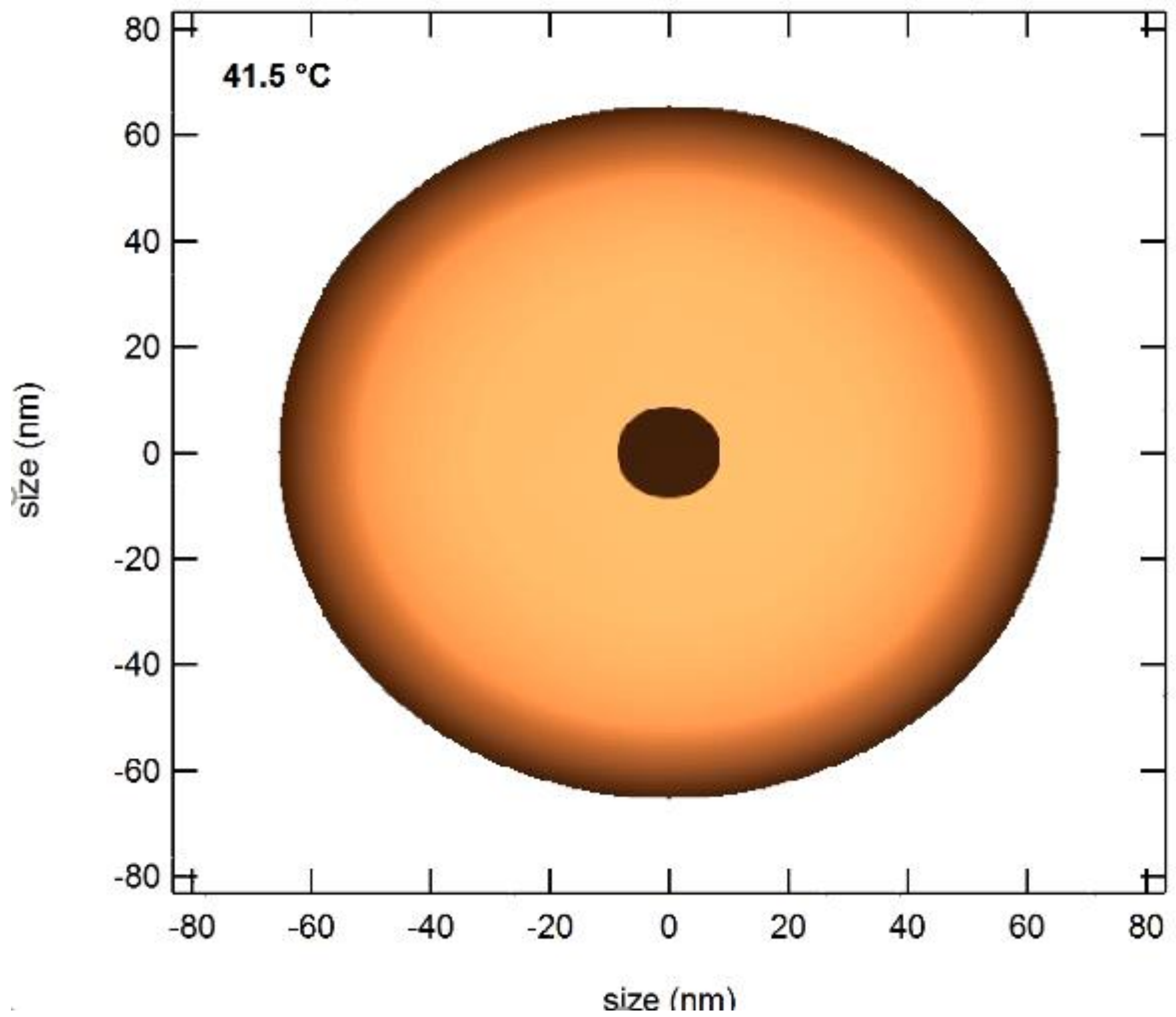


Evaporation rate is not reproduced in mixed precursor simulations

Is limonene SOA slowing down α-pinene SOA evaporation?

