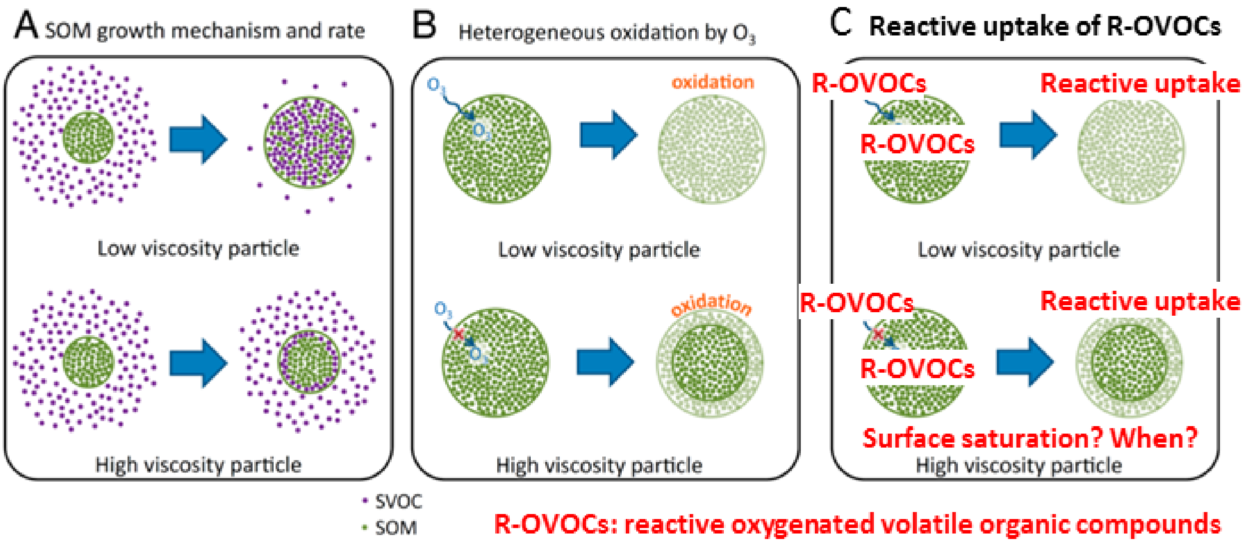
SOA Viscosity/Phase Focus Area

Leads: Scot Martin and Alla Zelenyuk

Effect of SOA Viscosity/Phase on SOA Formation, Properties, and Evolution



- Formation, properties, transformations, and temporal evolution of SOA particles depend strongly on SOA phase/viscosity
- Due to lack of data, models have assumed that SOA particles are low-viscosity solutions that maintain equilibrium with the gas-phase by rapid evaporation/ condensation and mixing
- Recent experimental evidence indicates that SOA particles are "semi-solid" with viscosity and diffusivities many orders of magnitude lower than assumed
- SOA viscosity depends on RH, temperature, SOA precursor, time/aging, etc.

SOA Viscosity/Phase Focus Area: Ongoing and Future Activities

1. Identify what techniques are available within our group to measure SOA phase and viscosity.

2. Identify what processes or endpoints that depend on SOA phase and viscosity can be measured.

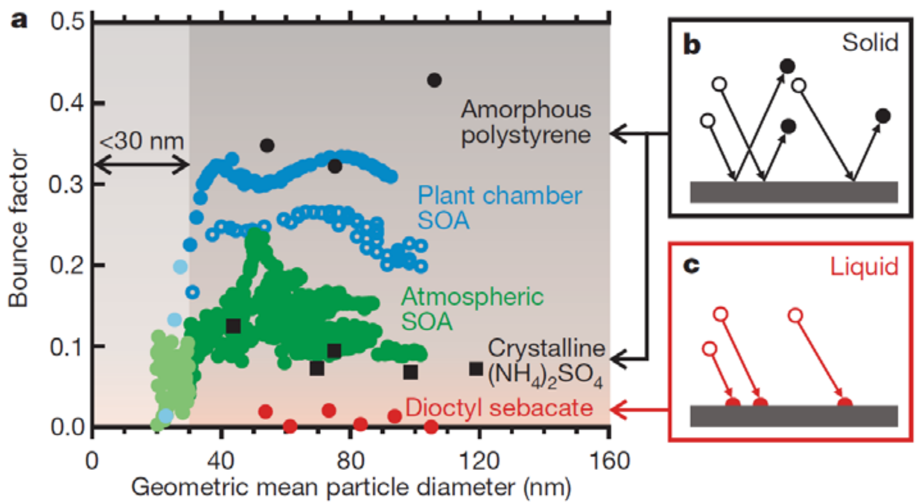
3. Identify what models are being used within are group at present time that either (a) already include a treatment of viscosity or (b) could be developed to include treatments of viscosity.

