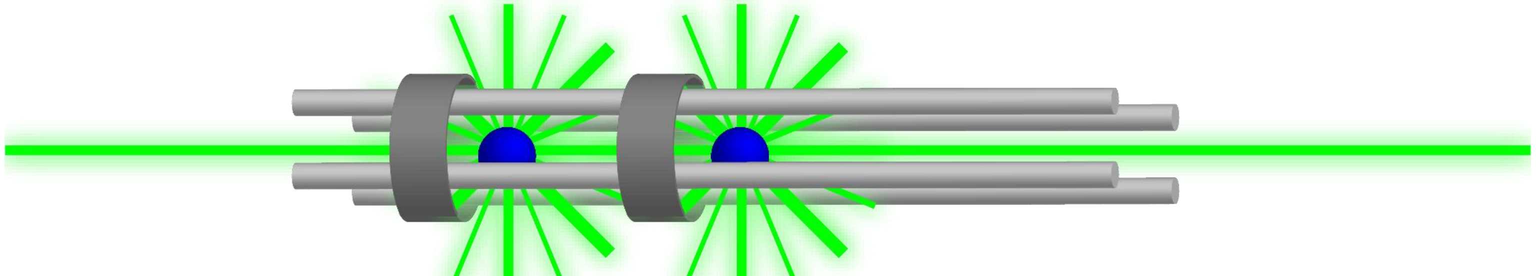
SAND2024-07436C

Exploring ion-molecule interactions in levitated aerosol particles



Ryan D. Davis, Katie Morton, Teresa Palacios Diaz, James Davies, Yi He

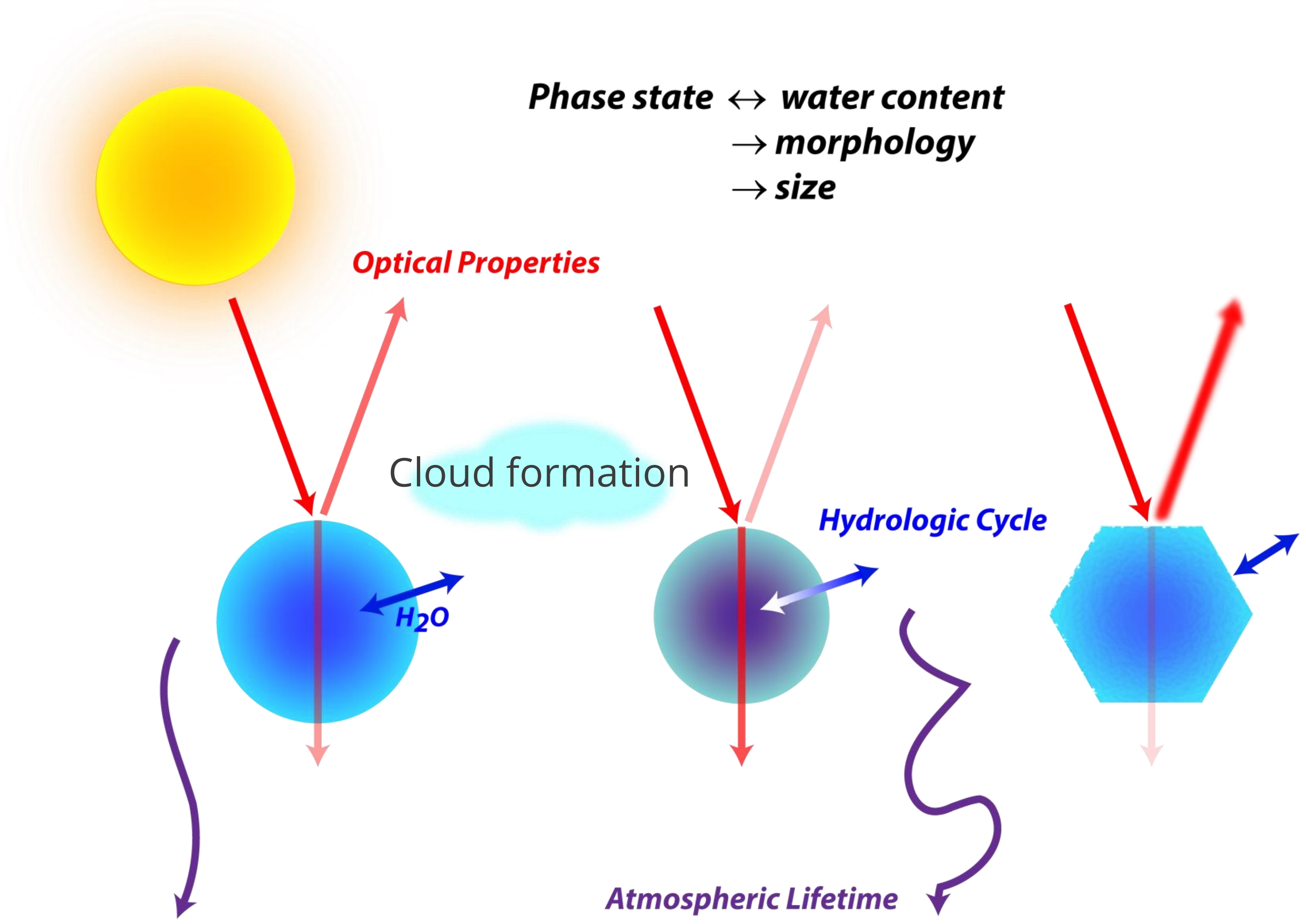
Sandia National Laboratories, Albuquerque, NM 87123

University of New Mexico, Albuquerque, NM 87131

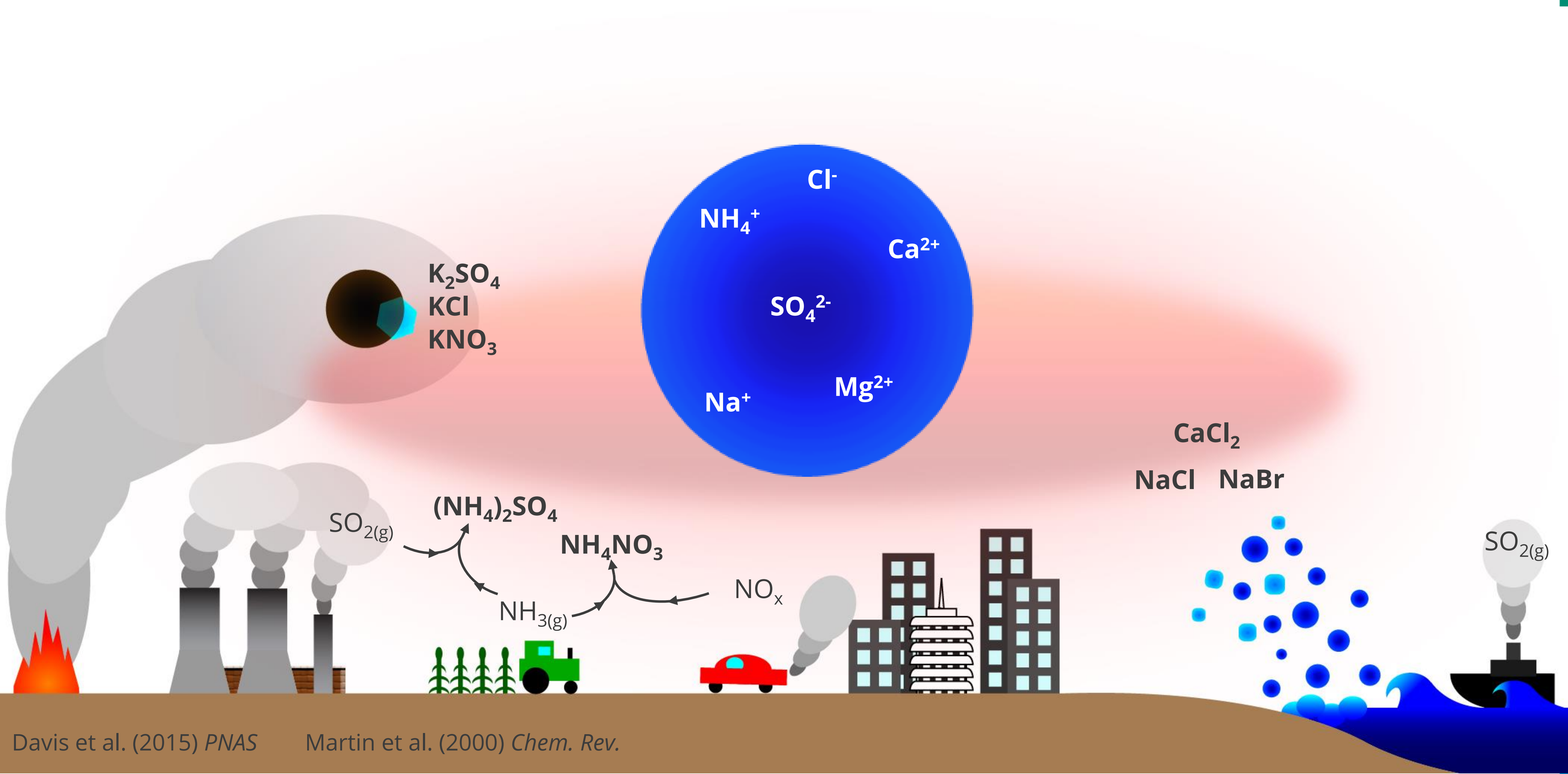
Trinity University, San Antonio, TX 78212

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Atmospheric aerosol directly and indirectly influence climate and air quality

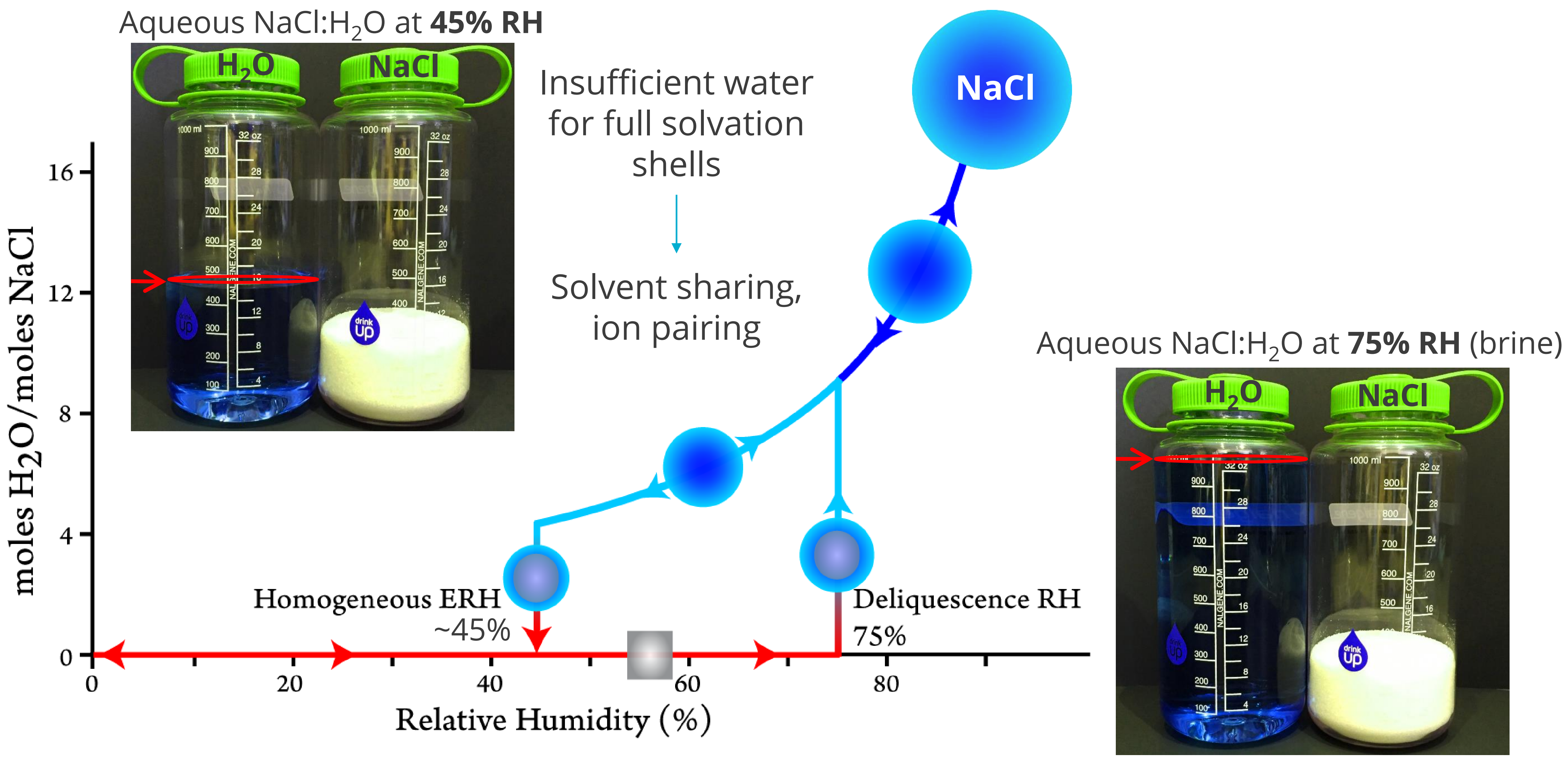


Inorganic ions are abundant in atmospheric aerosol

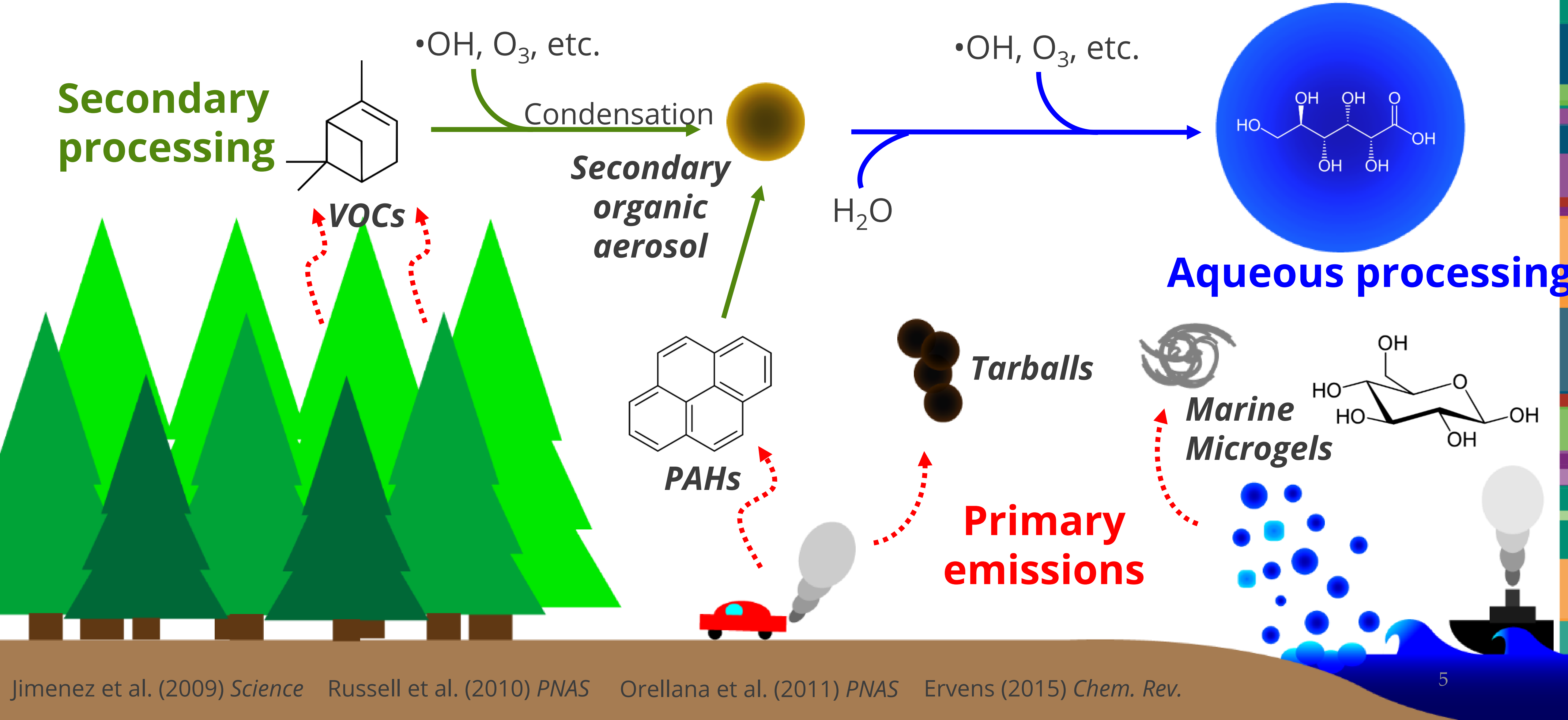


Davis et al. (2015) *PNAS* Martin et al. (2000) *Chem. Rev.*

Atmospheric aerosol can exist in a highly supersaturated state

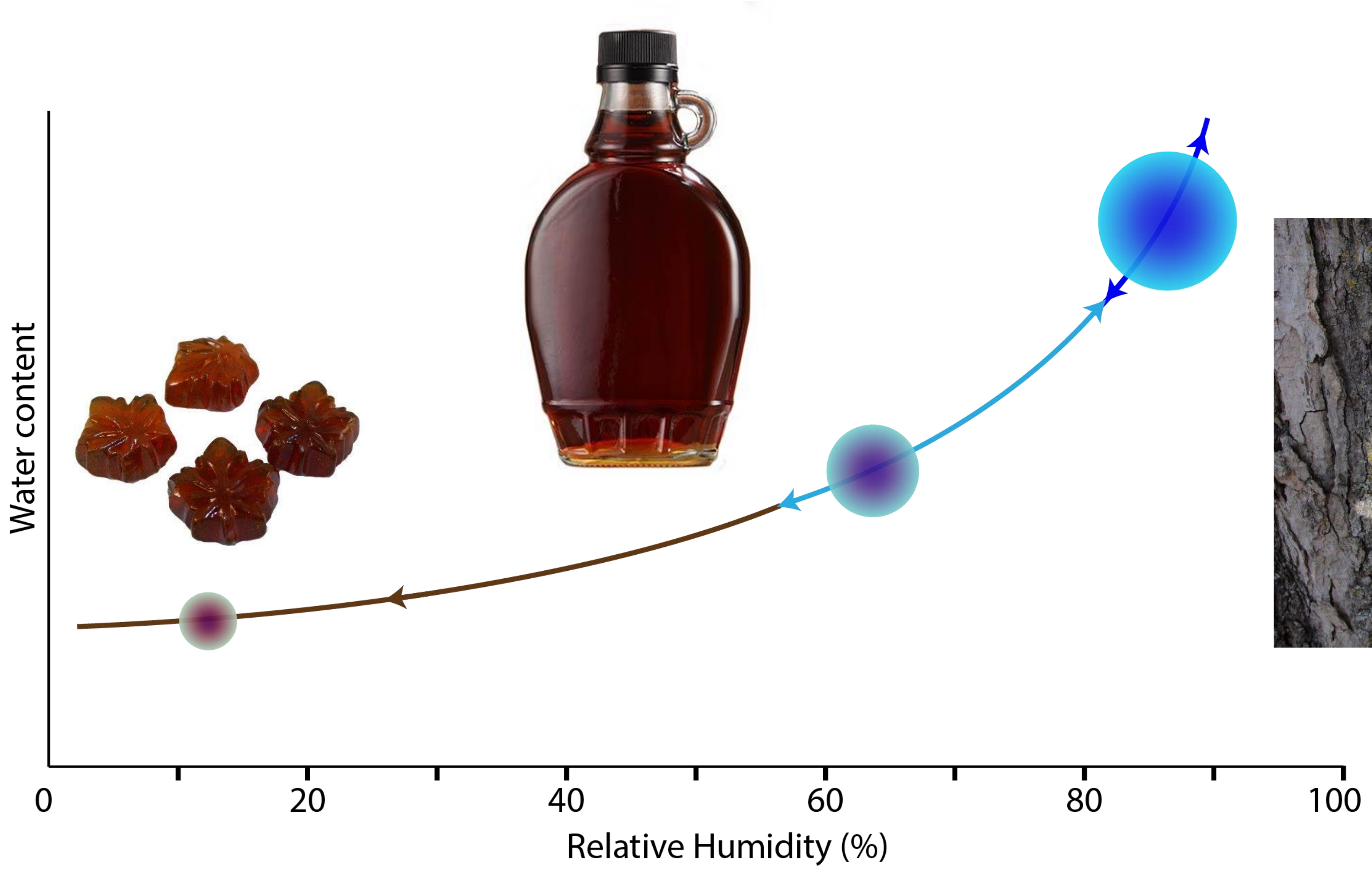


Organic compounds are abundant in the atmosphere



Jimenez et al. (2009) *Science* Russell et al. (2010) *PNAS* Orellana et al. (2011) *PNAS* Ervens (2015) *Chem. Rev.*

Organic aerosol respond to changes in relative humidity but tend to not have discrete phase transitions