Viscosity-Dependent Modelling Results

HIGH VISCOSITY PARTICLE



(A) **SOA formation is not strongly affected by viscous phase state.**

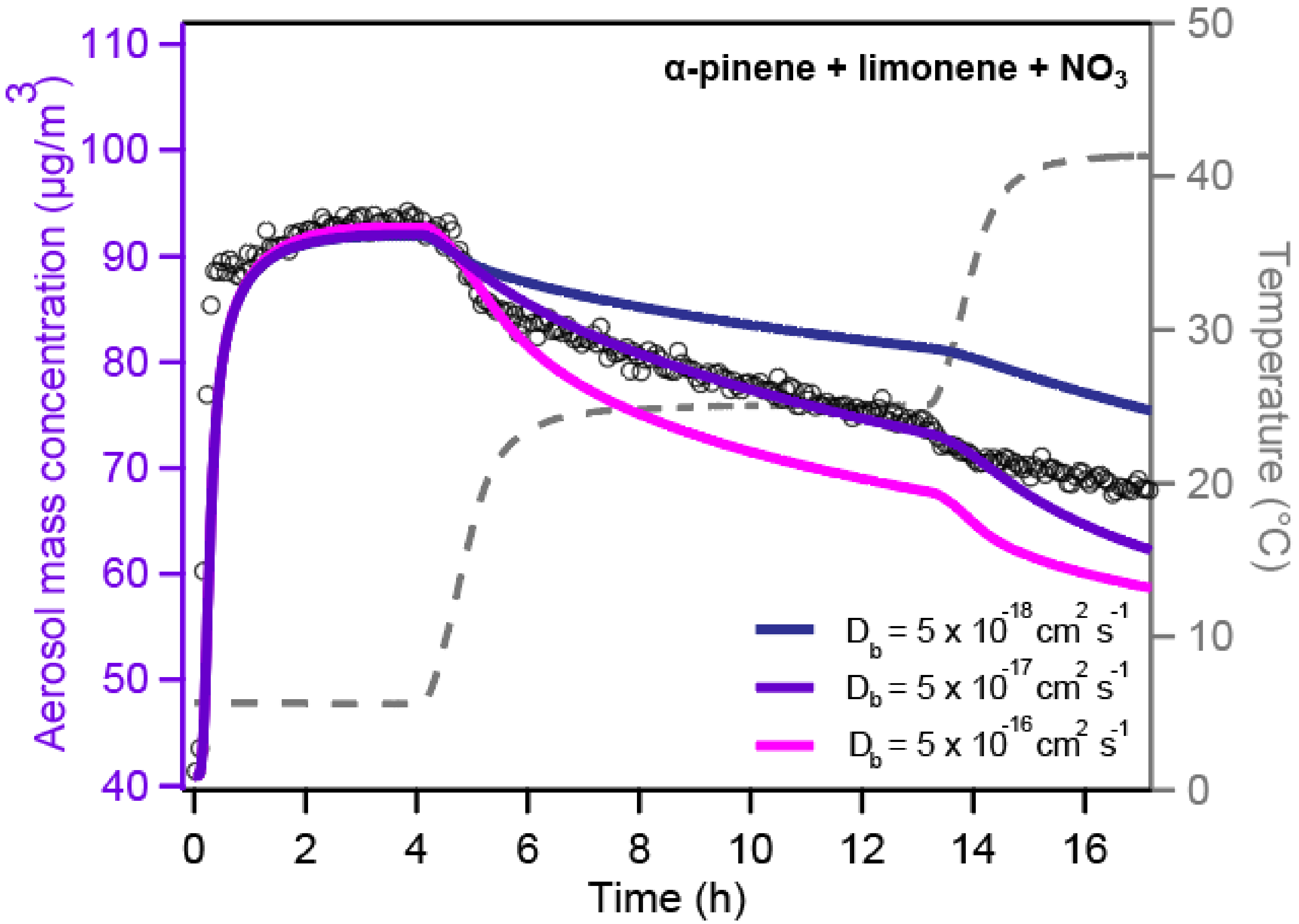
(B) **Semi-volatile molecules take longer to evaporate / are trapped inside.**