4. Design and conduct cooperative chamber experiments, in which the different techniques used to measure SOA phase and viscosity and study the processes that depends on SOA phase and viscosity (morphology/mixing state, gas-particle partitioning, evaporation, heterogeneous oxidation, reactive uptake, temperature of glass transition) will be simultaneously deployed.

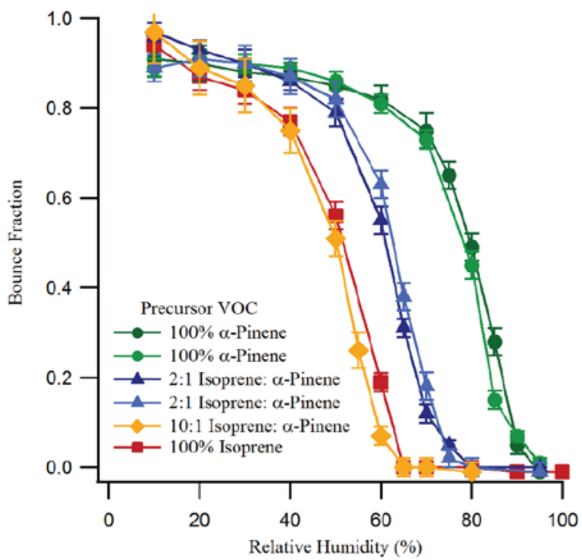
5. MOSAIC, and kinetic multi-layer models (ADCHAM, KM-GAP, PRA framework) will be used to provide a process level understanding of SOA formation, properties, and transformations and develop parameterization for implementation in larger scale models (WRF-Chem, CAM5.2)

6. Submitted 3 EMSL proposals, related to SOA phase and viscosity

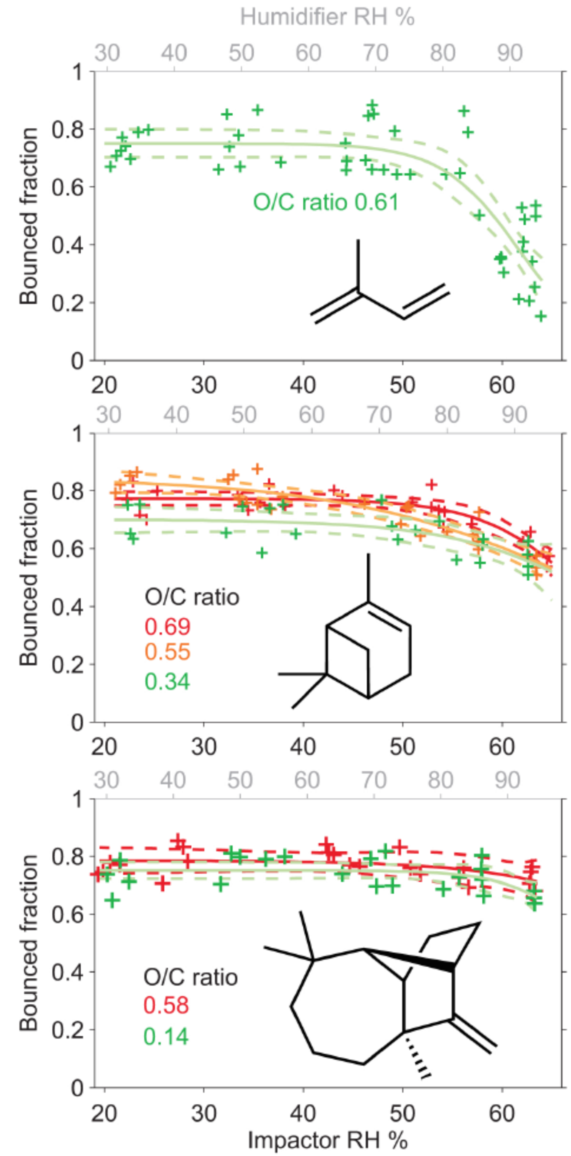
Measurements of SOA Phase: Particle Bounce



(Virtanen et al. Nature 2010)



(Bateman et al. 2013)