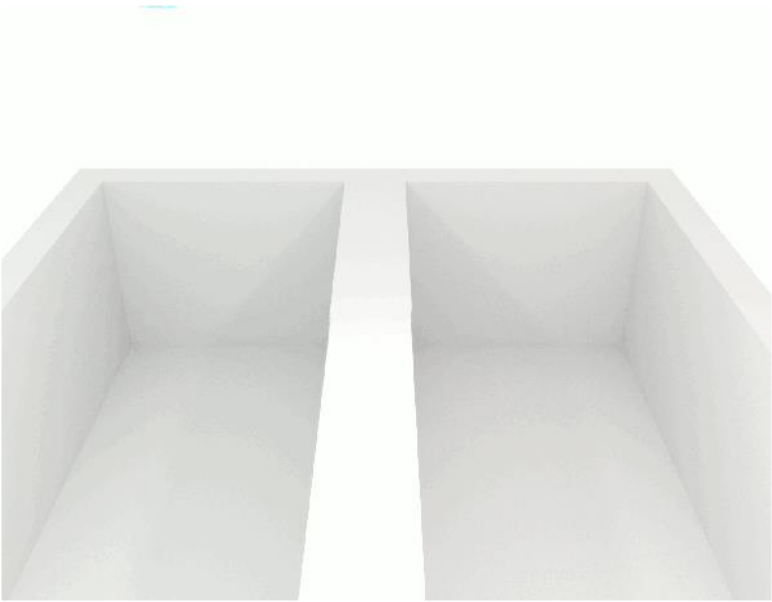


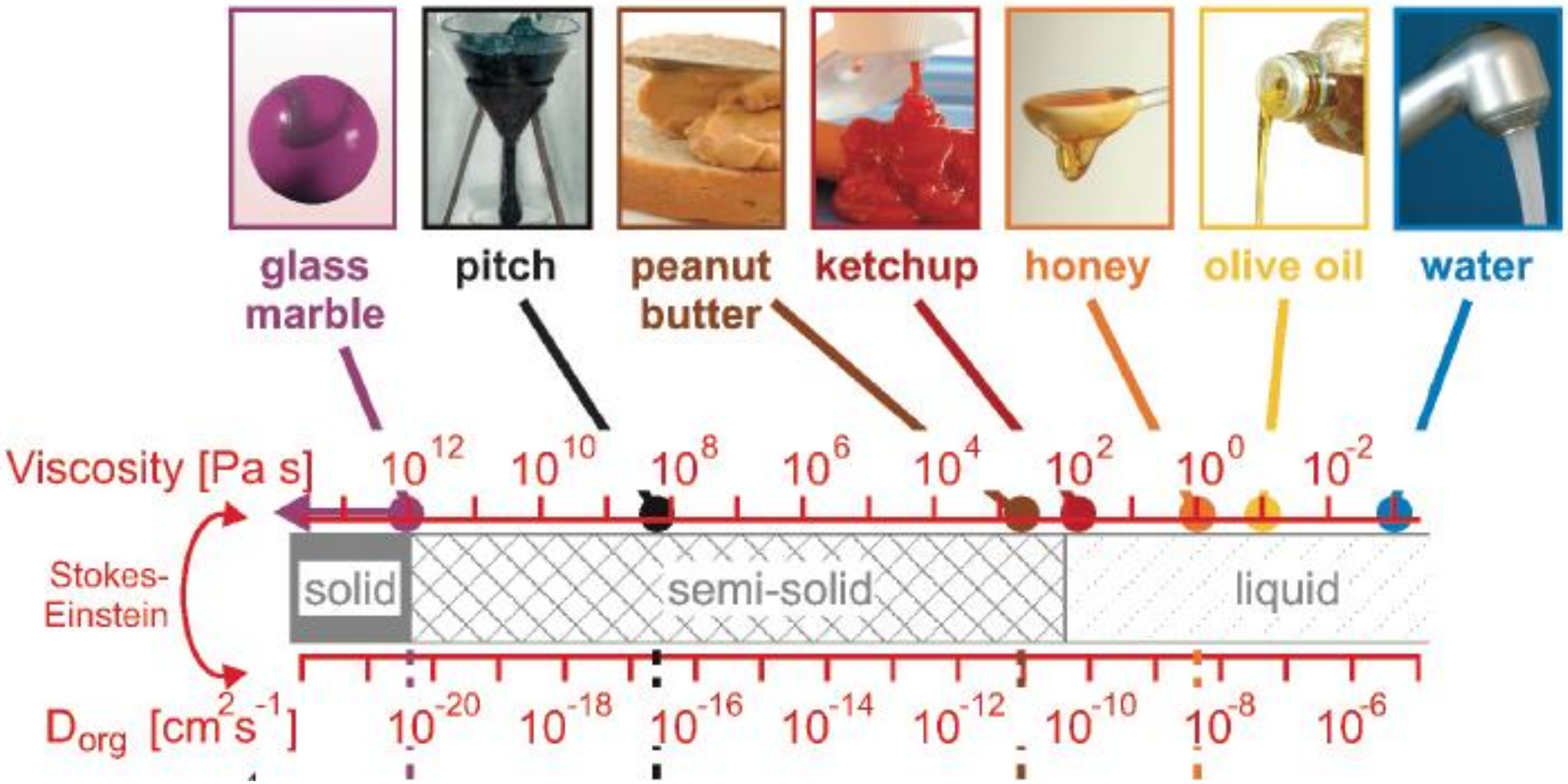
blog.scienceborealis.ca

Aerosol viscosity is a topic of interest in materials/atmospheric chemistry

Viscosity (η): resistance to deformation

Less viscous More viscous

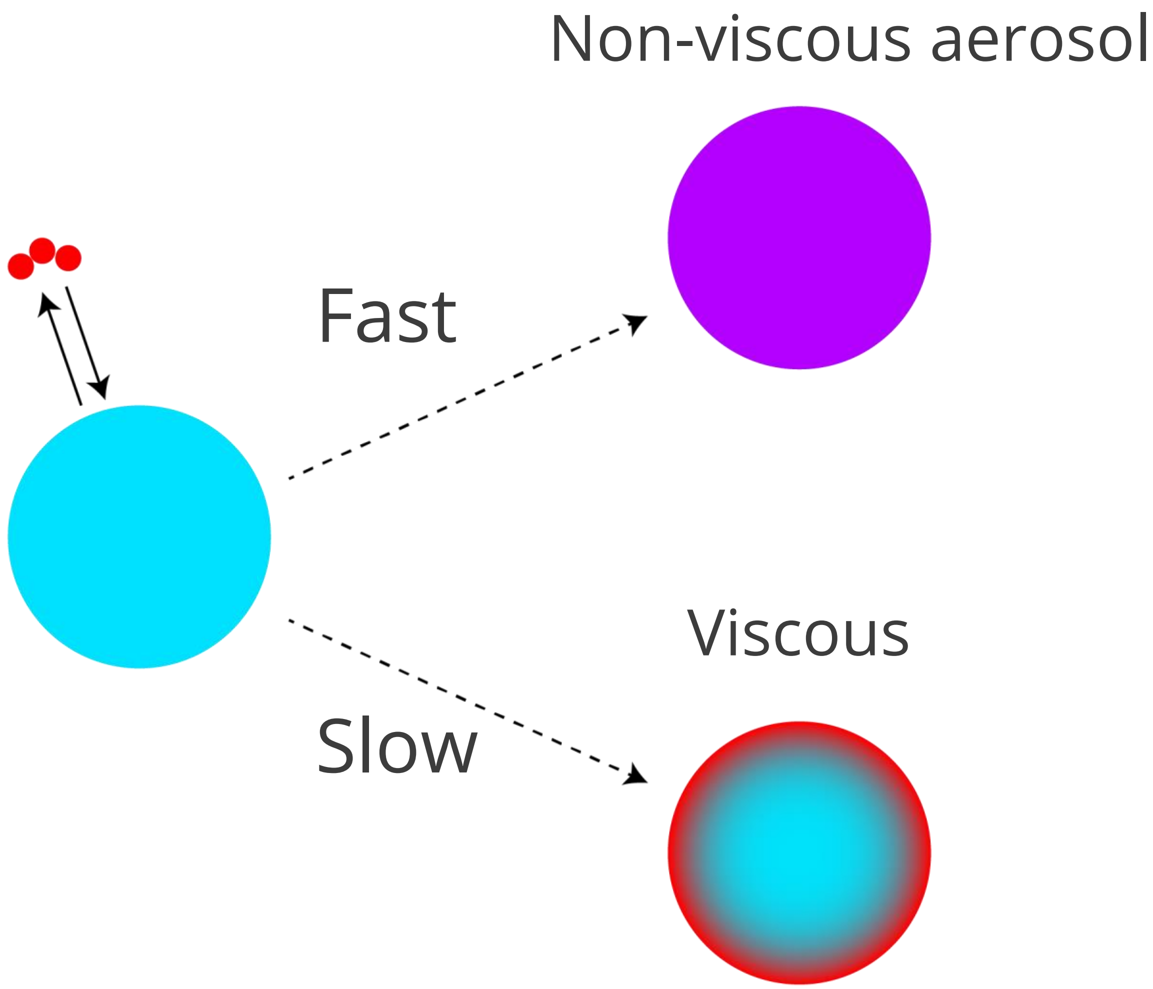




Koop et al., *PCCP*, 2011

GIF from wiki user Synapticrelay, image from user Cuk, CC BY-SA 4.0, wikipedia.org

Aerosol phase state and viscosity influence atmospheric chemistry



Relating viscosity (η) to diffusion constants (D):

$$\eta \propto \frac{1}{D}$$

Relationship to diffusional mixing time (τ_{mix}):

$$\tau_{mix} \propto \frac{1}{D} \propto \eta$$

Relationship to reaction rates:

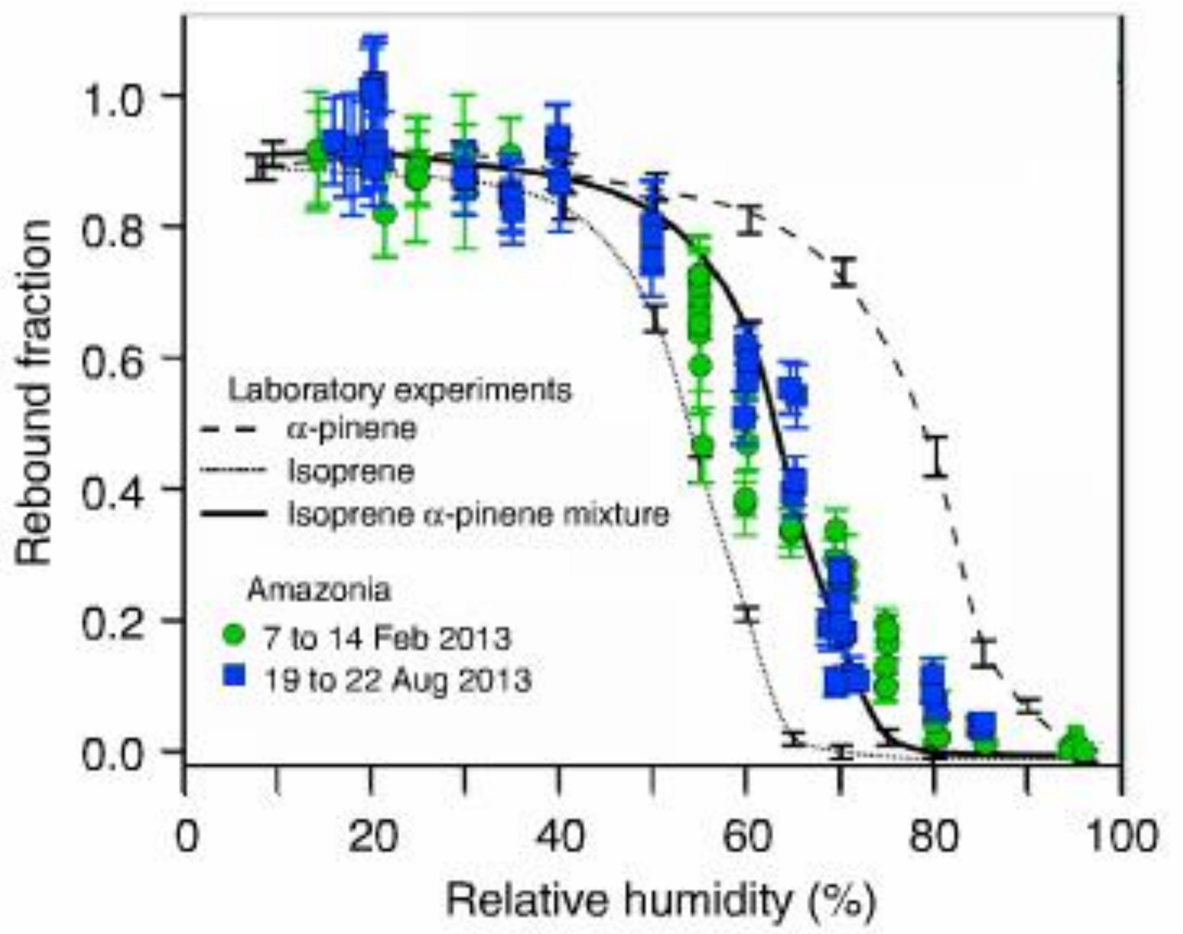
$$k \propto D \propto \frac{1}{\eta}$$

Reid et al., *Nature Comm.*, 2018

Large uncertainty exists regarding the viscosity of aerosol particles!
→ Fundamental laboratory studies are necessary

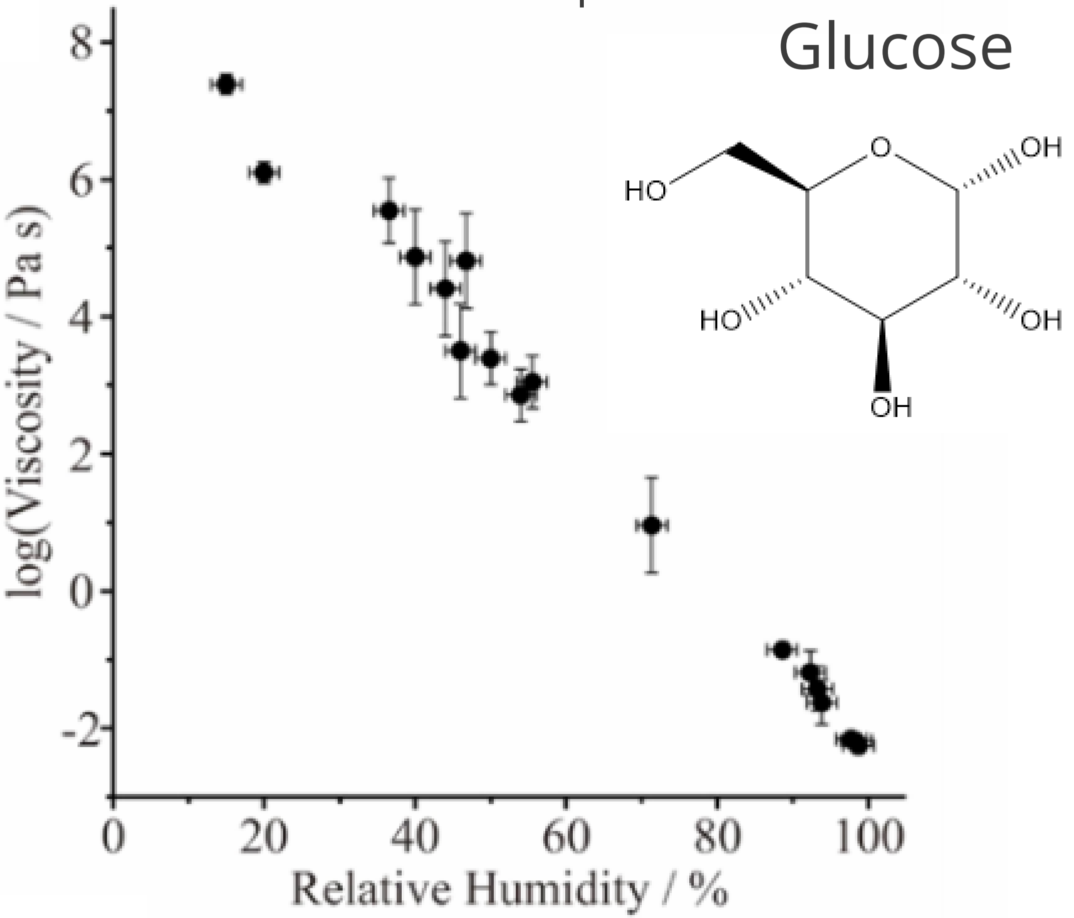
Consensus: Viscosity of organic aerosol increases with decreasing relative humidity (RH)

Field studies coupled with lab-generated proxies



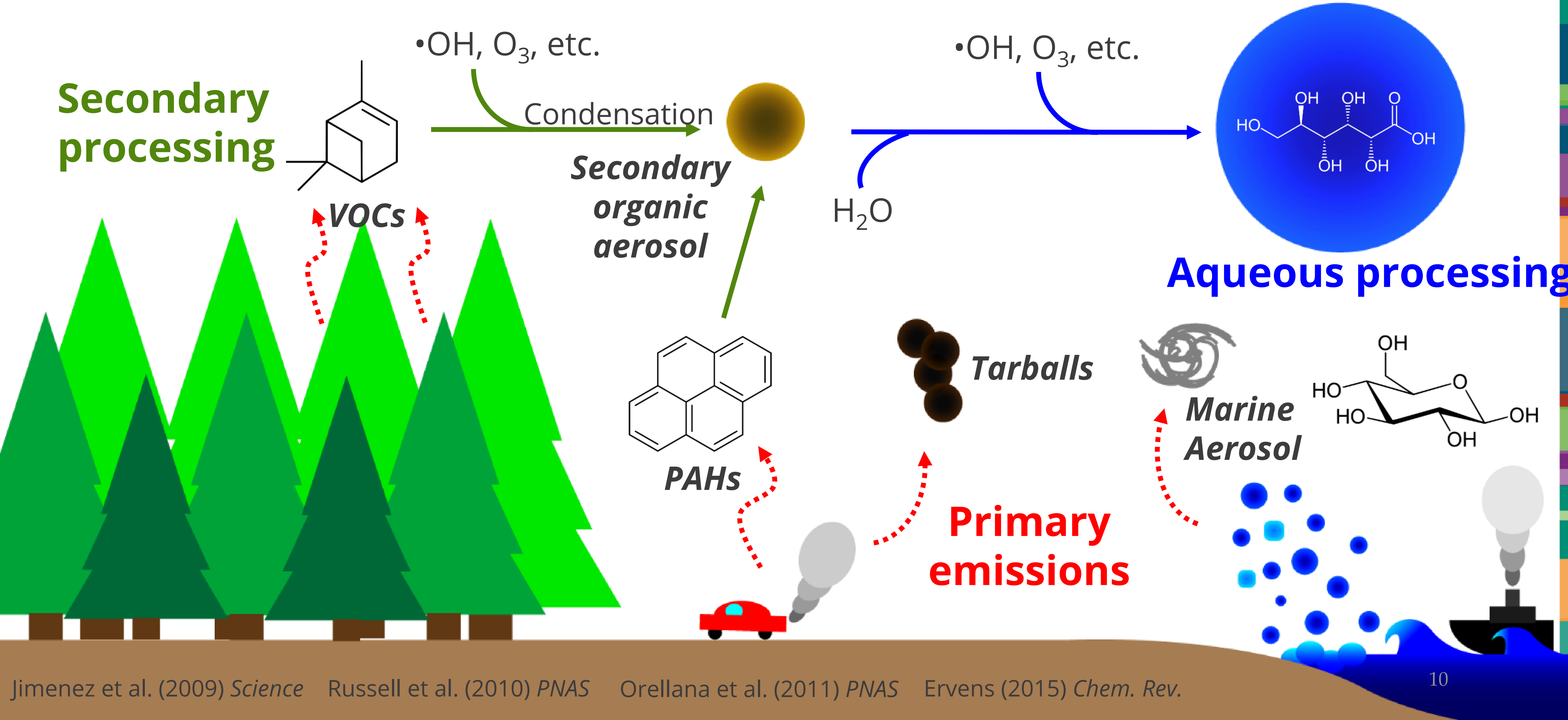
Bateman et al., *Nature Geosci.*, 2016

Aerosol optical tweezer measurements:
Model aerosol compounds



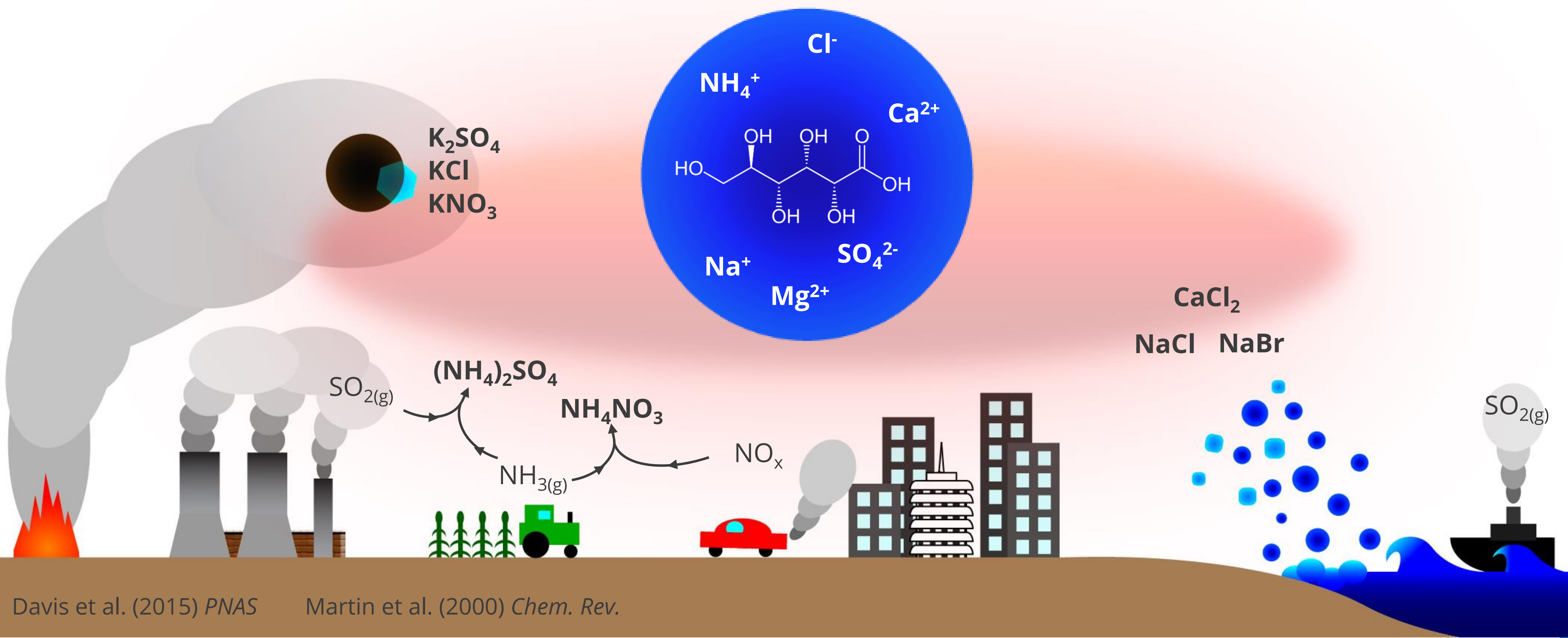
Song et al., *JPC.*, 2016

Organic compounds are abundant in the atmosphere



Jimenez et al. (2009) *Science* Russell et al. (2010) *PNAS* Orellana et al. (2011) *PNAS* Ervens (2015) *Chem. Rev.*