(C) **Diffusion barrier could increase over time due to crust formation.**

Color-Coded: Mean Volatility high low

Viscosity-Dependent Modelling Results – Sensitivity Study

3 SIMULTANEOUS OXIDATION

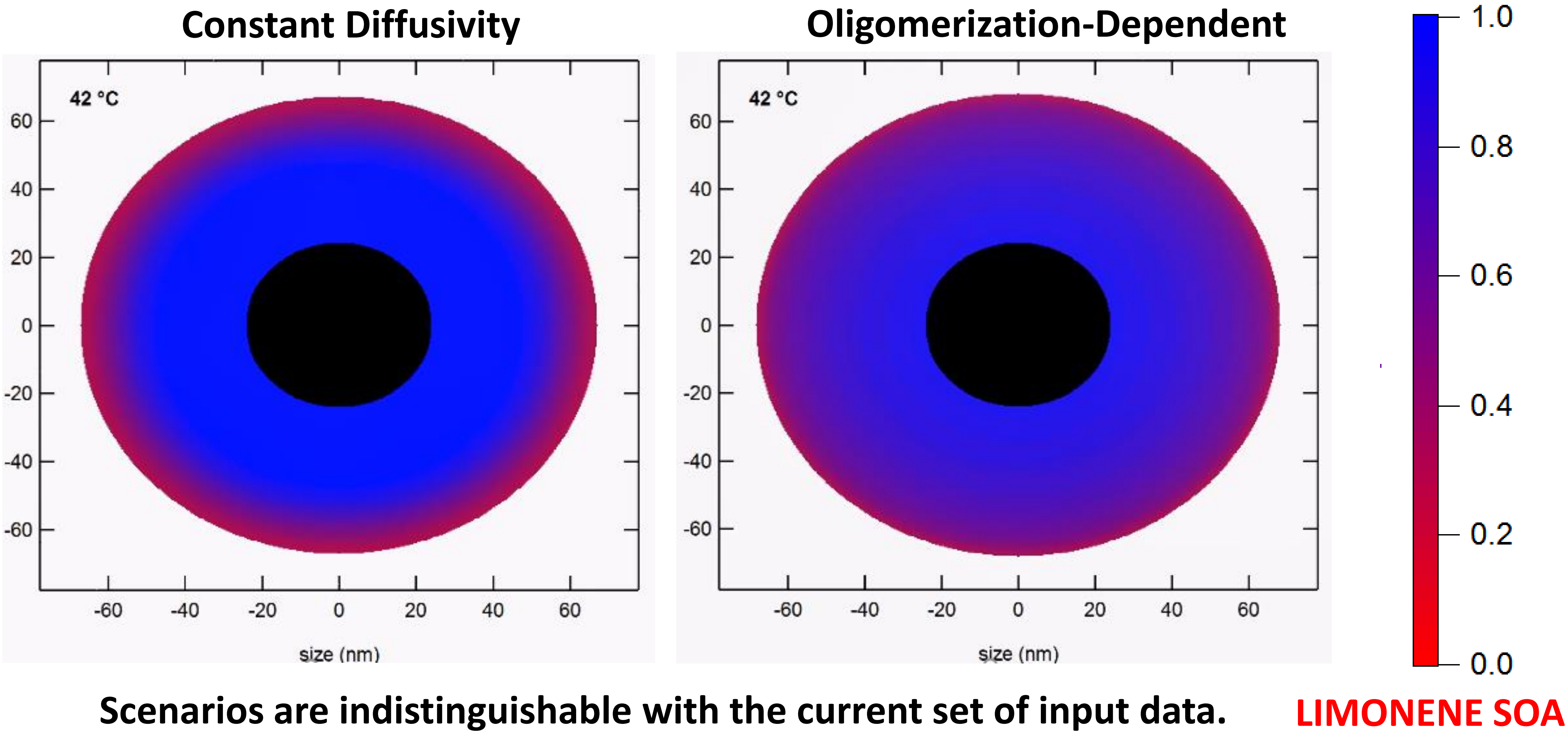


Elevated viscosity can explain slow evaporation of SOA

Application of **Stokes Einstein equation** yields **viscosity** of **10^8 Pa s**, typical for α-pinene SOA.

Viscosity-Dependent Modelling Results – Composition-Dependence

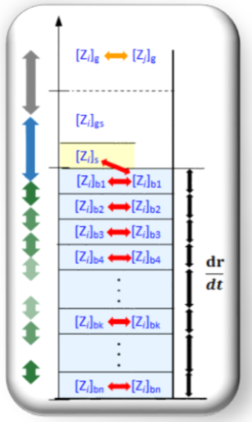
SEQUENTIAL EXPERIMENT: Core-Shell Morphology?



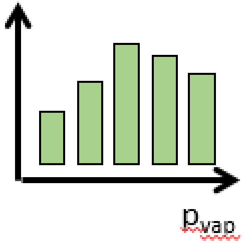
Scenarios are indistinguishable with the current set of input data.

Summary

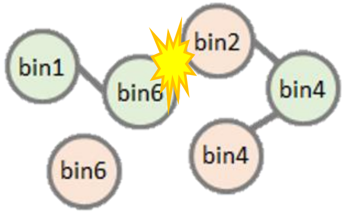
1 **Secondary Organic Aerosol (SOA) formation** from monoterpene precursor mixtures can be described using **kinetic multi-layer models**, but the gas-phase chemical mechanism has to be simplified.



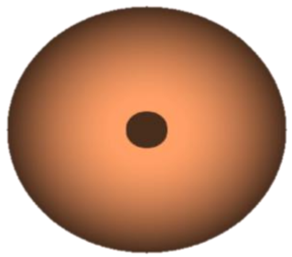
2 **SOA partitioning** can occur as **non-equilibrium process**, either due to **formation of oligomers** or **viscous phase state**.



3 **SOA yields** were mostly unaffected by mixing precursors in this study, but **evaporation behavior** was strongly affected.



4 **Oligomerization** and **diffusion effects** are difficult to separate from looking at SMPS data. There is a need to combine different experimental techniques to solve this puzzle.



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