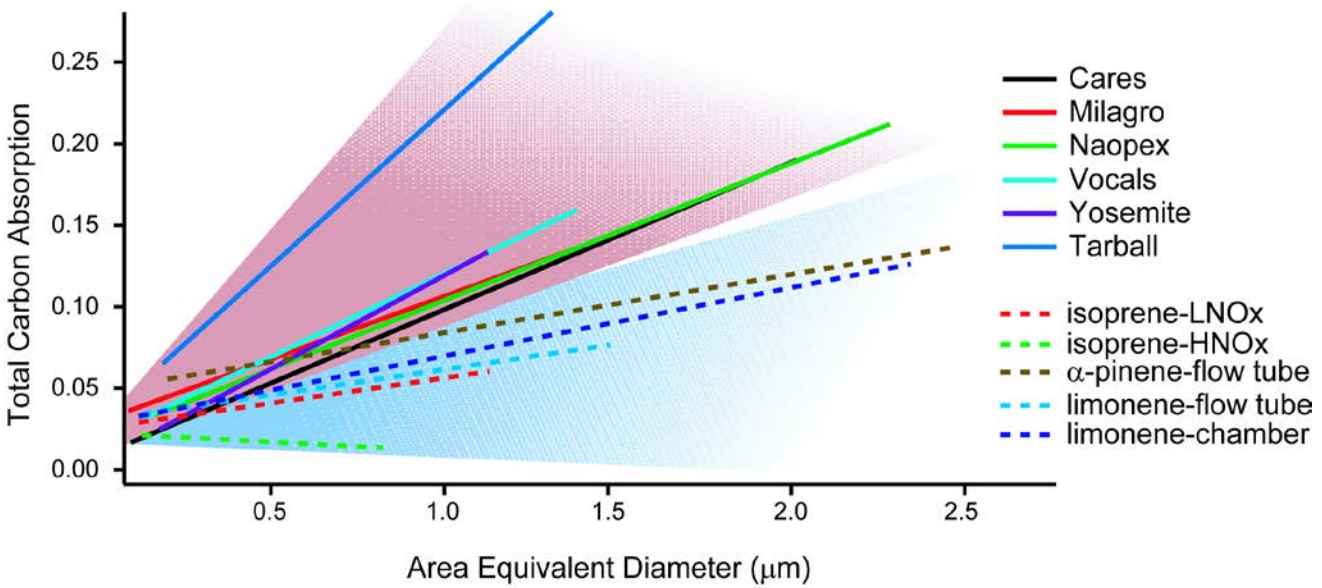


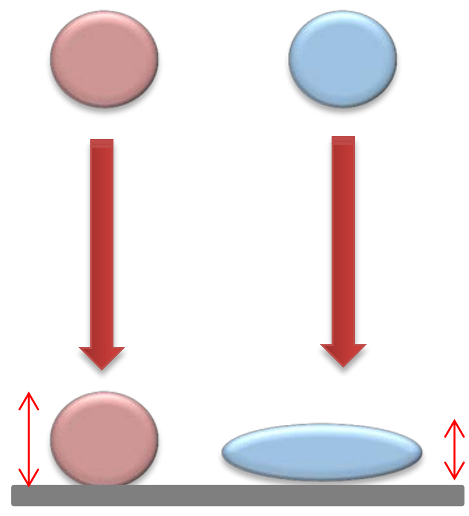
(Saukko et al. ACP 2012)

Measurements of SOA Phase: Particle Deformation

High viscosity - absorbance profile resembles a sphere maximum absorbance depends on particle diameter

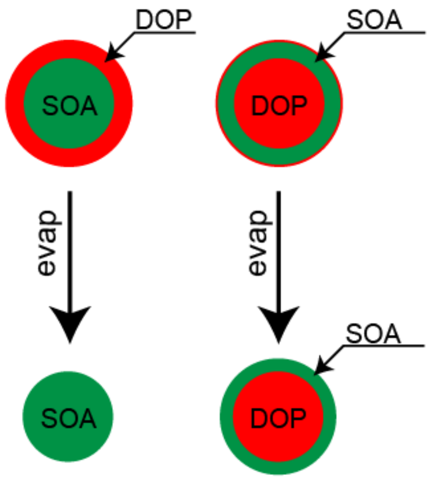
Low viscosity - particle flattens, lower maximum absorbance, weaker dependence of absorbance on particle diameter