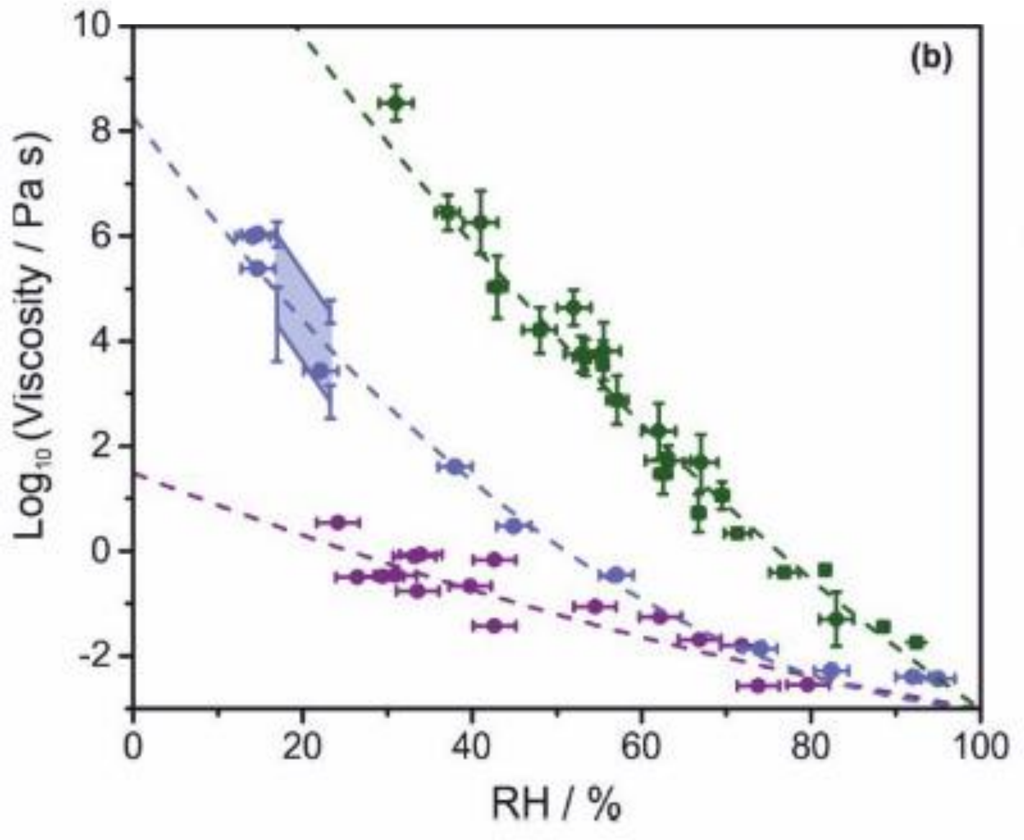
Inorganic compounds are often internally-mixed with organic compounds



Davis et al. (2015) *PNAS* Martin et al. (2000) *Chem. Rev.*

General consensus: the viscosity of organic-inorganic mixtures is reduced relative to the binary organic

Laboratory model compounds:
Sucrose-$NaNO_3$ mixture



Simple mixing approximation:

$NaNO_{3(aq)}$ | **$Sucrose_{(aq)}$ $NaNO_{3(aq)}$** | **$Sucrose_{(aq)}$**

$$\eta_{inorganic} < \eta_{mix} < \eta_{organic}$$

$$x_{H2O} > x_{H2O} > x_{H2O}$$

Rovelli et al. *Analytical Chemistry*, 2019

General consensus: the viscosity of organic-inorganic mixtures is reduced relative to the binary organic

Mixing approximations do not consider supramolecular, ion-organic interactions

$NaNO_{3(aq)}$

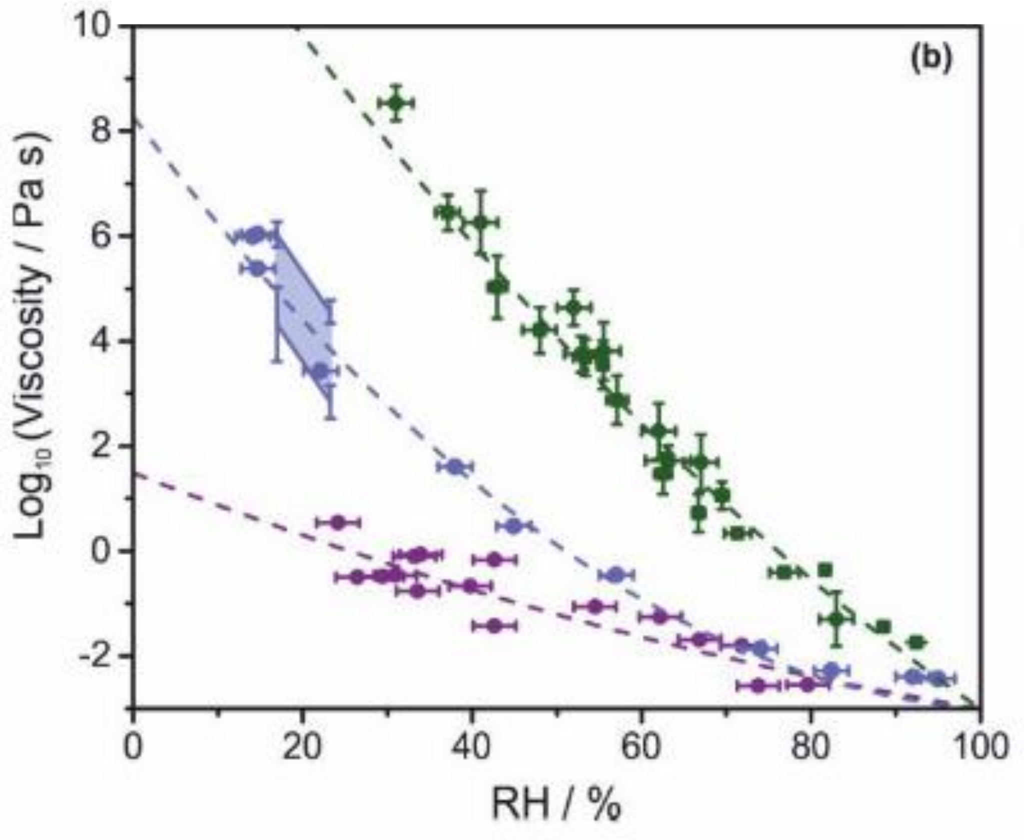
$Sucrose_{(aq)}$ $NaNO_{3(aq)}$

$Sucrose_{(aq)}$

$$\eta_{inorganic} < \eta_{mix} < \eta_{organic}$$

$$x_{H2O} > x_{H2O} > x_{H2O}$$

Laboratory model compounds:
Sucrose-$NaNO_3$ mixture

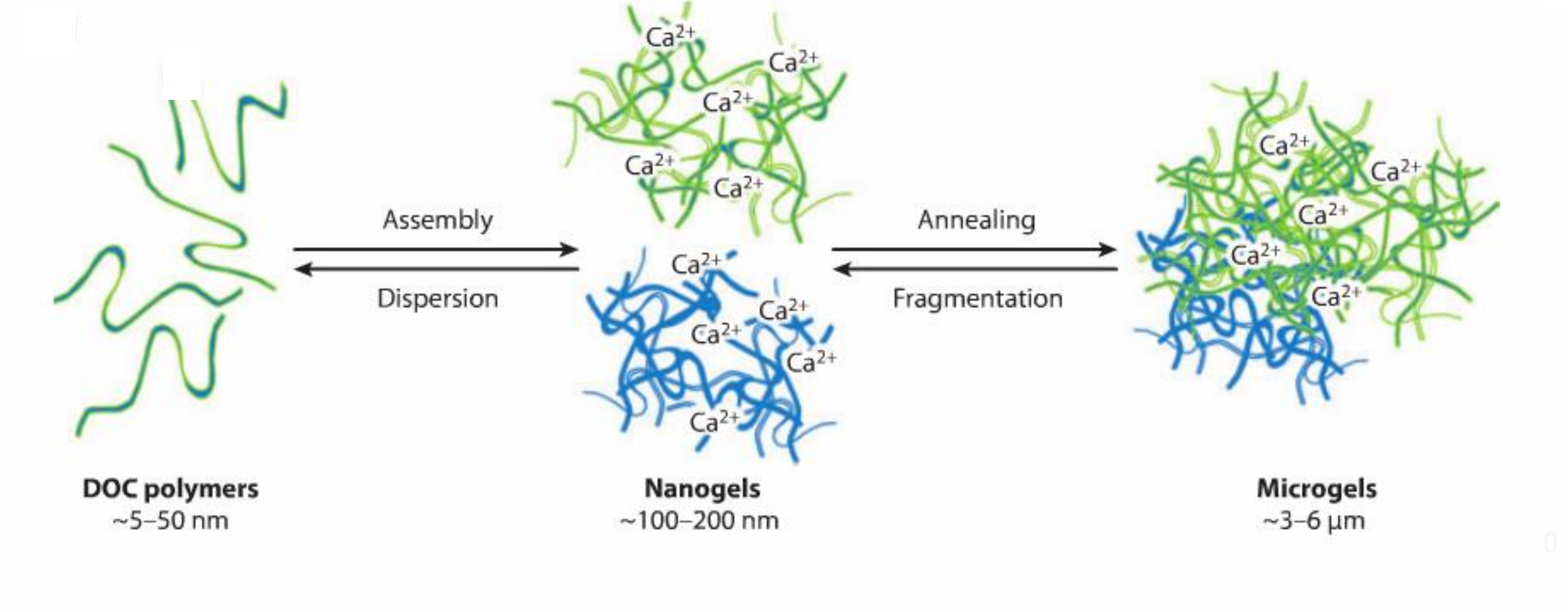


Rovelli et al. *Analytical Chemistry*, 2019

General consensus: the viscosity of organic-inorganic mixtures is reduced relative to the binary organic

Supramolecular assemblies include non-covalent interactions between two species

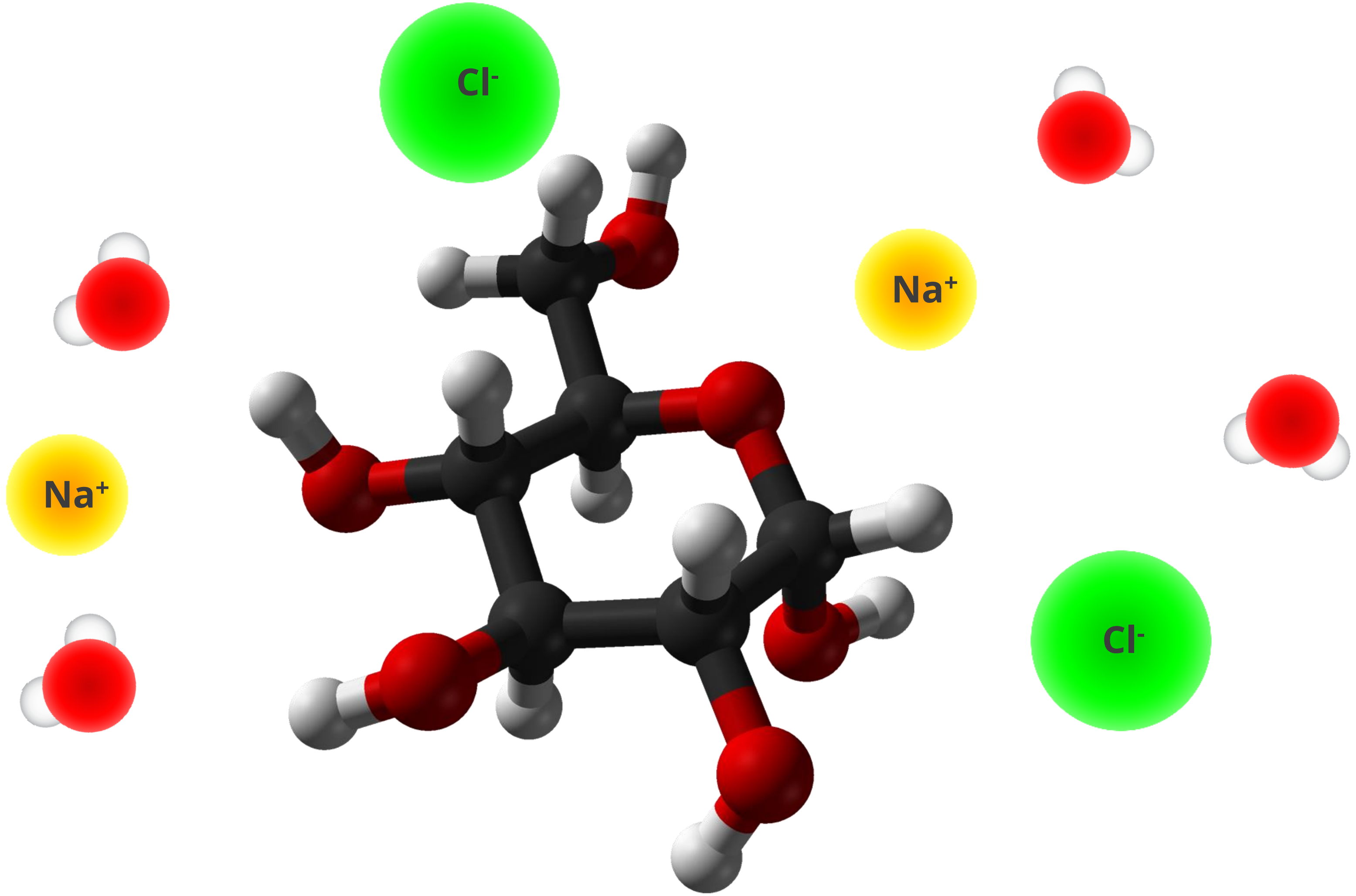
Example: marine microgels crosslinked by Ca^{2+}



Verdugo, *Annu. Rev. Marine Sci.*, 2012

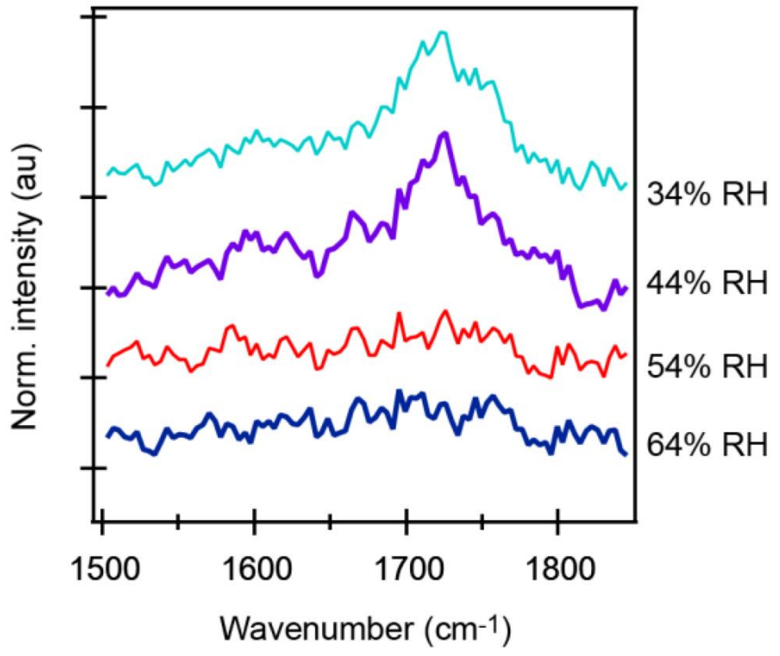
Low water content may facilitate solute-solute interactions

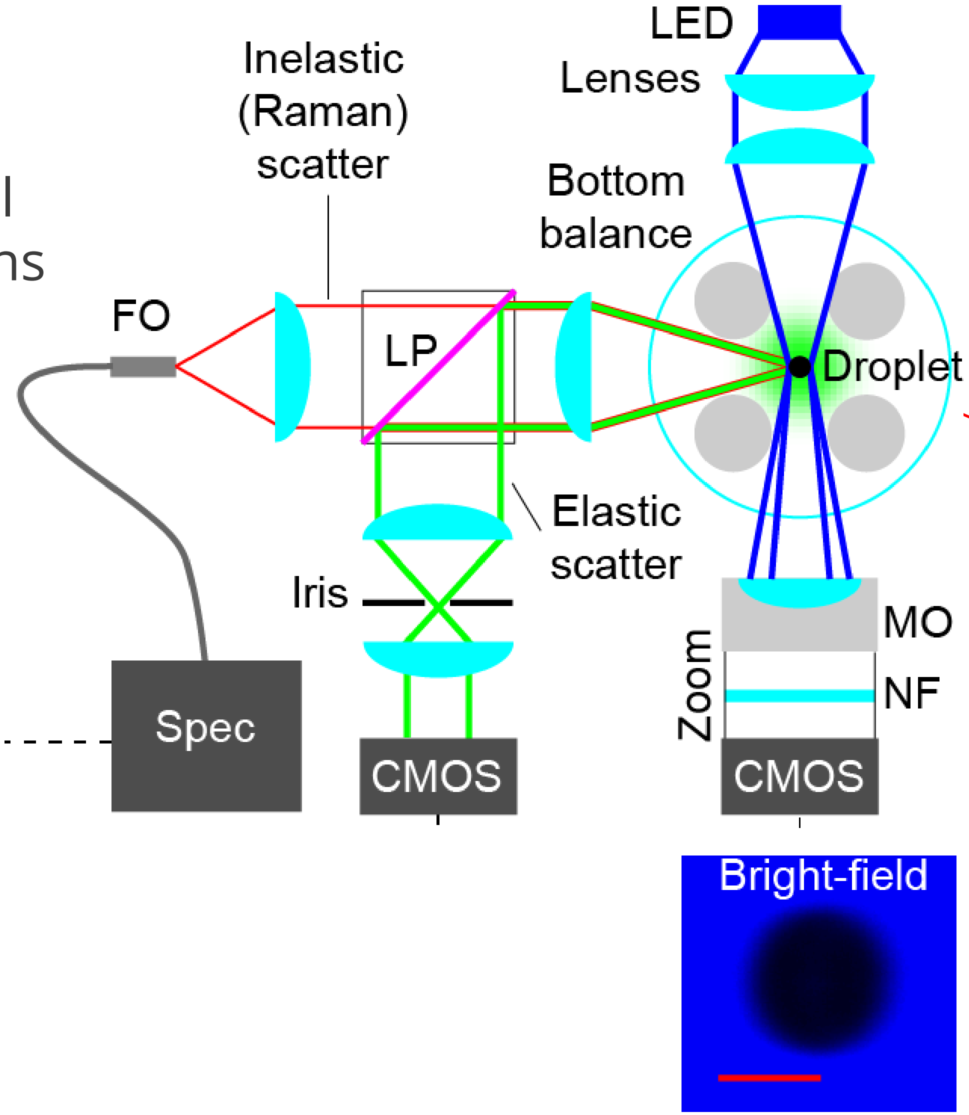
Research question: to what extent does ion-molecule clustering influence the properties of aerosol?

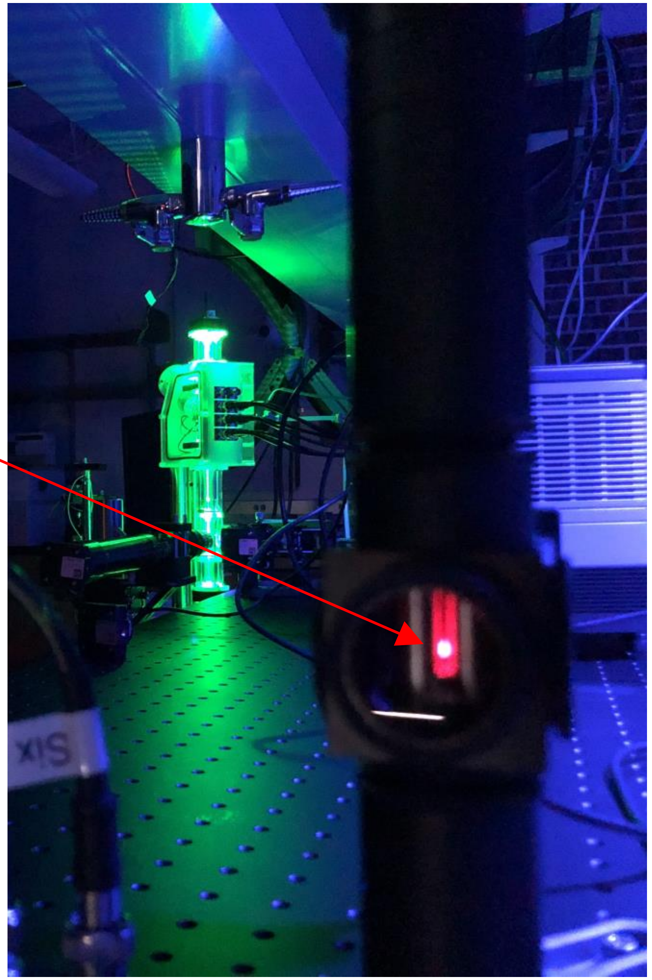


Aerosol levitation enables the study of molecular interactions under highly concentrated supersaturated conditions

Raman spectroscopy can reveal insight into molecular interactions





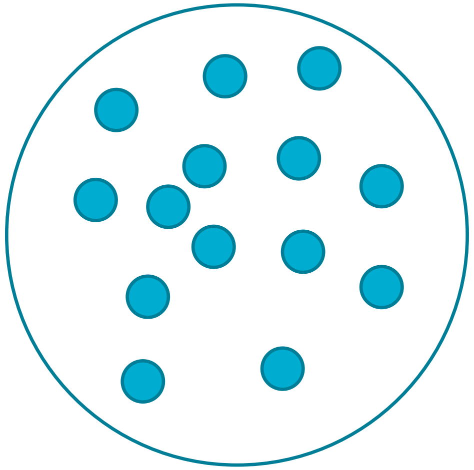


Micro-rheology provides a macroscopic observable that can be related to micro-structure

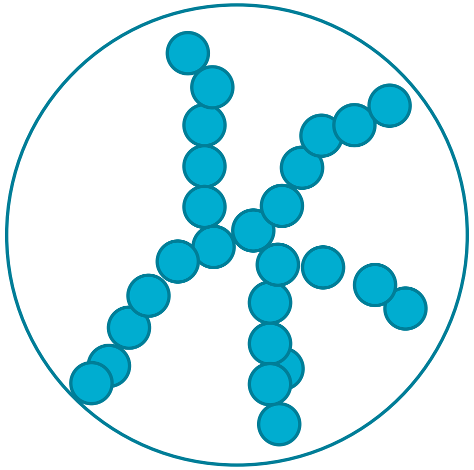
Rheological observations

↓

Micro-structure



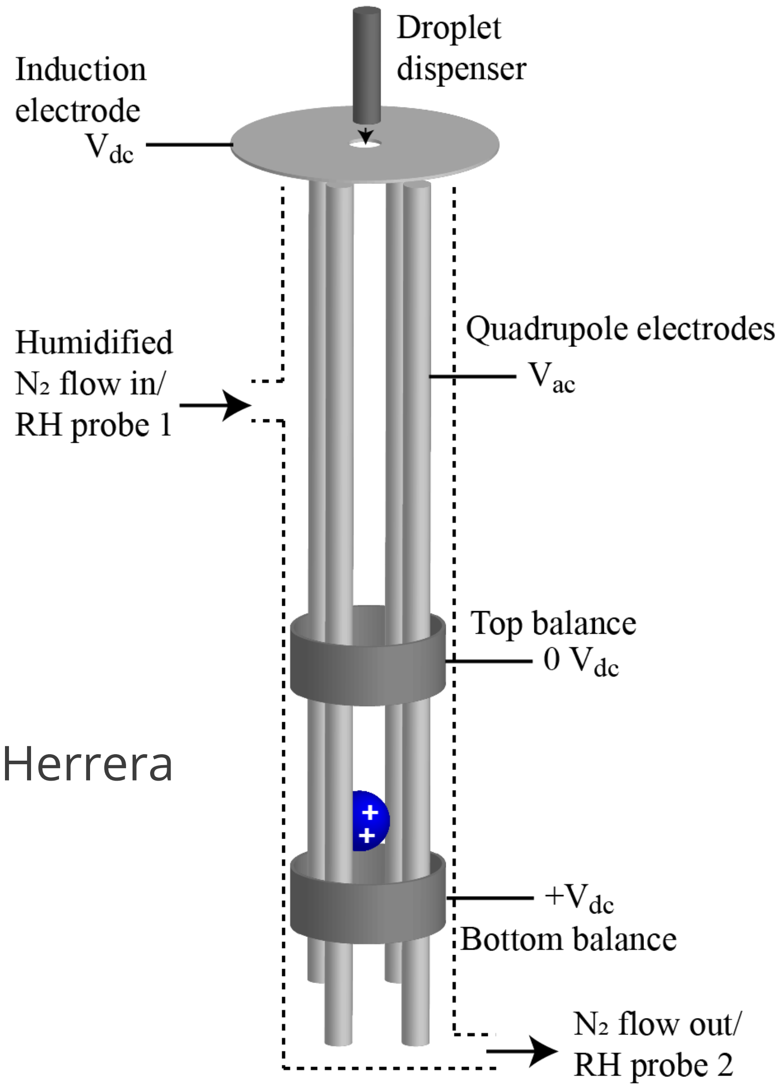
Less resistant to flow



More resistant to flow

Aerosol rheology was studied in a electrodynamic balance by merging particles

Dual-balance linear quadrupole electrodynamic balance (DBQ-EDB)