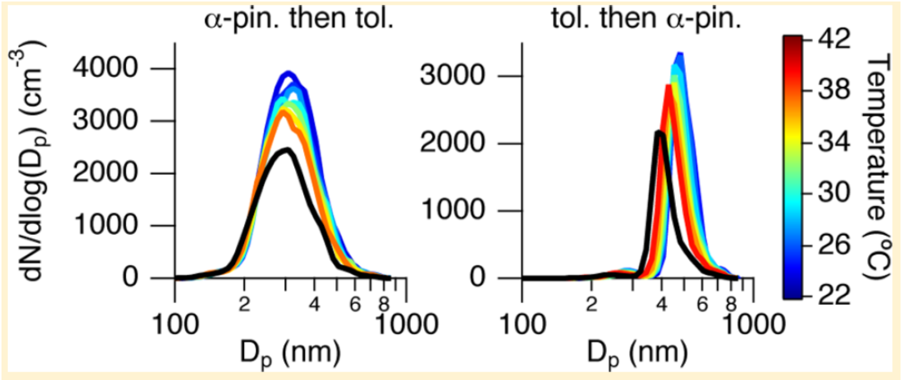


R. E. O'Brien A. Neu, S. A. Epstein, A. MacMillan, S. Nizkorodov, A. l Laskin, R. C. Moffet, M. K. Gilles, in prep for submission to GRL

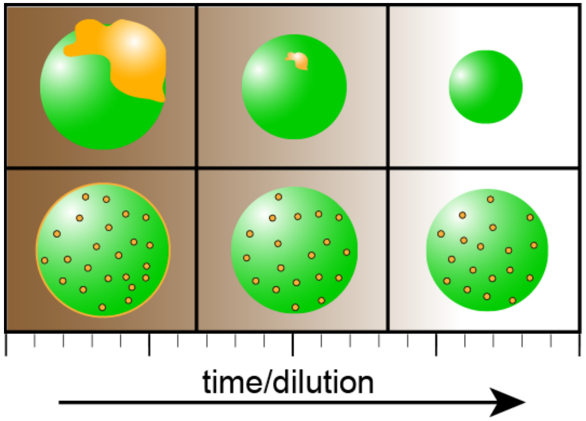
Measurements of SOA Phase: Particle Morphology, Mixing, Shape, and Evaporation Behavior



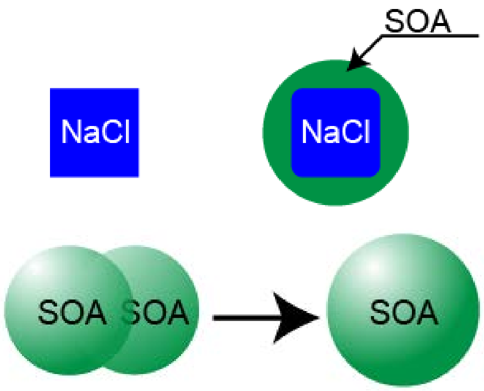
(Vaden et al. PNAS 2010)



(Loza et al. ES&T 2013)

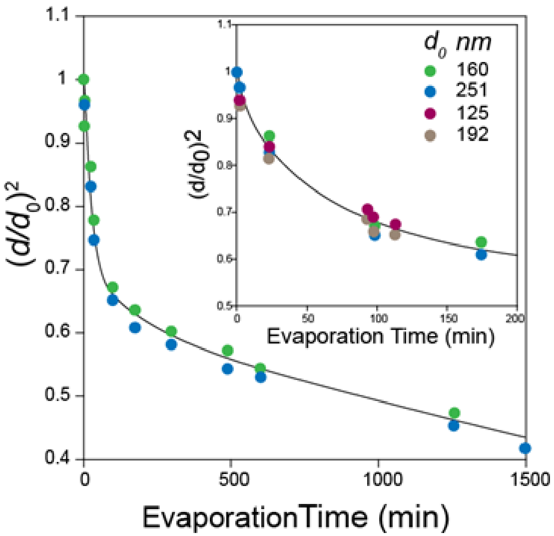


(Zelenyuk et al. ES&T 2012)

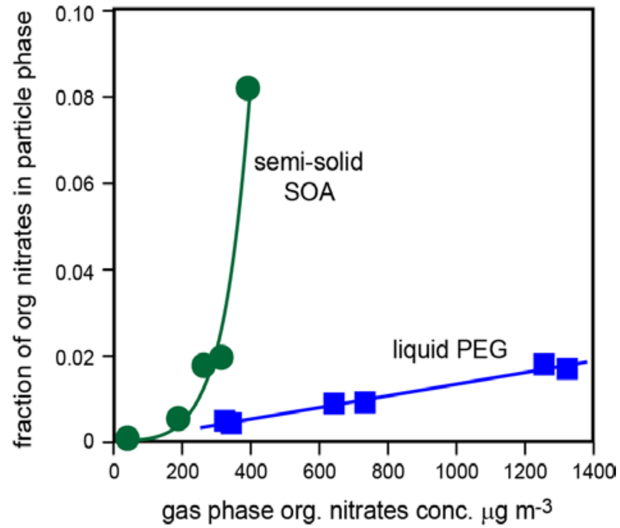


Zelenyuk et al. ES&T (2008, 2012) Vaden et al. PNAS 2010

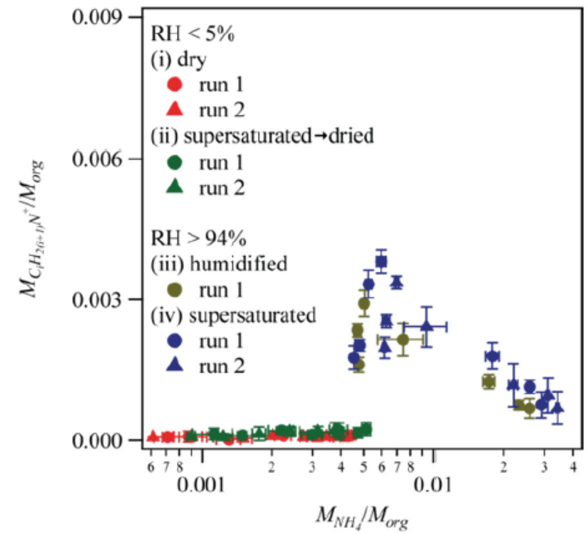
Measurements of SOA Phase: Particle Composition, Evaporation Behavior, and Size Distribution



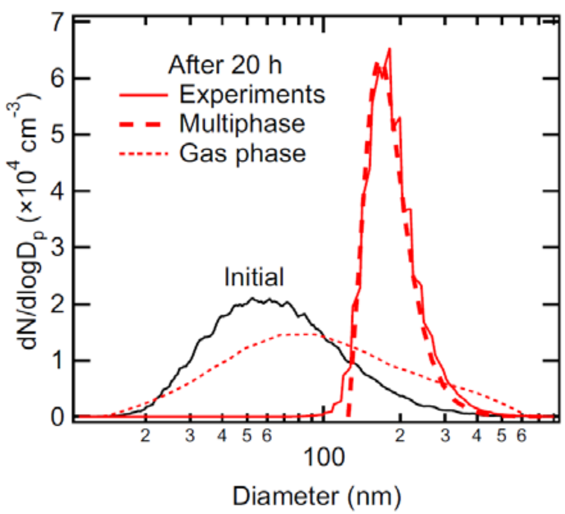
(Vaden et al. PNAS 2011)



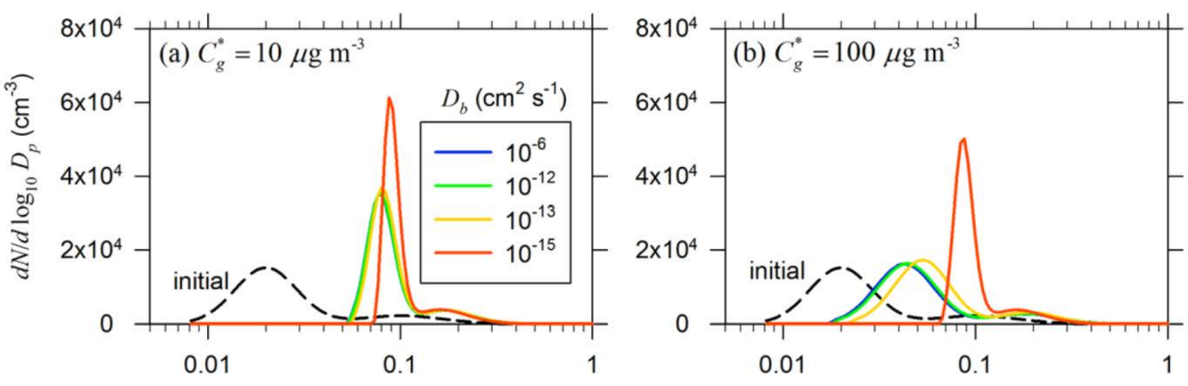
(Perraud et al. PNAS 2012)



(Kuwata and Martin, PNAS 2012)