A new system developed by:
Kristin Trobaugh Josefina Hajek-Herrera

At a constant RH:

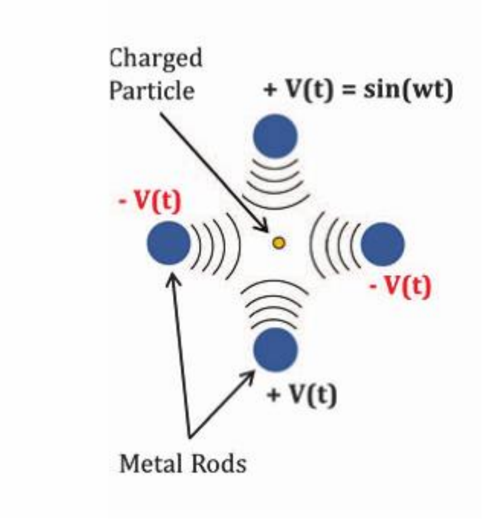
1. **Trap droplet (~30 µm) in bottom balance**
2. Trap droplet (of opposite polarity) in top
3. Equilibrate both droplets
4. Merge
5. Determine micro-rheological properties

Richards et al., *Analytical Chemistry*, 2020
Richards et al., *Science Advances*, 2020

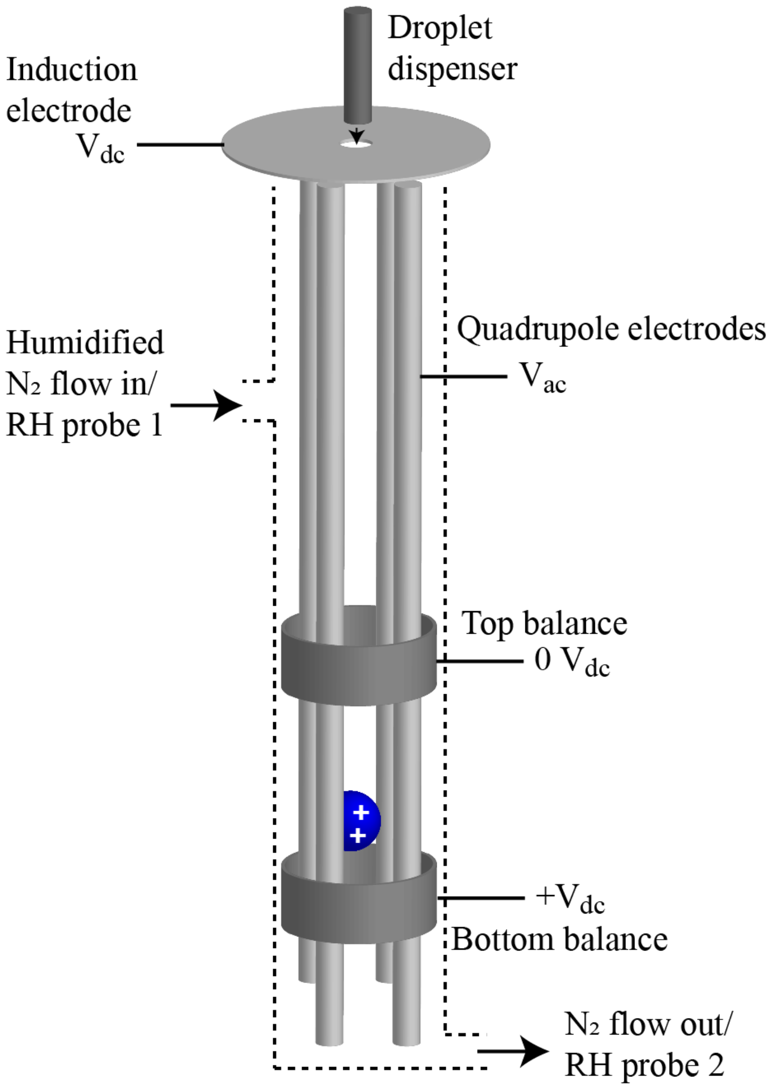
Aerosol rheology was studied in a electrodynamic balance by merging particles

Dual-balance linear quadrupole electrodynamic balance (DBQ-EDB)

Radial confinement (top view)



Hart et al. (2015) *Applied Optics*



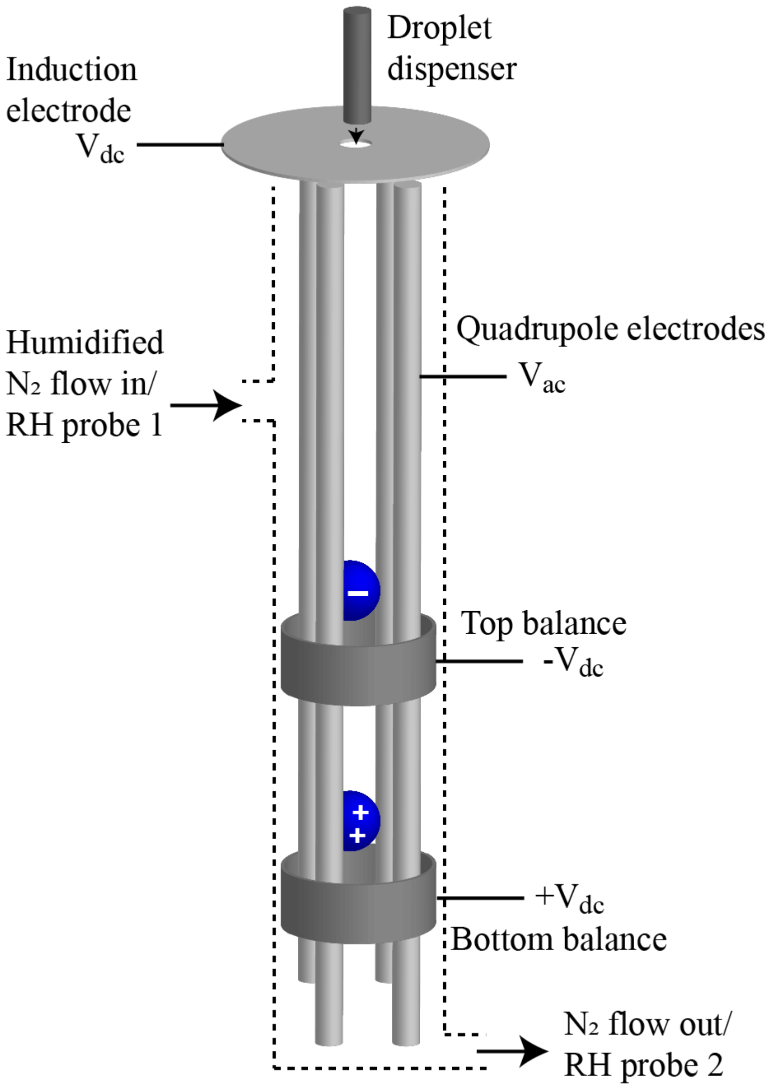
At a constant RH:

1. **Trap droplet (~30 µm) in bottom balance**
2. Trap droplet (of opposite polarity) in top
3. Equilibrate both droplets
4. Merge
5. Determine micro-rheological properties

Richards et al., *Analytical Chemistry*, 2020
Richards et al., *Science Advances*, 2020

Aerosol rheology was studied in a electrodynamic balance by merging particles

Dual-balance linear quadrupole electrodynamic balance (DBQ-EDB)



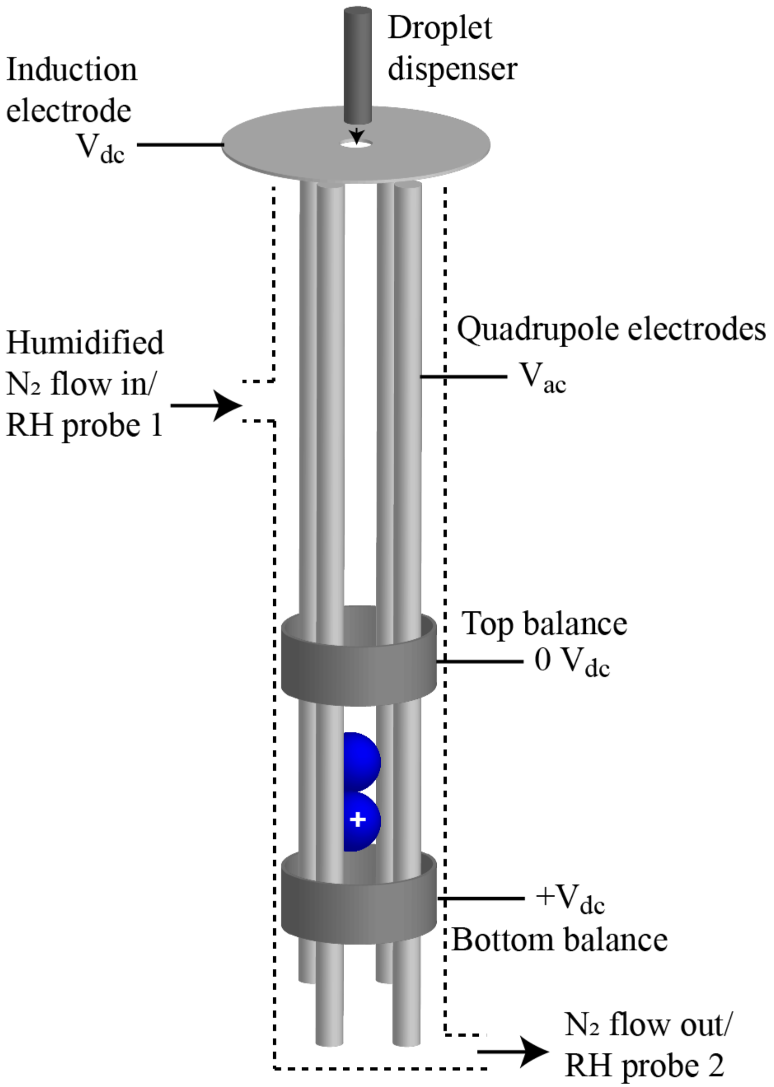
At a constant RH:

1. Trap droplet (~30 μm) in bottom balance
2. **Trap droplet (of opposite polarity) in top**
3. **Equilibrate both droplets**
4. Merge
5. Determine micro-rheological properties

Richards et al., *Analytical Chemistry,* 2020
Richards et al., *Science Advances,* 2020

Aerosol rheology was studied in a electrodynamic balance by merging particles

Dual-balance linear quadrupole electrodynamic balance (DBQ-EDB)

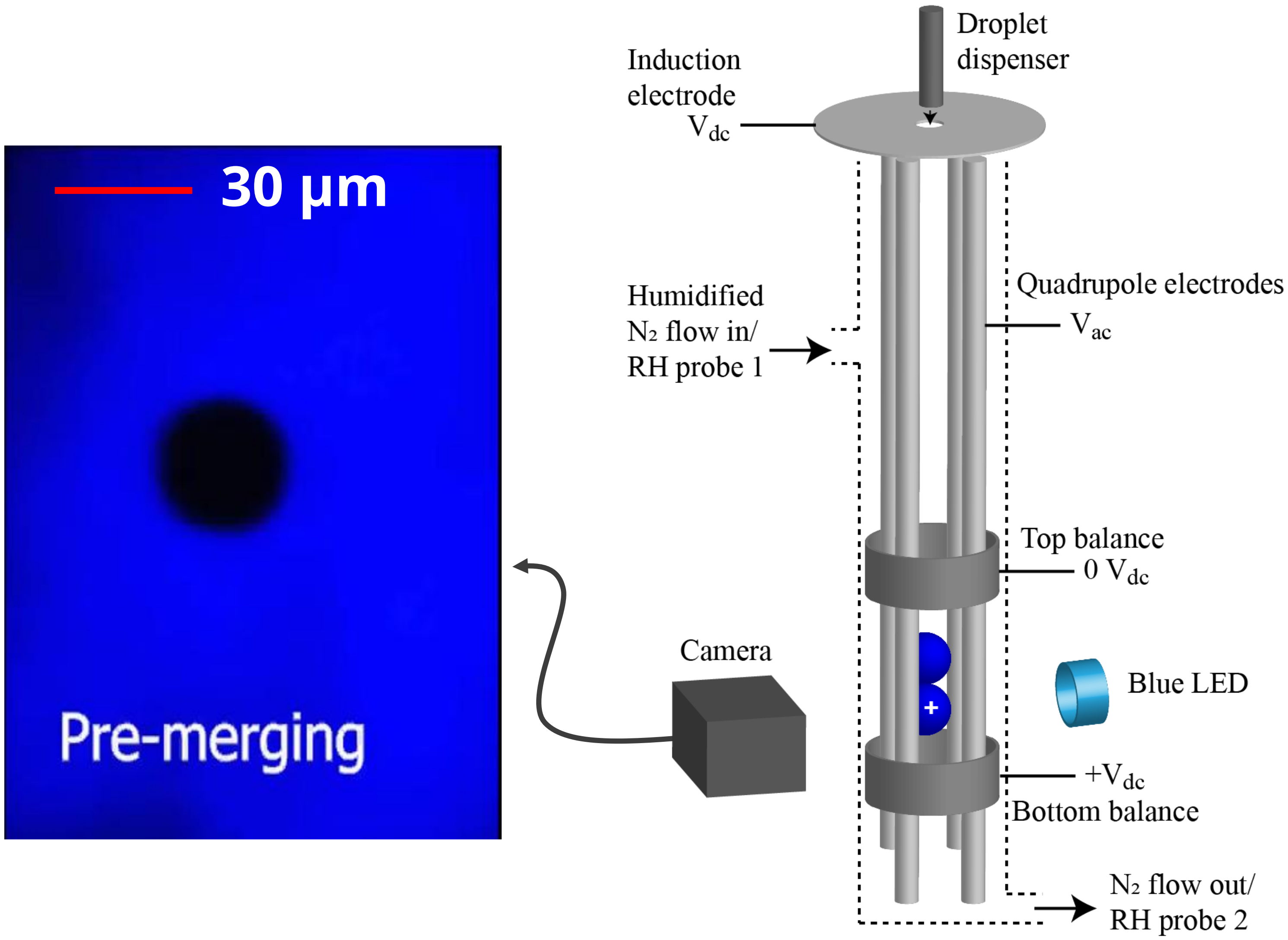


At a constant RH:

1. Trap droplet (~30 μm) in bottom balance
2. Trap droplet (of opposite polarity) in top
3. Equilibrate both droplets
4. **Merge**
5. Determine micro-rheological properties

Richards et al., *Analytical Chemistry*, 2020
Richards et al., *Science Advances*, 2020

Optical microscopy was used to monitor the fluid flow of merged dimers as a function of time

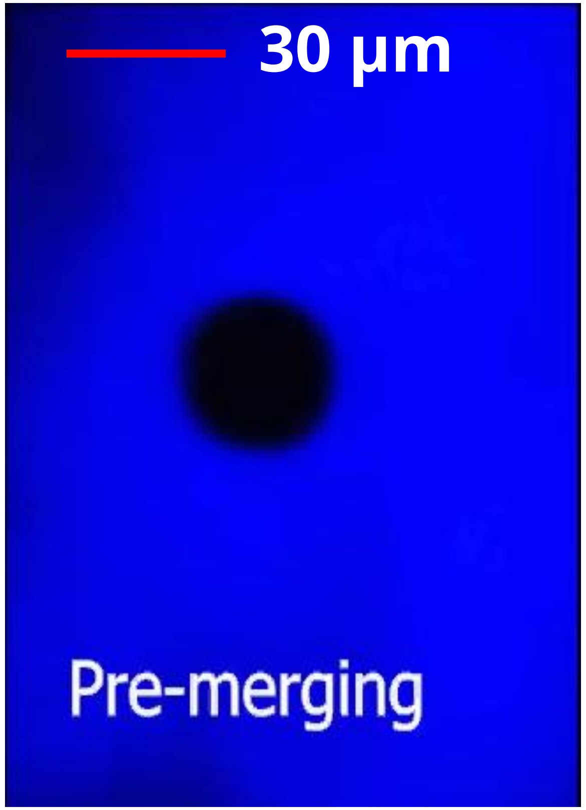


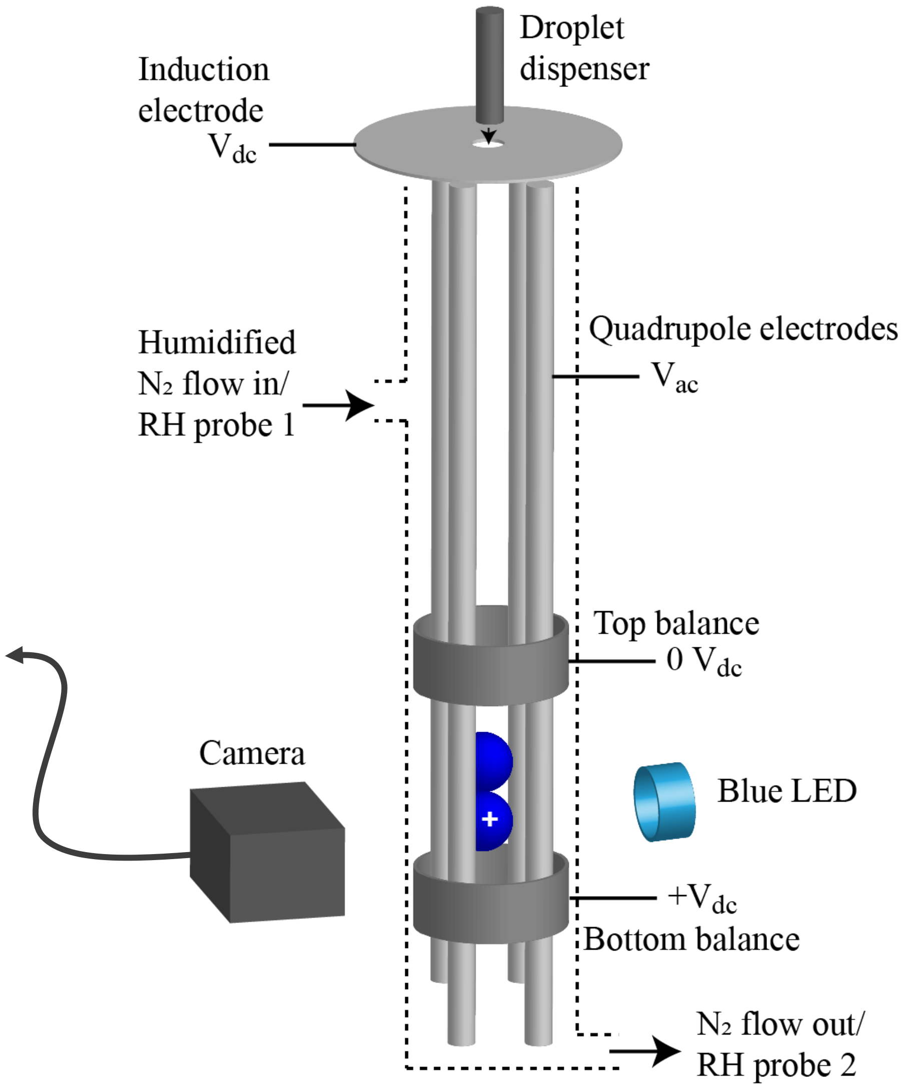
At a constant RH:

1. Trap droplet (~30 µm) in bottom balance
2. Trap droplet (of opposite polarity) in top
3. Equilibrate both droplets
4. Merge
5. **Determine micro-rheological properties**

Richards et al., *Analytical Chemistry*, 2020
Richards et al., *Science Advances*, 2020

Optical microscopy was used to monitor the fluid flow of merged dimers as a function of time





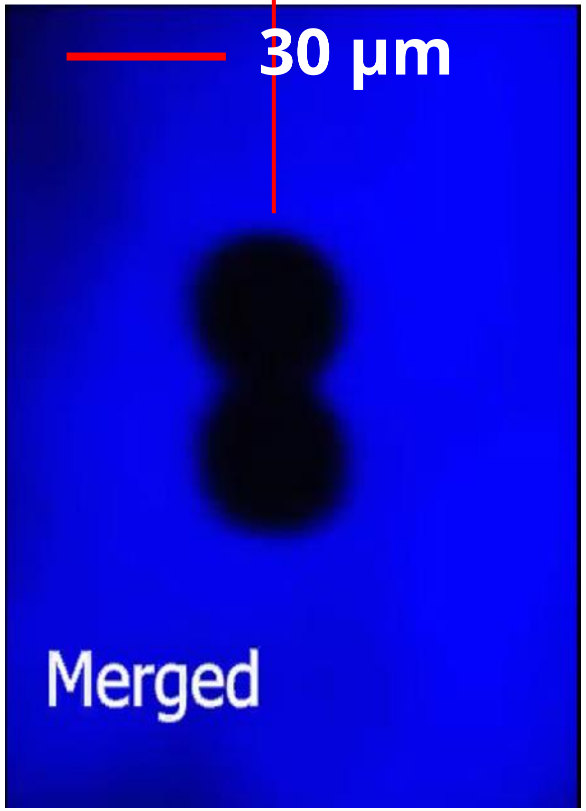
At a constant RH:

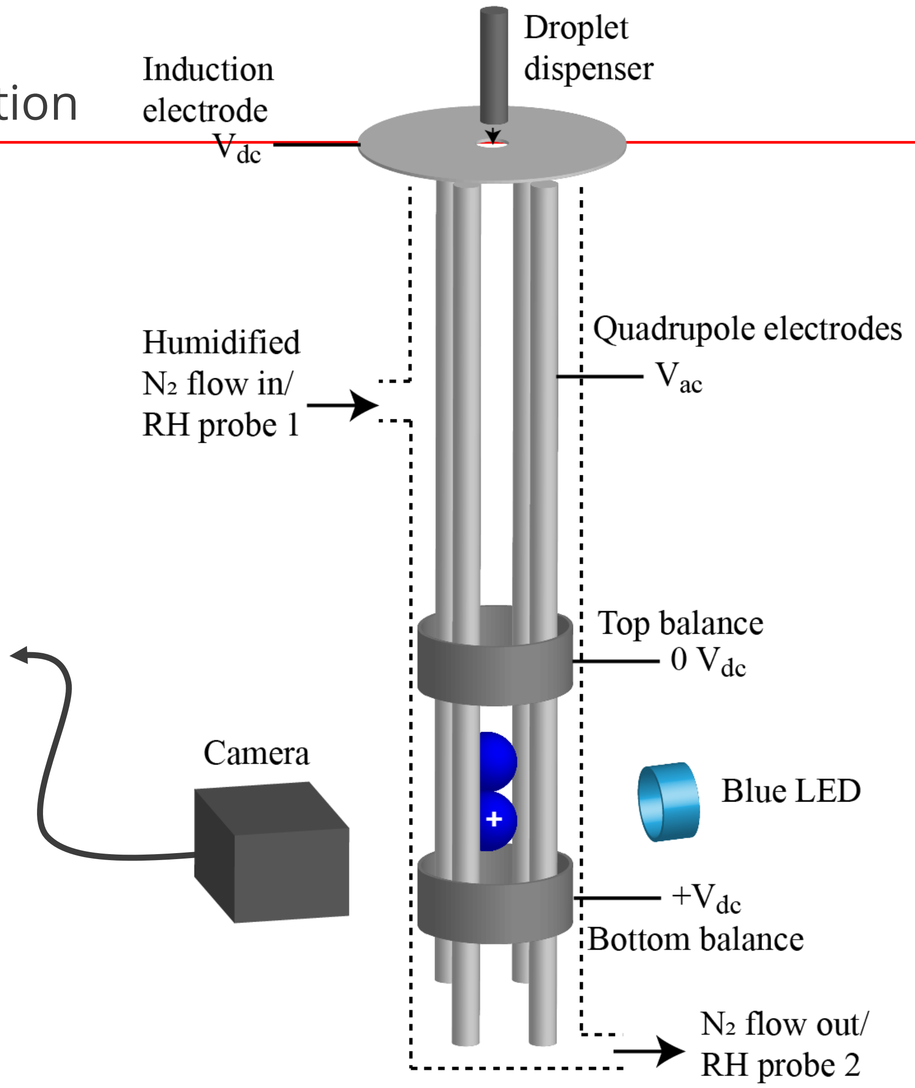
1. Trap droplet (~30 μm) in bottom balance
2. Trap droplet (of opposite polarity) in top
3. Equilibrate both droplets
4. Merge
5. **Determine micro-rheological properties**

Richards et al., *Analytical Chemistry*, 2020
Richards et al., *Science Advances*, 2020

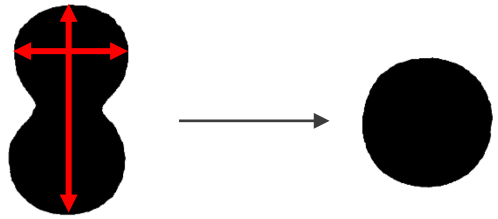
Optical microscopy was used to monitor merged dimer micro-rheology as a function of time

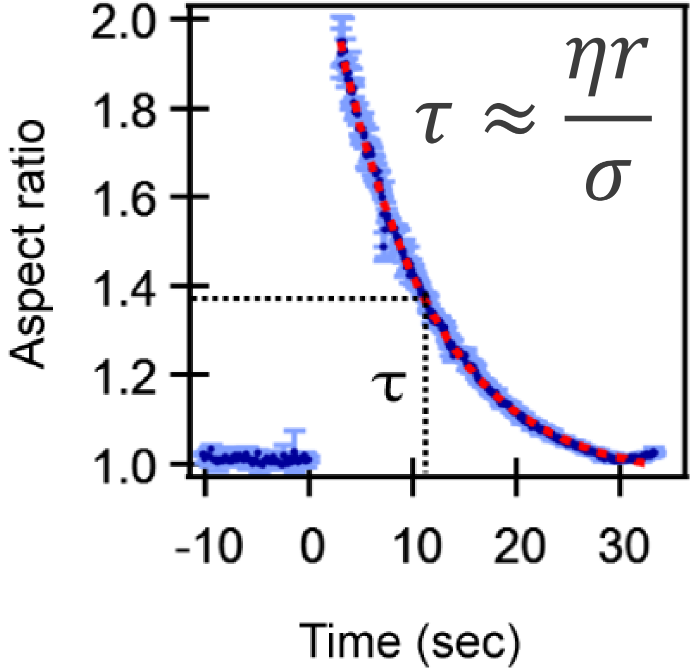
Binarization



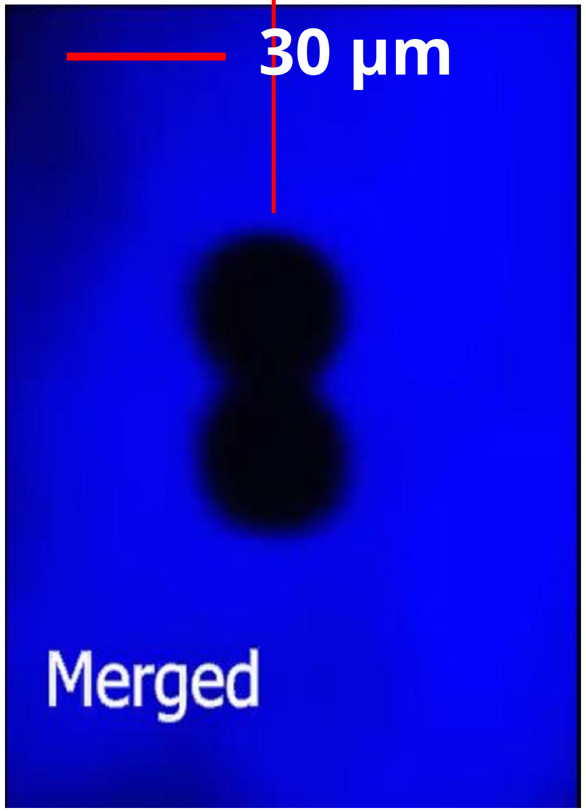


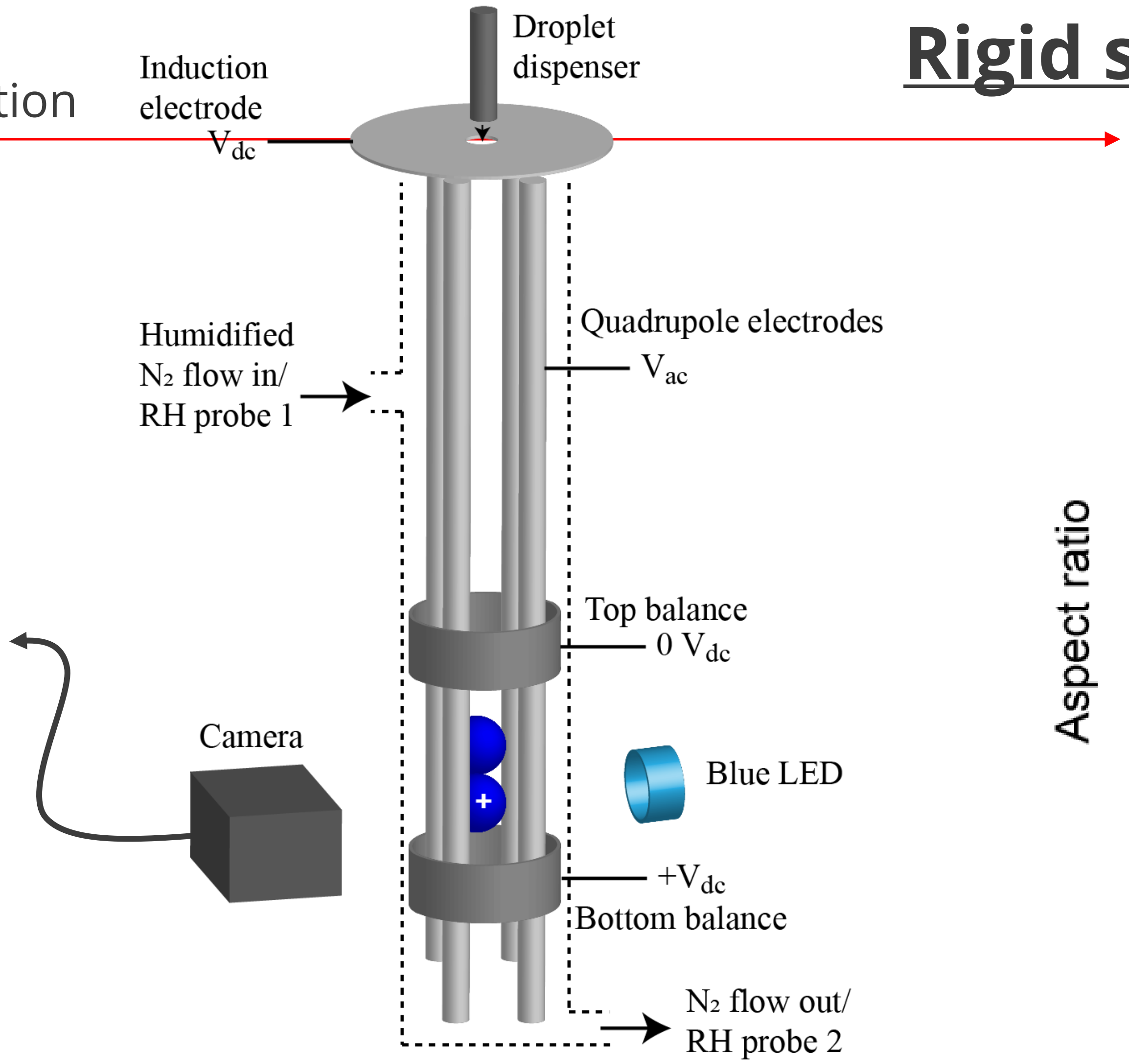
Viscous fluids:





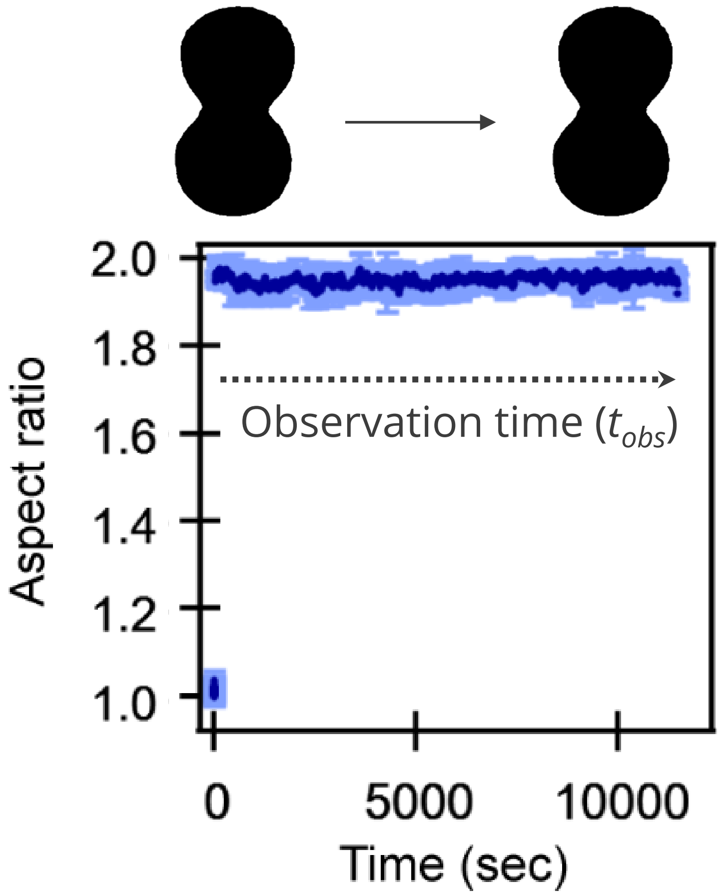
Optical microscopy was used to monitor merged dimer micro-rheology as a function of time





Rigid strucutures:

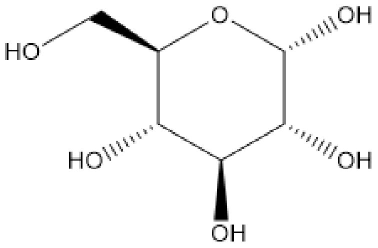
$MgSO_{4(aq)}$
~30% RH



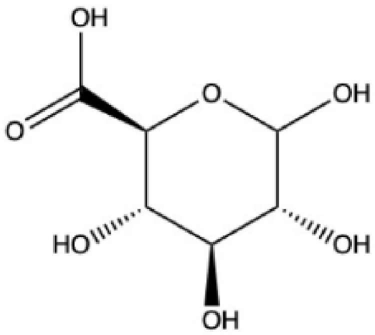
Model atmospheric/ marine aerosol compounds were used to explore the effects of ion-molecule interactions

Organics:

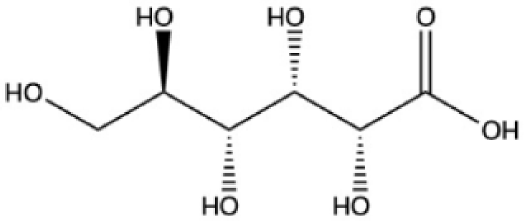
D-glucose:



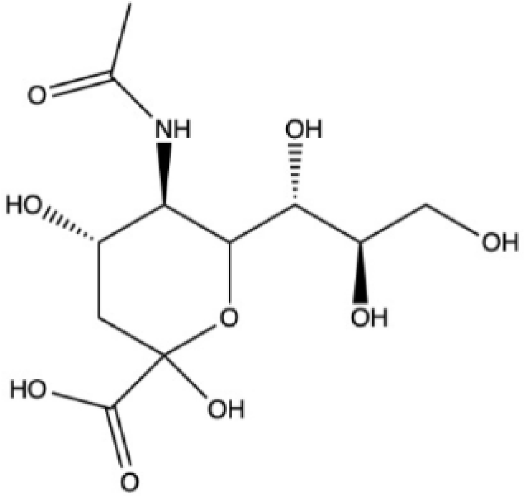
D-glucuronic acid:



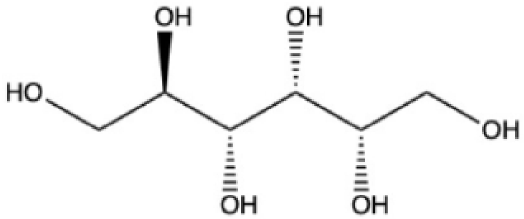
D-gluconic acid:



N-acetylneuraminic acid:



D-sorbitol:



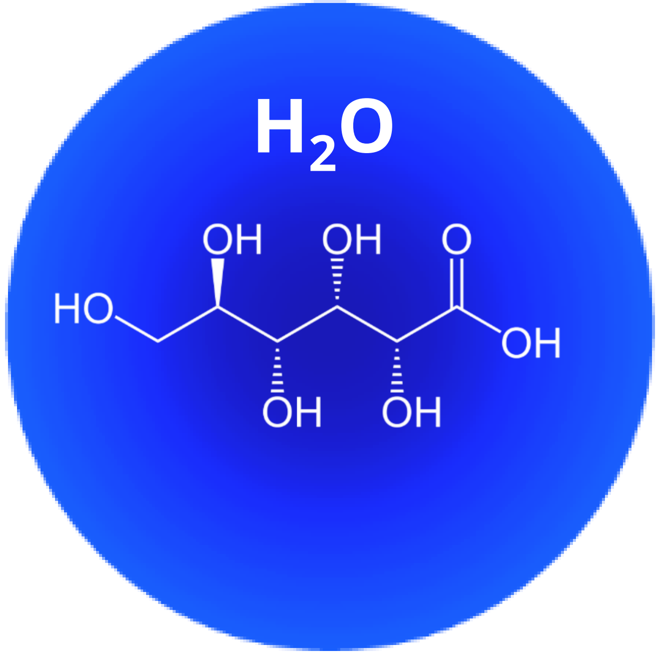
Inorganics:

$CaCl_2$

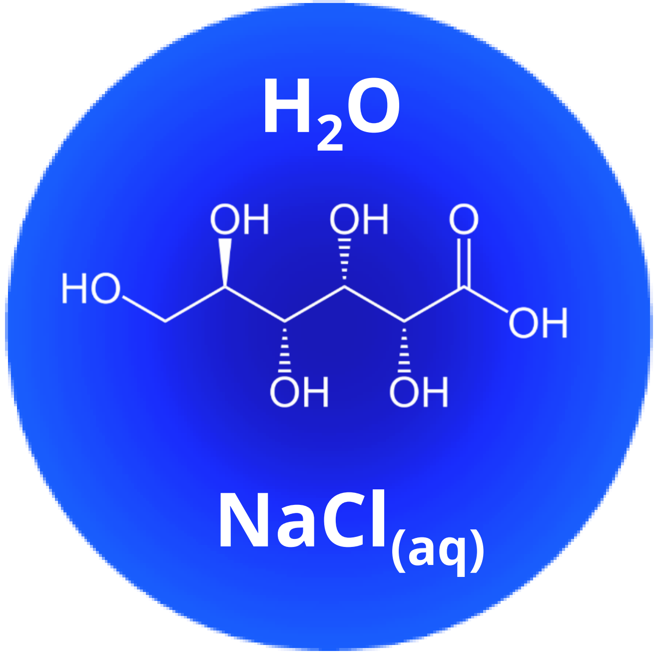
Richards et al., 2020, *Science Advances*

Model atmospheric/ marine aerosol compounds were used to explore gel formation

Binary monosaccharide droplets

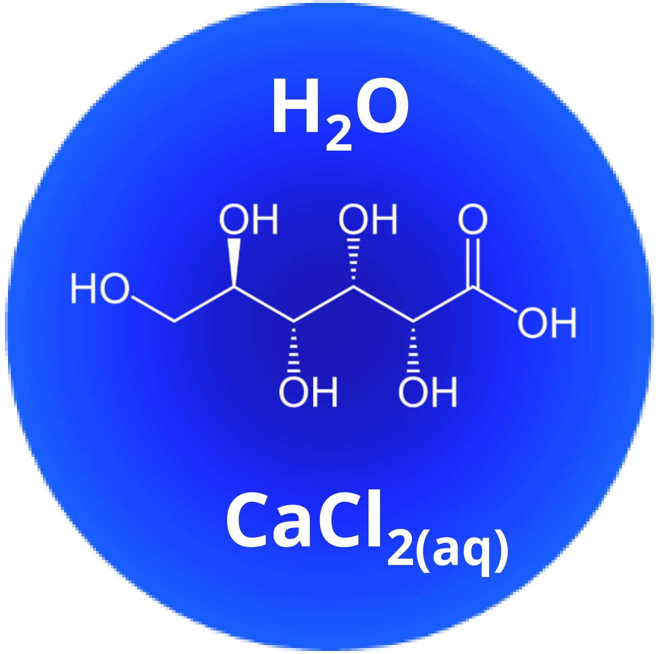


Ternary NaCl-monosaccharide droplets



1:1 (by mole) NaCl:sugar

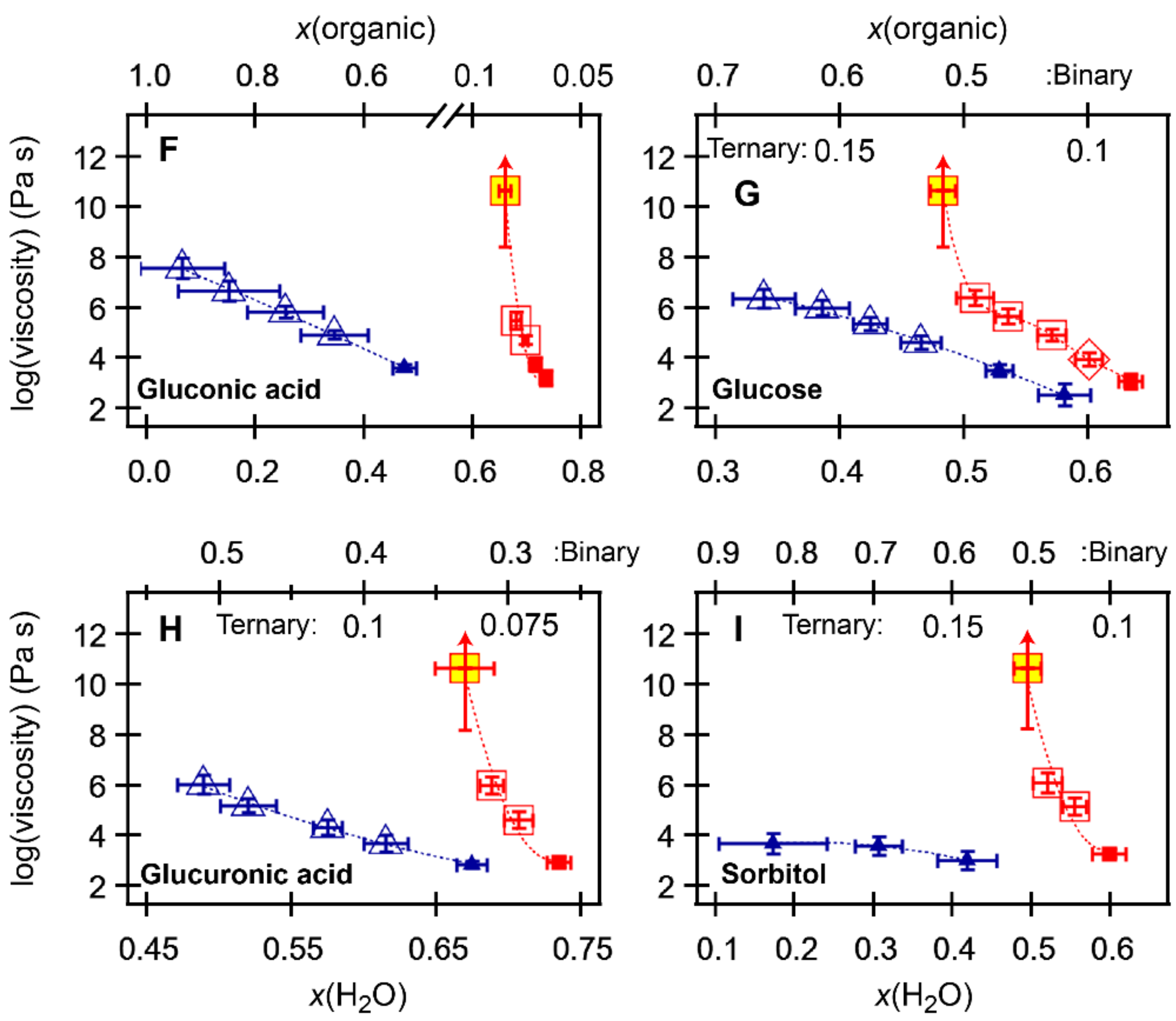
Ternary $CaCl_2$-monosaccharide droplets