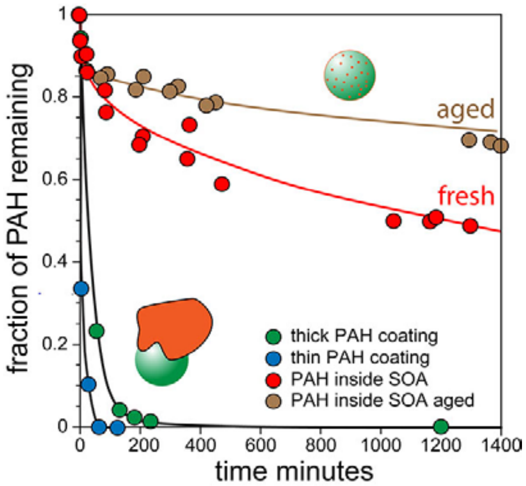
(Shiraiwa et al. PNAS 2013)



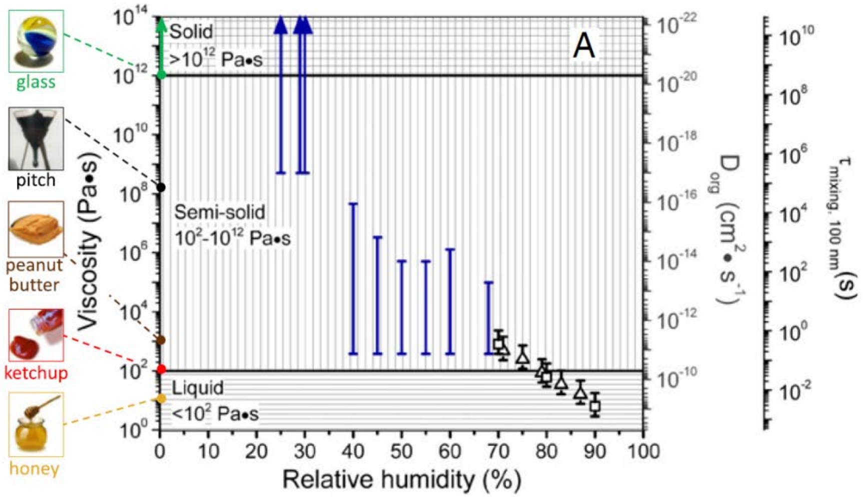
(Zaveri et al. ACPD 2013)

Measurements of SOA Viscosity

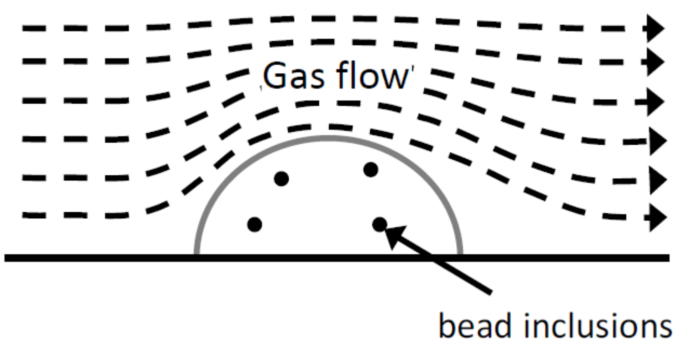
Diffusivity - D=2.5 10^{-21} m^2 s^{-1}
Viscosity 10^8 Pa-s, harden with time



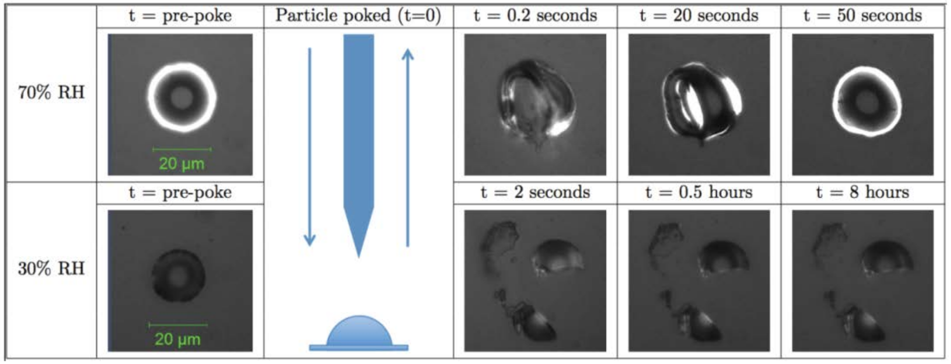
Abramson et al. PCCP 2013



Renbaum-Wolff et al. PNAS 2013



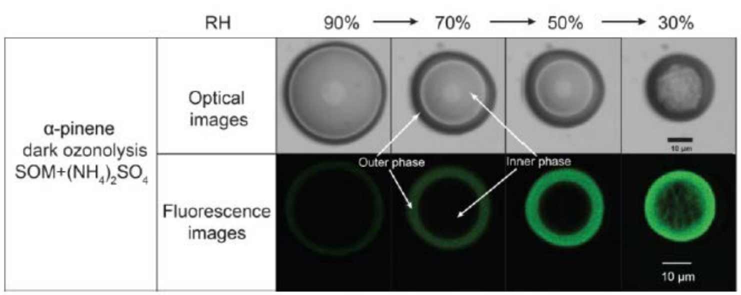
Renbaum-Wolff et al. ACP 2013



Renbaum-Wolff et al. PNAS 2013

Other Processes that Depend on SOA Phase/Viscosity

- Gas-particle partitioning, multiphase chemical reactions, reactive uptake coefficients (NO_3, O_3, OH, ammonia, carbonyls, organic acids, SVOC)
- Liquid-liquid phase separation
- Glass transition points measured by the onsets of deposition ice nucleation and water uptake, as a function of RH and T
- The microfluidic platforms that can be used to mimic atmospherically relevant liquid-liquid and liquid-vapor interfaces and measure surface tension, dilatational viscosity, and dynamic interfacial moduli, under a range of thermal conditions and chemical compositions
- The timescales of required for a viscous organic particles to equilibrate with the humidified gas phase
- The influence of viscosity on the observed relationship between critical supersaturation and dry diameter



(You et al. PNAS 2012)

SOA Phase/Viscosity: Modeling Approaches

- The MOSAIC aerosol model includes a new kinetic (dynamic) SOA partitioning framework that can include treatments of phase state, viscosity/diffusivity, and particle-phase reactions. The model framework is capable of simulating the following climate-relevant end points:
  - Mass concentrations,
  - Number-diameter distributions,
  - Size-resolved composition and mixing state
  - Size- and mixing state-resolved hygroscopicity (kappa), and
  - Size- and mixing-state-resolved optical properties.

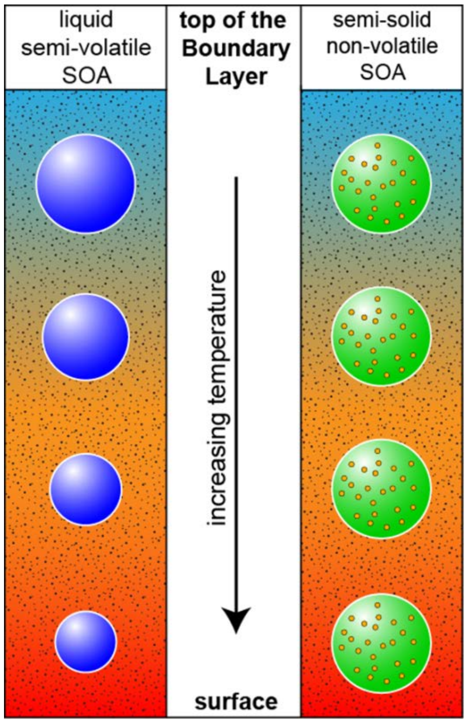
- While the kinetic mass transfer and thermodynamics treatments for inorganic species are already in place, the framework currently awaits specification of gas- and particle-phase chemistries relevant to SOA formation and the associated treatments for phase state and viscosity (diffusivity)
- As part of this focus area, MOSAIC can be used to bridge laboratory measurements of viscosity/diffusivity and phase state to some of the above end points. As part of the cross-cutting activities focus area, it can serve to connect outcomes from other focus areas (growth mechanisms, sulfate as trigger) as well as other focus groups (aerosol mixing state, absorbing aerosols) into a common framework.

(Zaveri et al. ACPD 2013)

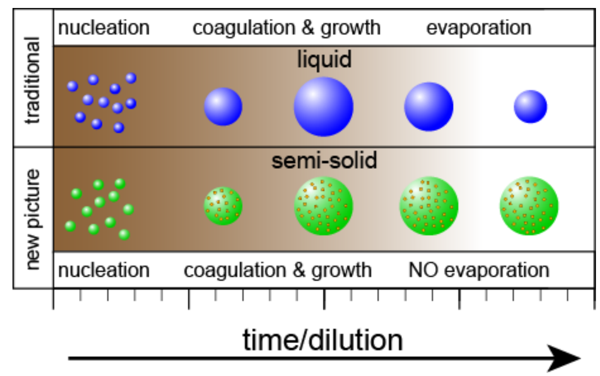
SOA Phase/Viscosity: Modeling Approaches