1:1 (by mole) $CaCl_2$:suga

Richards et al., 2020, *Science Advances*

Ternary Ca^{2+} - organic droplets are more viscous than binary organic droplets

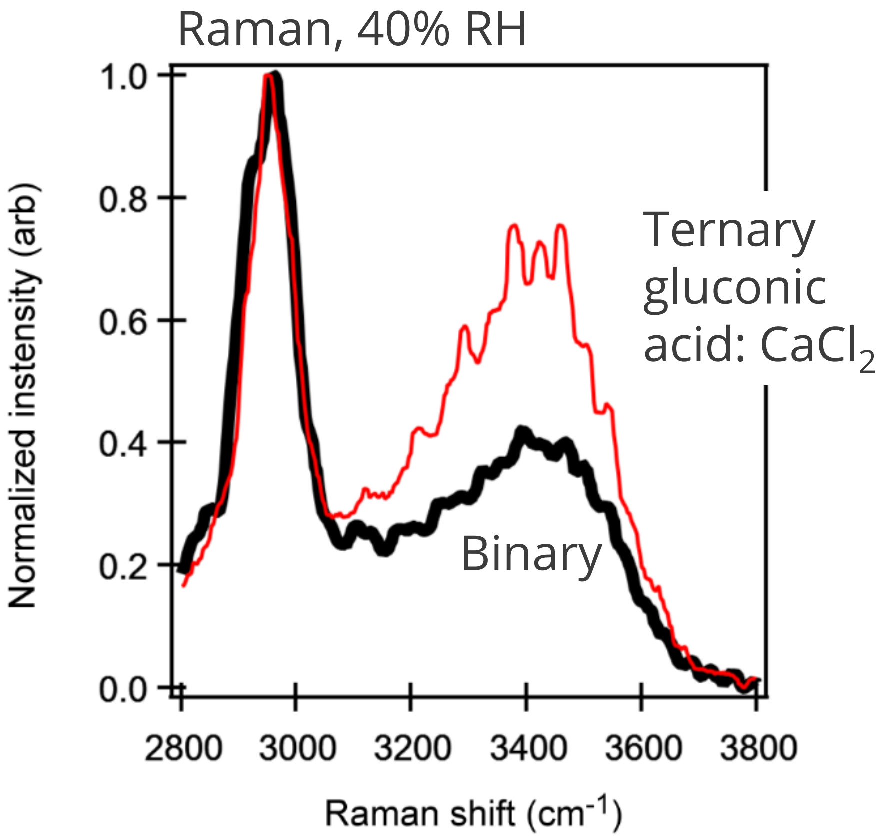


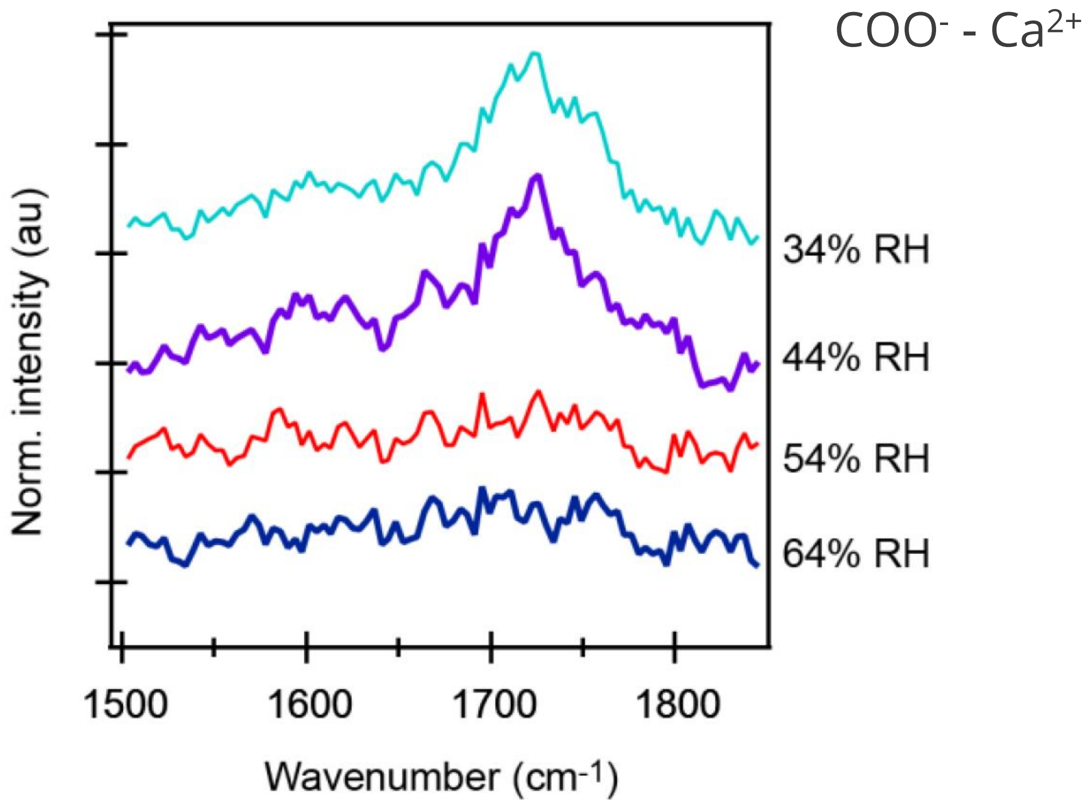
Data collection by David Richards

Ca^{2+}-organic phase behavior is not predicted by simple mixing approximations

Richards et al. (2020) *Sci. Adv.*

Ternary $CaCl_2$-organic droplets transition to rigid micro-structures



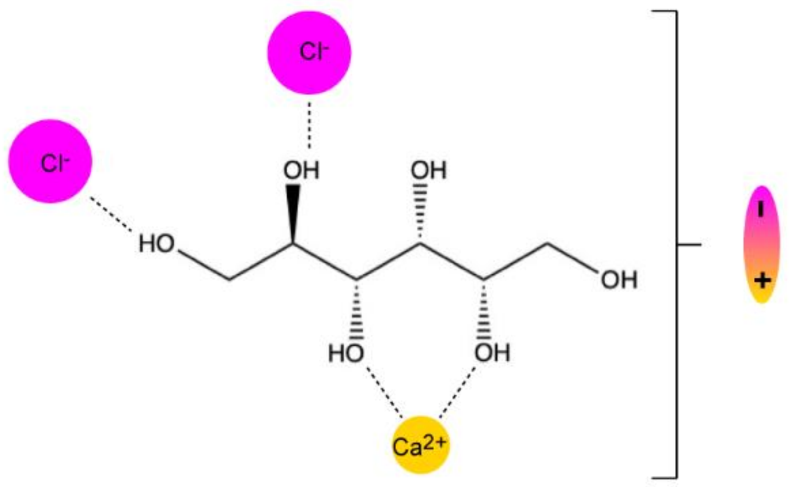


More water, more rigid, and evidence for ion pairing → **long range networks?**

Richards et al. (2020) *Sci. Adv.*

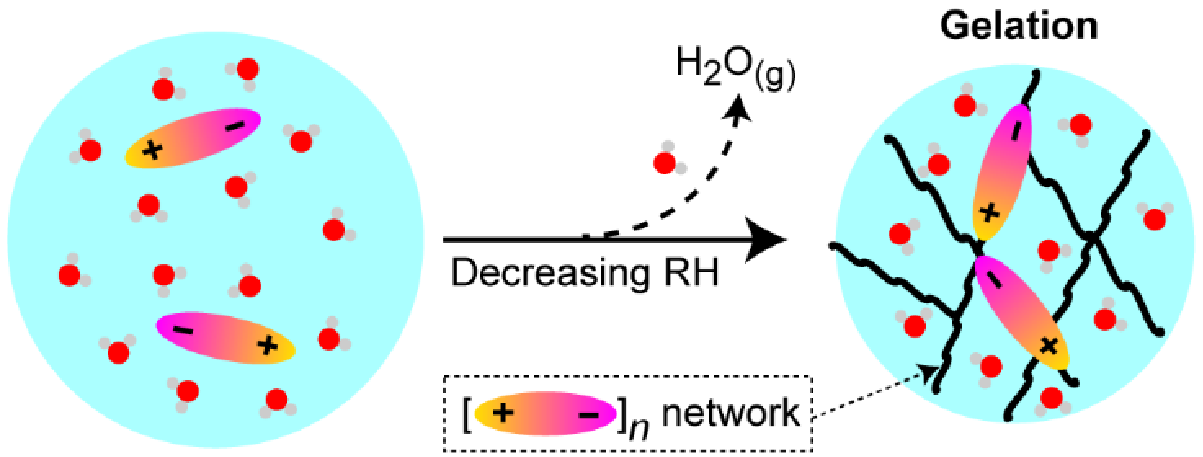
Cooperative ion-solute interactions facilitate gelation of low-mass molecules in concentrated droplets

Ion-organic complex



Symons et al, 1982, *J. Chem. Soc. Faraday Trans.*

Long-range assembly with decreasing RH via ion-paired networks

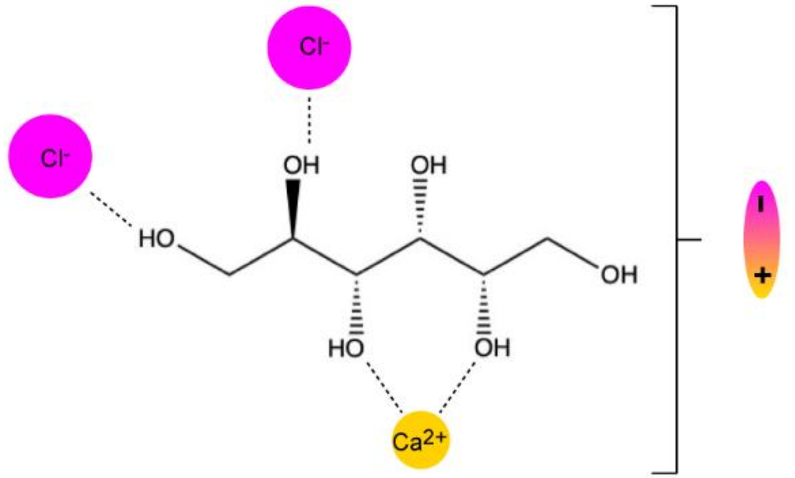


Analogous to mechanism of $MgSO_4$ gelation

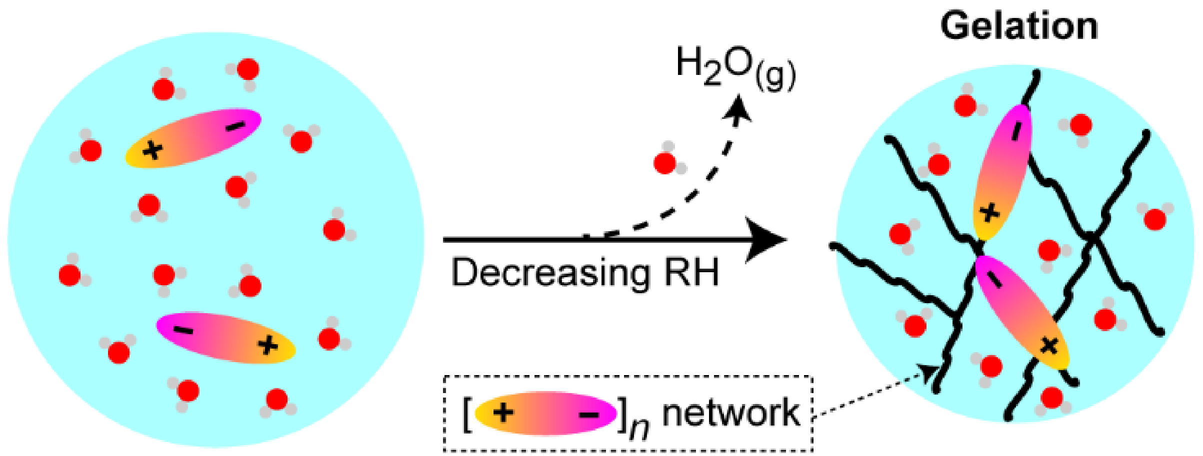
Richards et al. (2020) *Sci. Adv.*

Cooperative ion-solute interactions facilitate gelation of low-mass molecules in concentrated droplets

Ion-organic complex



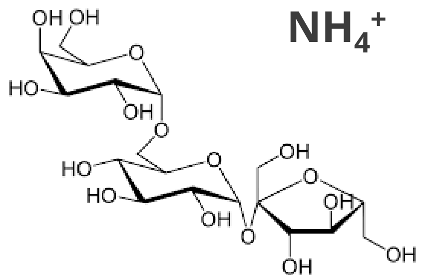
Long-range assembly with decreasing RH via ion-paired networks



- Provides a pathway for assembly of molecules that do not form networks in bulk
- Not predicted from simple mixing rules of individual components
- Diffusion expected to be hindered

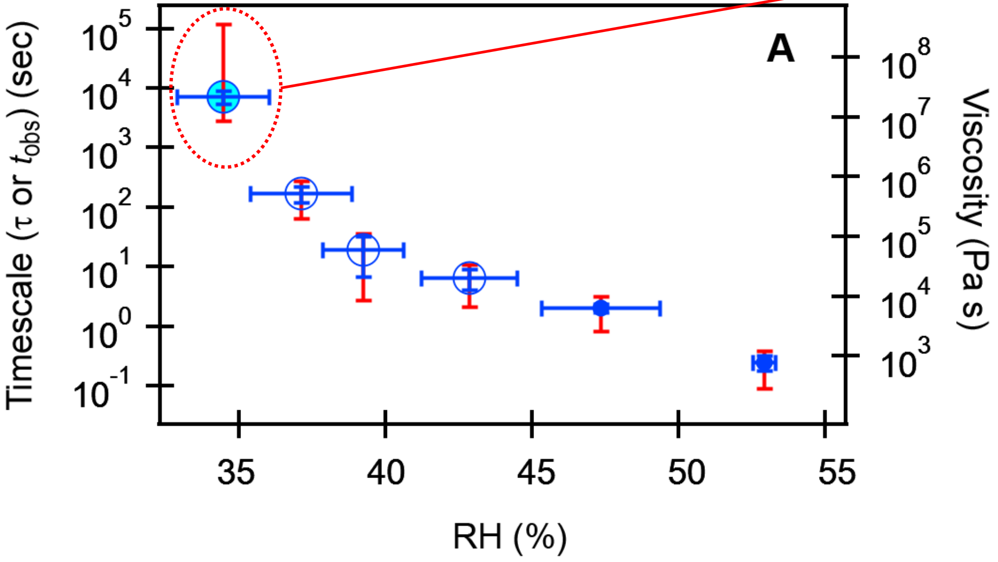
Richards et al. (2020) *Sci. Adv.*

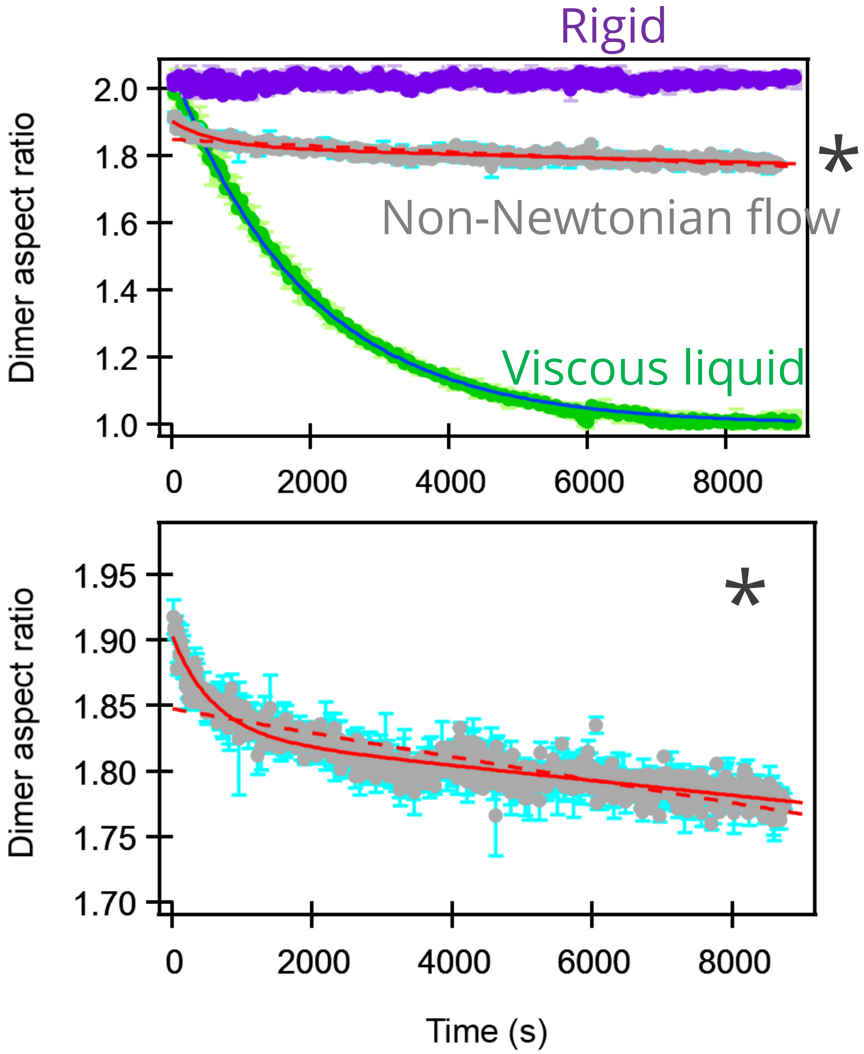
Ammonium sulfate-raffinose mixtures exhibit complex phase behavior at low RH



NH_4^+ SO_4^{2-} NH_4^+

1:1 (by wt.) AS:raffinose
No efflorescence





Erik Huynh

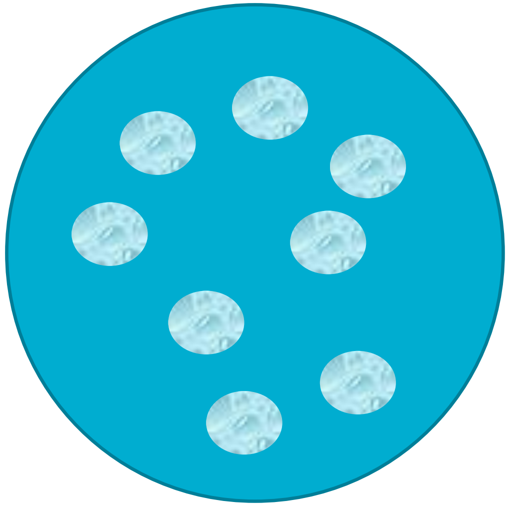
Ushijima (CU-B), Huynh (TU) et al., (2021) *JPCA.*

Non-Newtonian flow indicates inhomogeneities

For example, a slurry exhibits non-Newtonian flow

Possibilities:

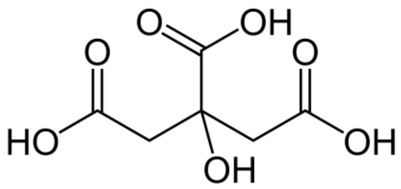
Clusters or aggregates?



Discontinuous network

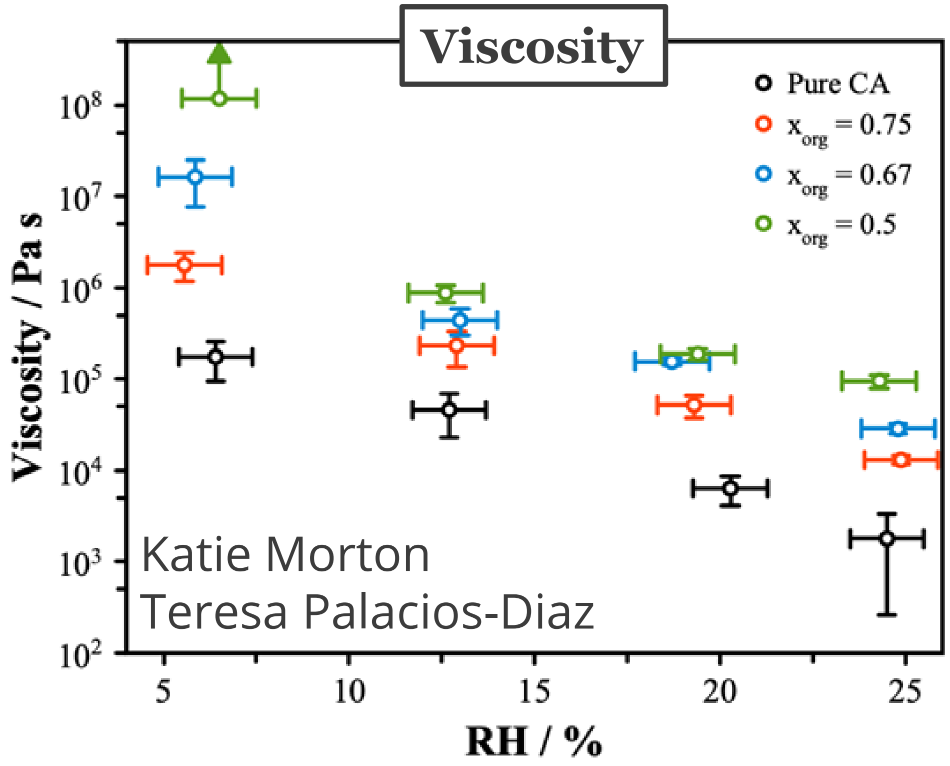
Ammonium sulfate- citric acid mixtures also show deviations from behavior expected based on bulk predictions

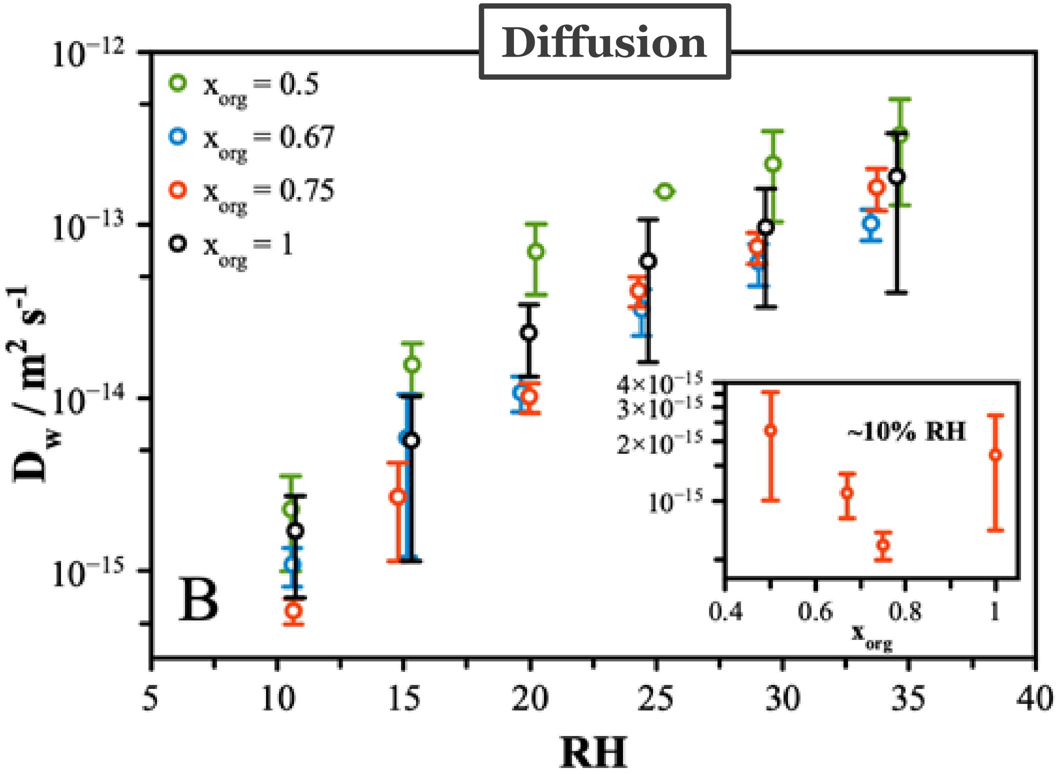
Citric acid: a common proxy for oxidized atmospheric aerosol



NH_4^+ SO_4^{2-} NH_4^+

Addition of ammonium sulfate increases viscosity and hinders water diffusion in citric acid mixtures





Sheldon et al. (2023) *Env. Sci. Atmos.*

Data: Craig Sheldon (UC-Riverside)

Ion pairing at low RH may be responsible for deviations from bulk expectations

- The **Stokes-Einstein relationship** is commonly used to predict **diffusion** rates based on **viscosity**:

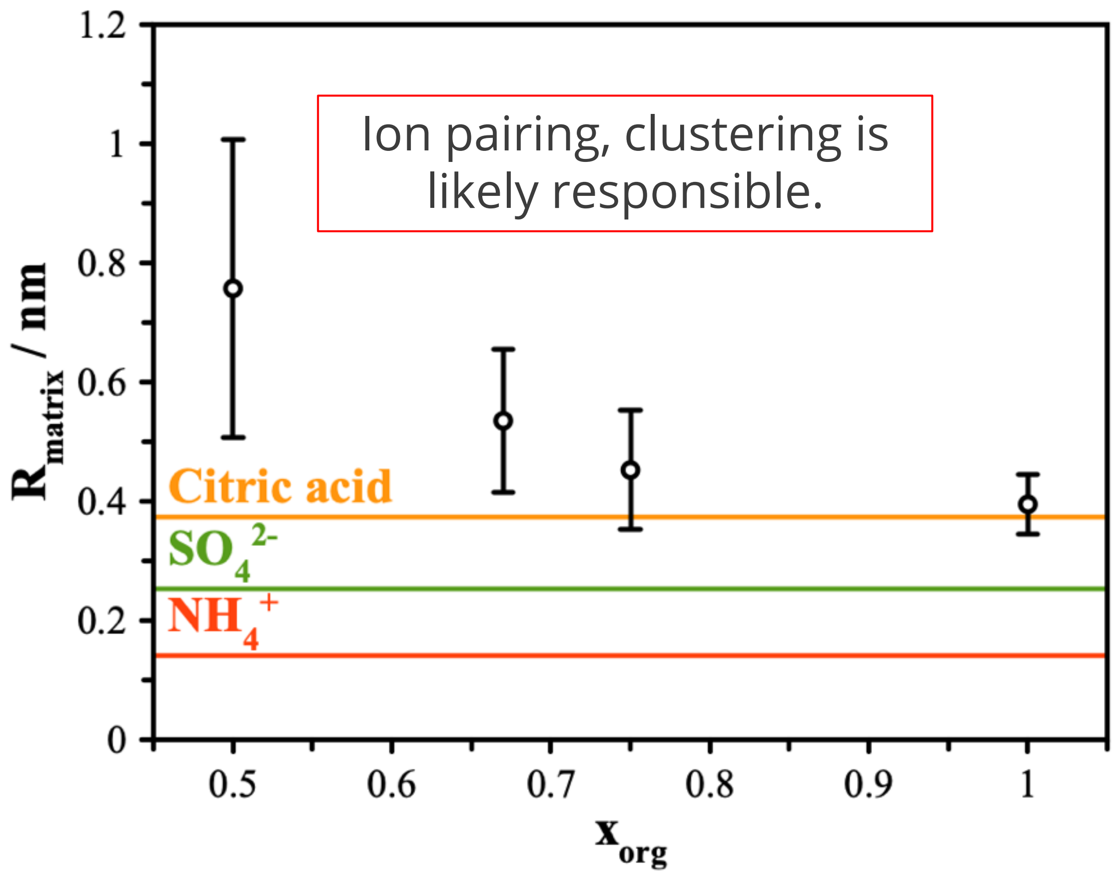
$$D = \frac{kT}{6\pi\eta R_{\mathrm{diff}}}$$

- The **fractional Stokes-Einstein** relationship is better suited for this system:

$$\frac{D}{D_0} = \left(\frac{\eta_0}{\eta}\right)^{\xi}$$

- The exponent related to the **size of the diffusing molecule** and the **<u>size of molecules in the matrix</u>** ($\xi = 1$ indicates purely S-E behavior) :

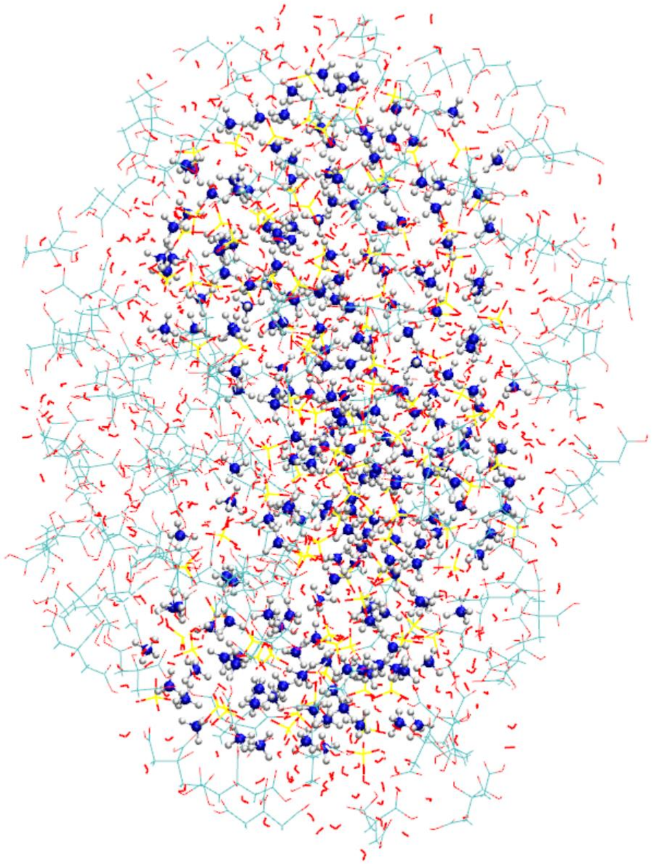
$$\xi = 1 - A.e^{-B\times\frac{R_{\mathrm{diff}}}{R_{\mathrm{matrix}}}}$$

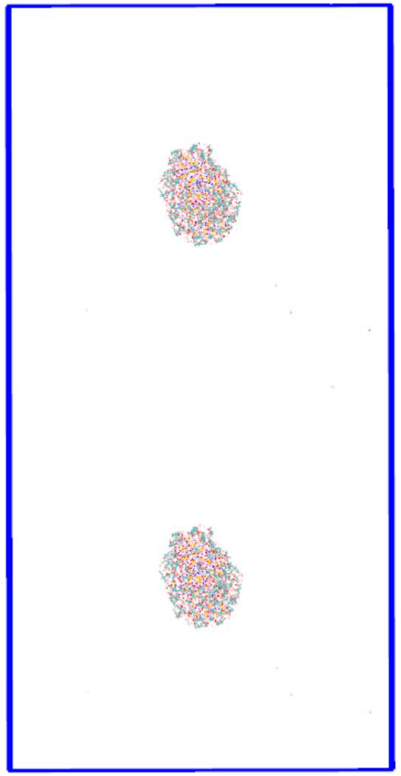


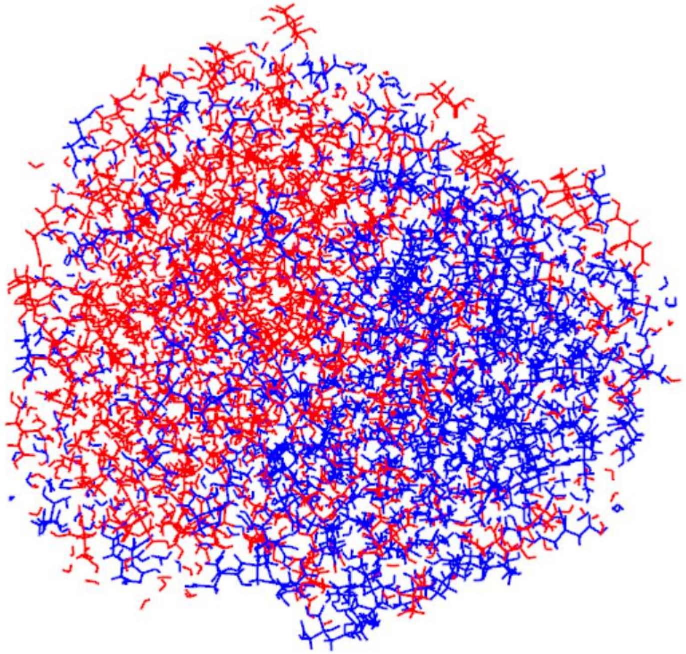
Sheldon et al. (2023) *Env. Sci. Atmos.*

Slide courtesy of Prof. James Davies, UCR

Molecular dynamics simulations suggest a (generally) well mixed solution at intermediate RH that has fluid properties



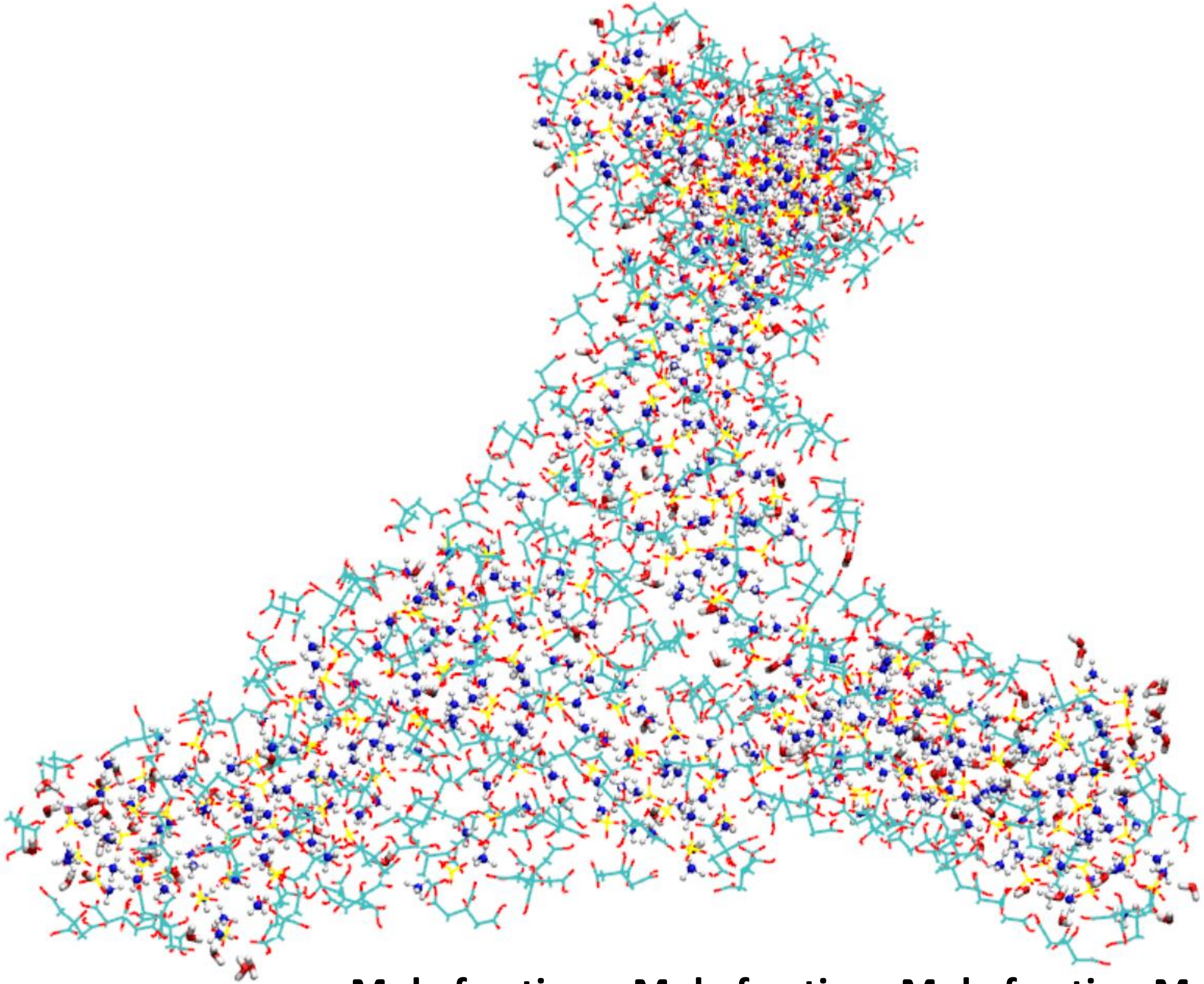


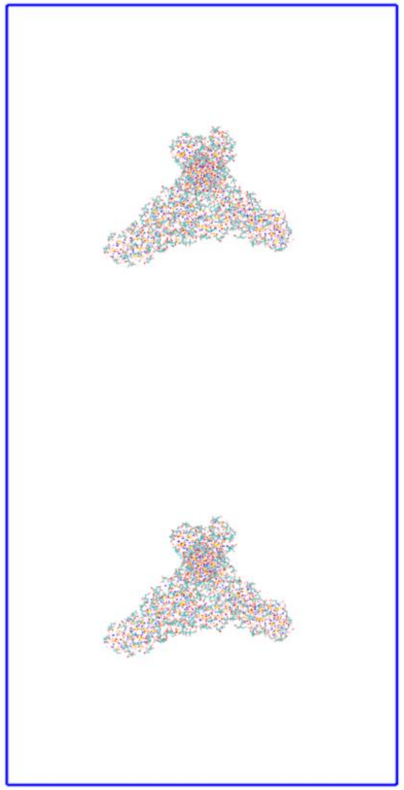


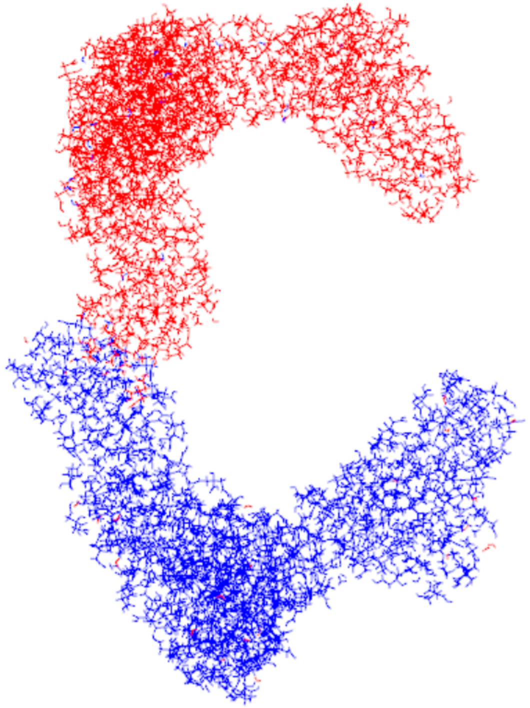
RH (%)	Mole fraction of water	Mole fraction of citric acid	Mole fraction of NH4+	Mole fraction of sulfate
51	538	115	224	112

Simulations by Yi He, UNM

At low RH, MD simulations show clustering and a viscous state



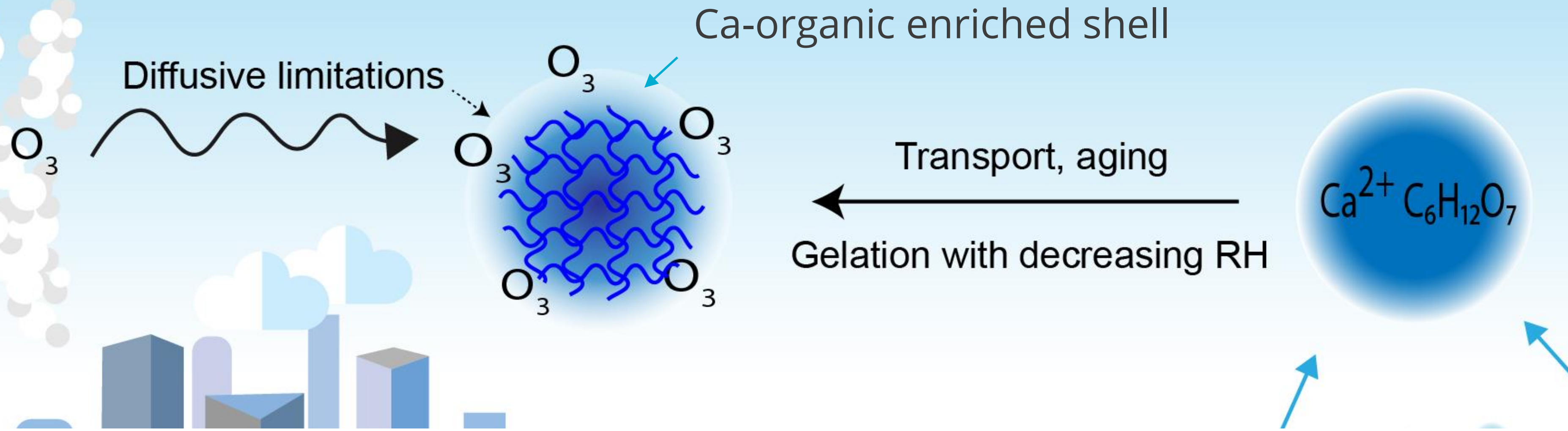




RH (%)	Mole fraction of water	Mole fraction of citric acid	Mole fraction of NH4+	Mole fraction of sulfate
9	130	218	408	204

Simulations by Yi He, UNM

Supramolecular interactions are likely influencing the phase and viscosity of atmospheric aerosol



- Low water content in aerosol facilitates solute-solute interactions
- Ion-molecule clustering can lead to hindered diffusion in aerosol
- Long-range networks can develop from such interactions
- Micro-rheology combined with computational tools can elucidate molecular-level details

Thank you for your time

Davis Research Group (2021)

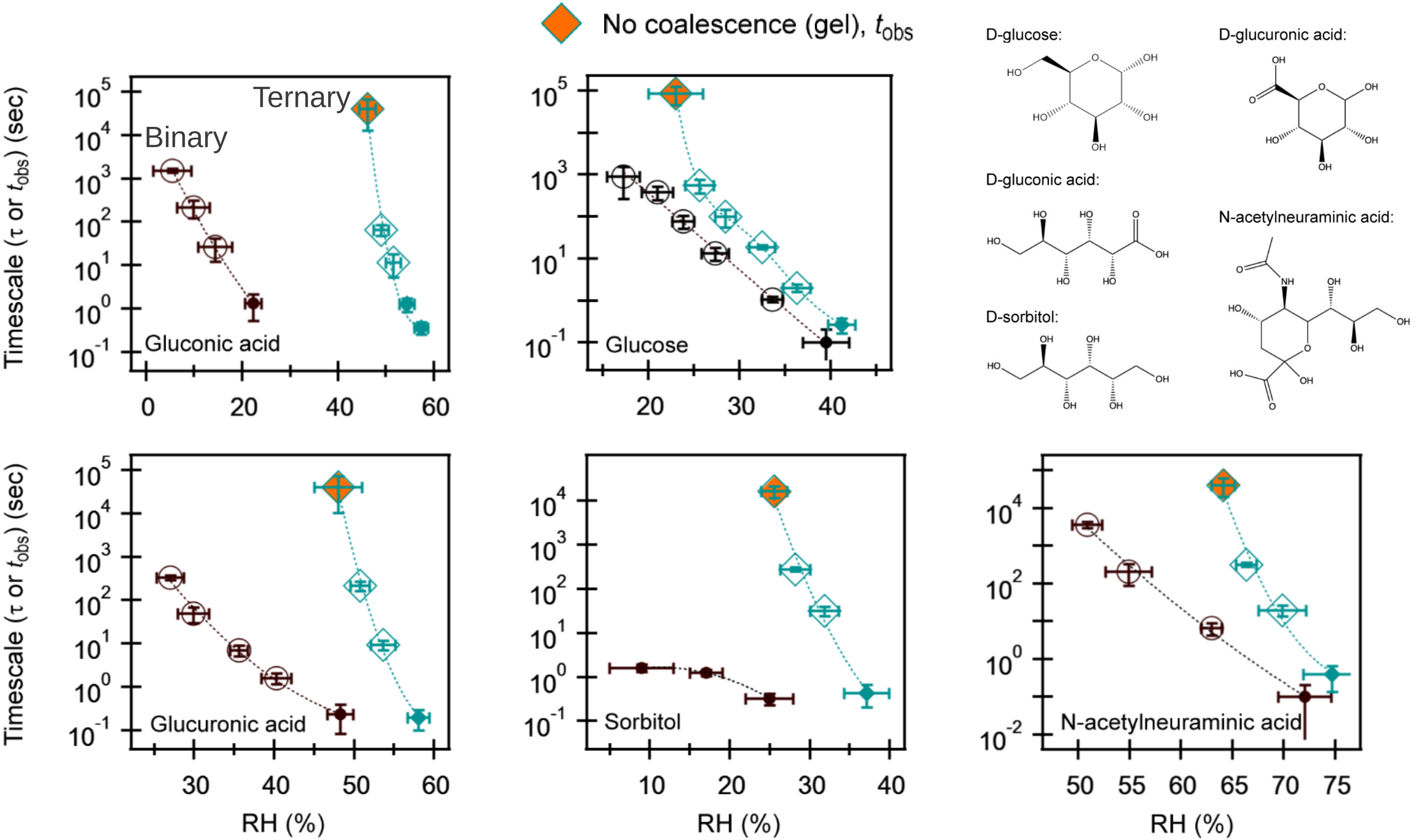
Senior collaborators:
James Davies, UC-Riverside
Yi He, U. New Mexico