- The Aerosol Dynamics, gas- and particle- phase chemistry model for laboratory CHAMber studies (ADCHAM) combines the detailed gas phase Master Chemical Mechanism version 3.2, an aerosol dynamics and particle phase chemistry module (acid catalysed oligomerization, heterogeneous oxidation reactions and non-ideal interactions between organic compounds, water and inorganic ions) and a kinetic multilayer module for diffusion limited transport of compounds between the gas phase, particle surface and particle bulk phase (*Roldin et al. ACPD 2014).*
- Kinetic multi-layer model of gas-particle interactions in aerosols and clouds (KM-GAP, Shirawa et al. ACP 2012) treats explicitly all steps of mass transport and chemical reactions of semi-volatile species partitioning between gas phase, particle surface, and particle bulk.
- Kinetic flux-based model ("PRA" model framework) provides a process level understanding of uptake mechanism and estimates of physicochemical parameters such as diffusion coefficient estimates (Shiraiwa et al., EST, 2012).
- PRA framework was applied to urban plume box models (based on RADM2) and a particle resolved model. This allows direct implementation of the physicochemical parameters and their effect on heterogeneous kinetics (see e.g. Springmann et al, ACP, 2009, Kaiser et al., ACP 2011). The results can be parameterized for implementation in larger scale models with less detailed chemistry.
- SOA and HULIS glass transition point estimates (parameterizations) could be implemented in atmospheric chemistry models.

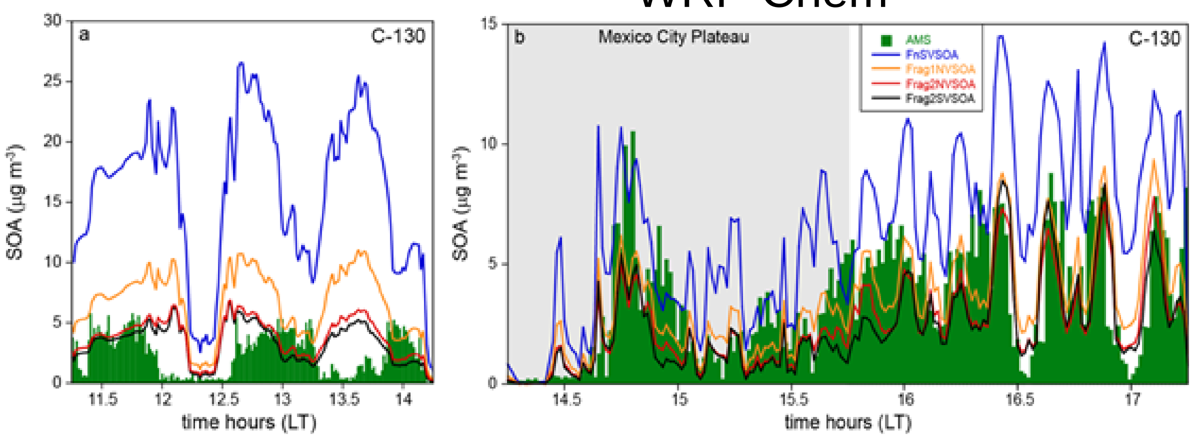
SOA Phase/Viscosity: Modeling Approaches



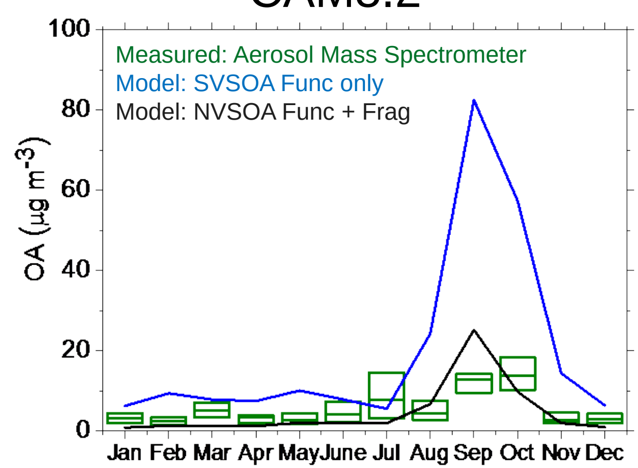
- Recent laboratory findings on SOA phase and volatility were incorporated into 3D Chemical Transport Models
- This modeling framework treats SOA particles as non-absorbing, semi-solid, and non-volatile and incorporates fragmentation reactions.



WRF-Chem



CAM5.2



(Shrivastava et al. JGR 2013)

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