Grad students:
Ravleen Kaur Kohli, UC-Riverside
Jack Choczynski, UC-Riverside
Craig Sheldon, UC-Riverside
Chelsea Price, UC-Riverside

rddavis@sandia.gov

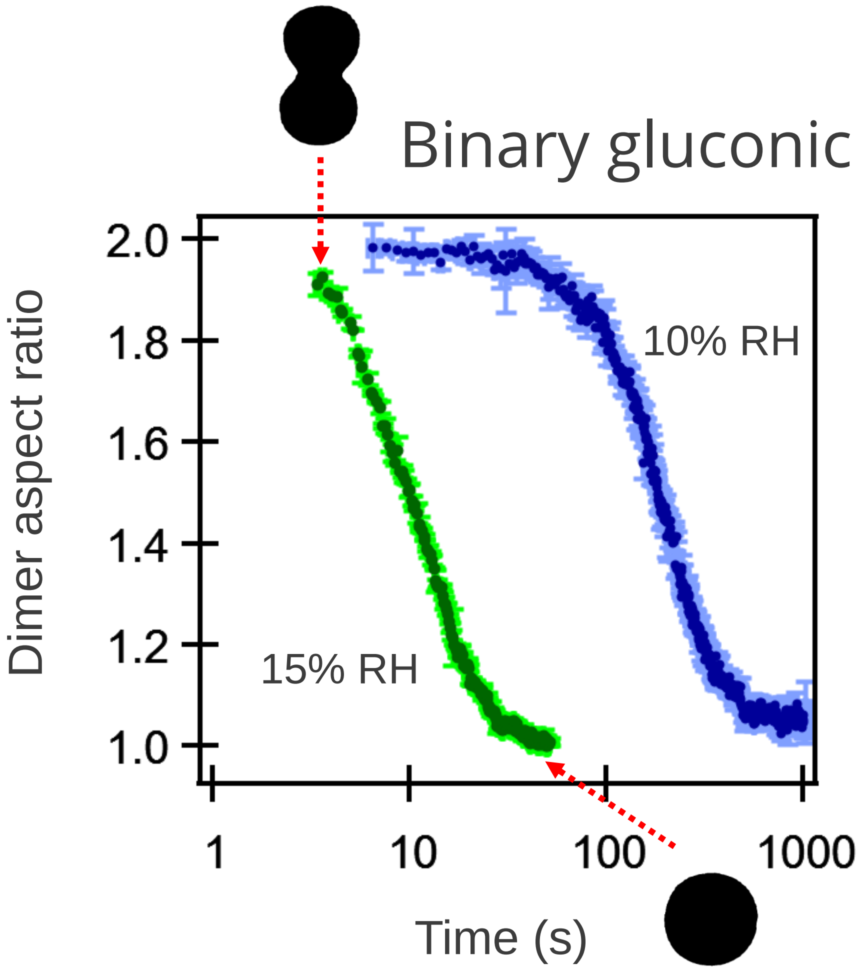
Back up slides

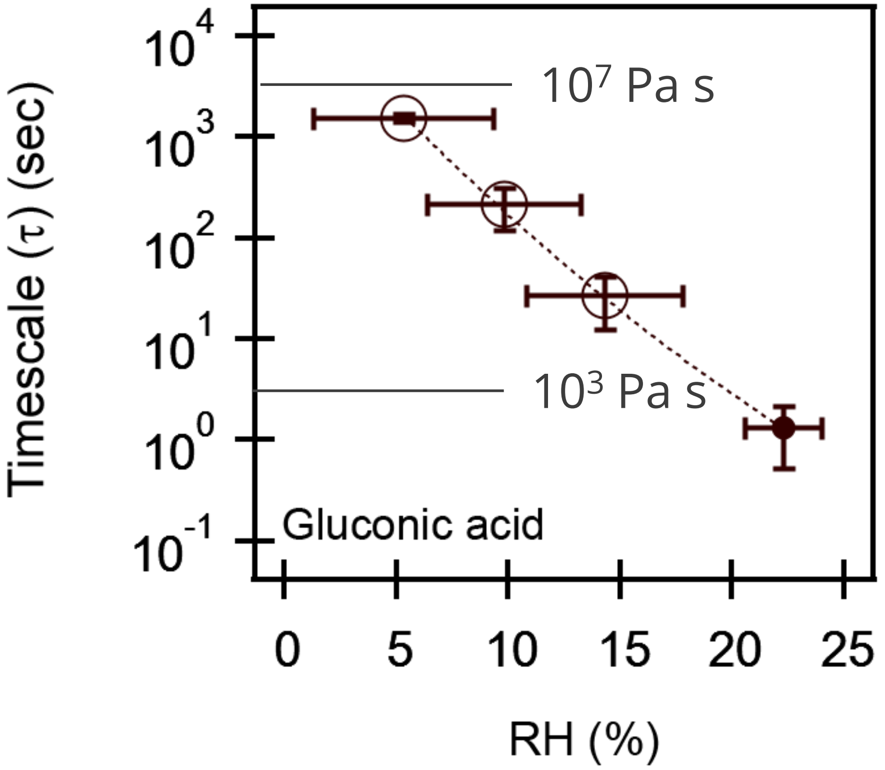
All $CaCl_2$-organic mixtures exhibited a gel transition



Richards et al. (2020) *Sci. Adv.*

Binary organic droplets gradually increase in coalescence timescale (and viscosity) with decreasing RH

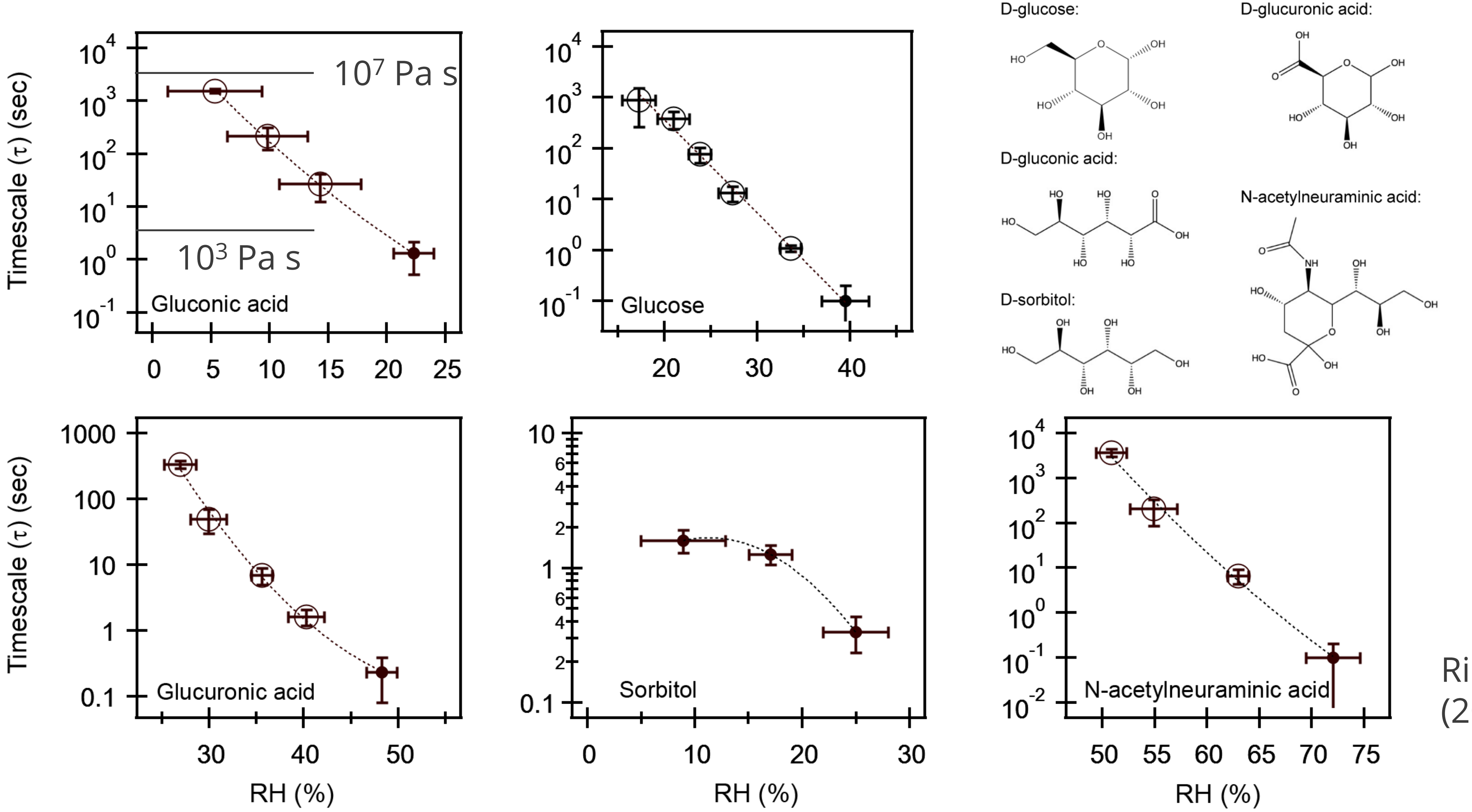




Data collection by David Richards

Richards et al., 2020, *Science Advances*

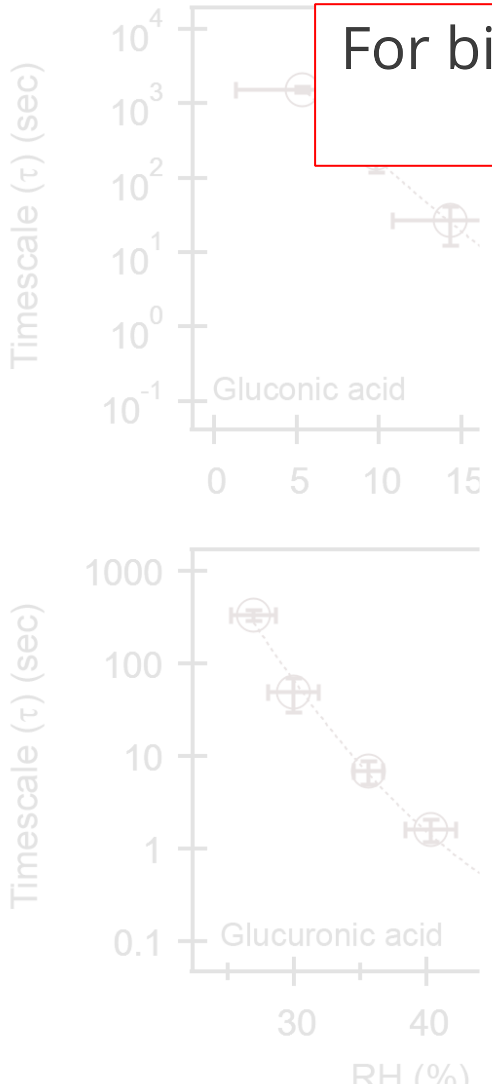
Binary organic droplets gradually increase in coalescence time (and viscosity) with decreasing RH

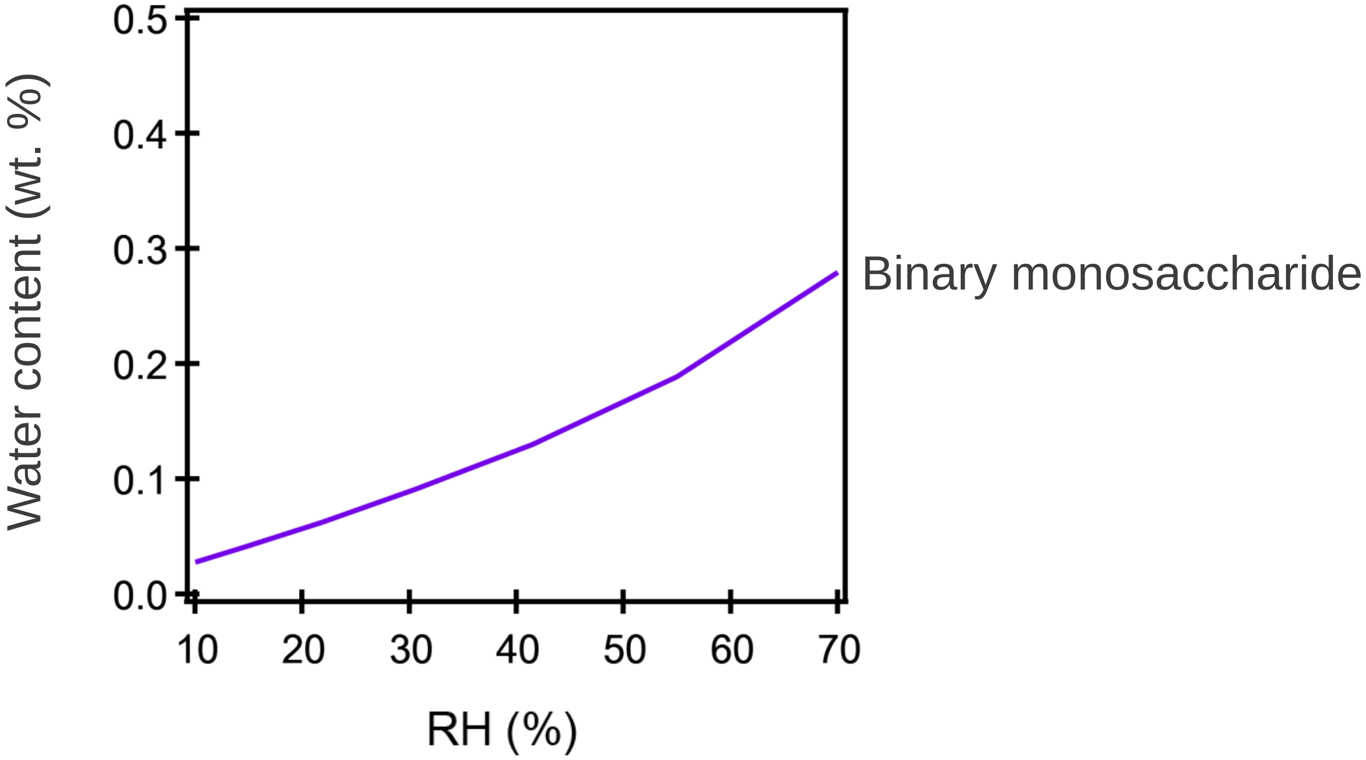


Richards et al. (2020) *Sci. Adv.*

Binary organic droplets gradually increase in coalescence time (and viscosity) with decreasing RH

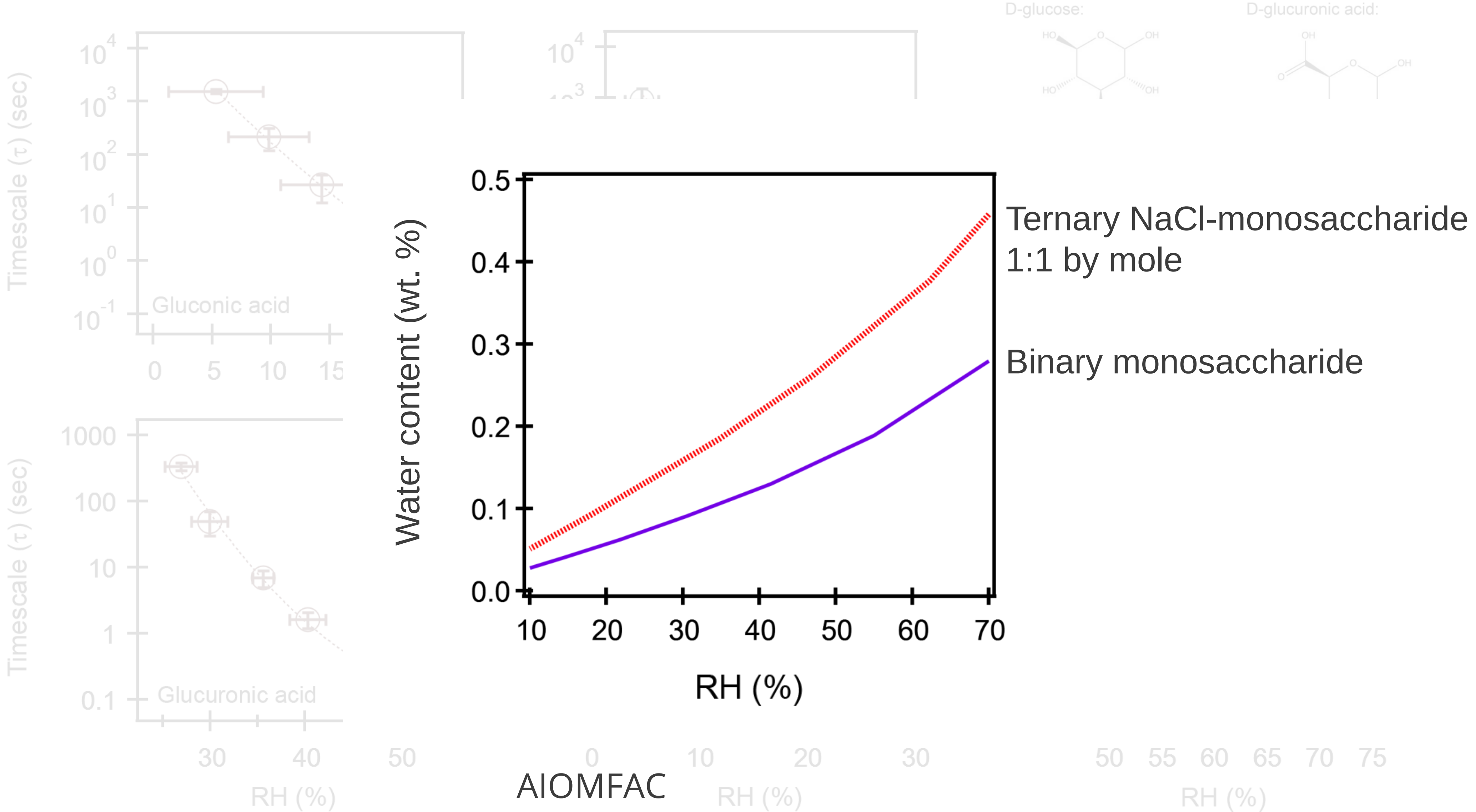
For binary mixtures: As water content decreases, coalescence time (viscosity) increases





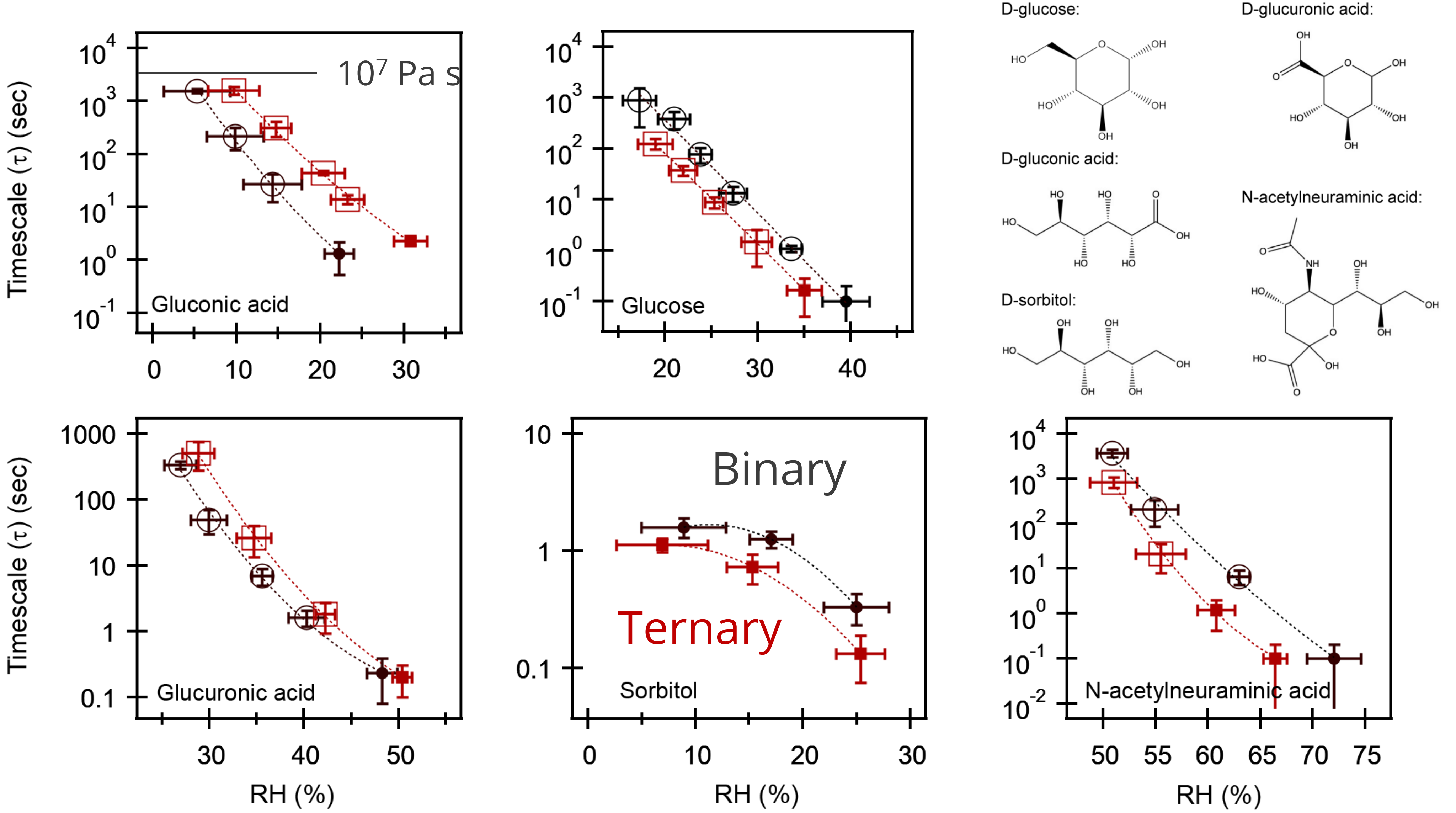
AIOMFAC

Binary organic droplets gradually increase in coalescence time (and viscosity) with decreasing RH



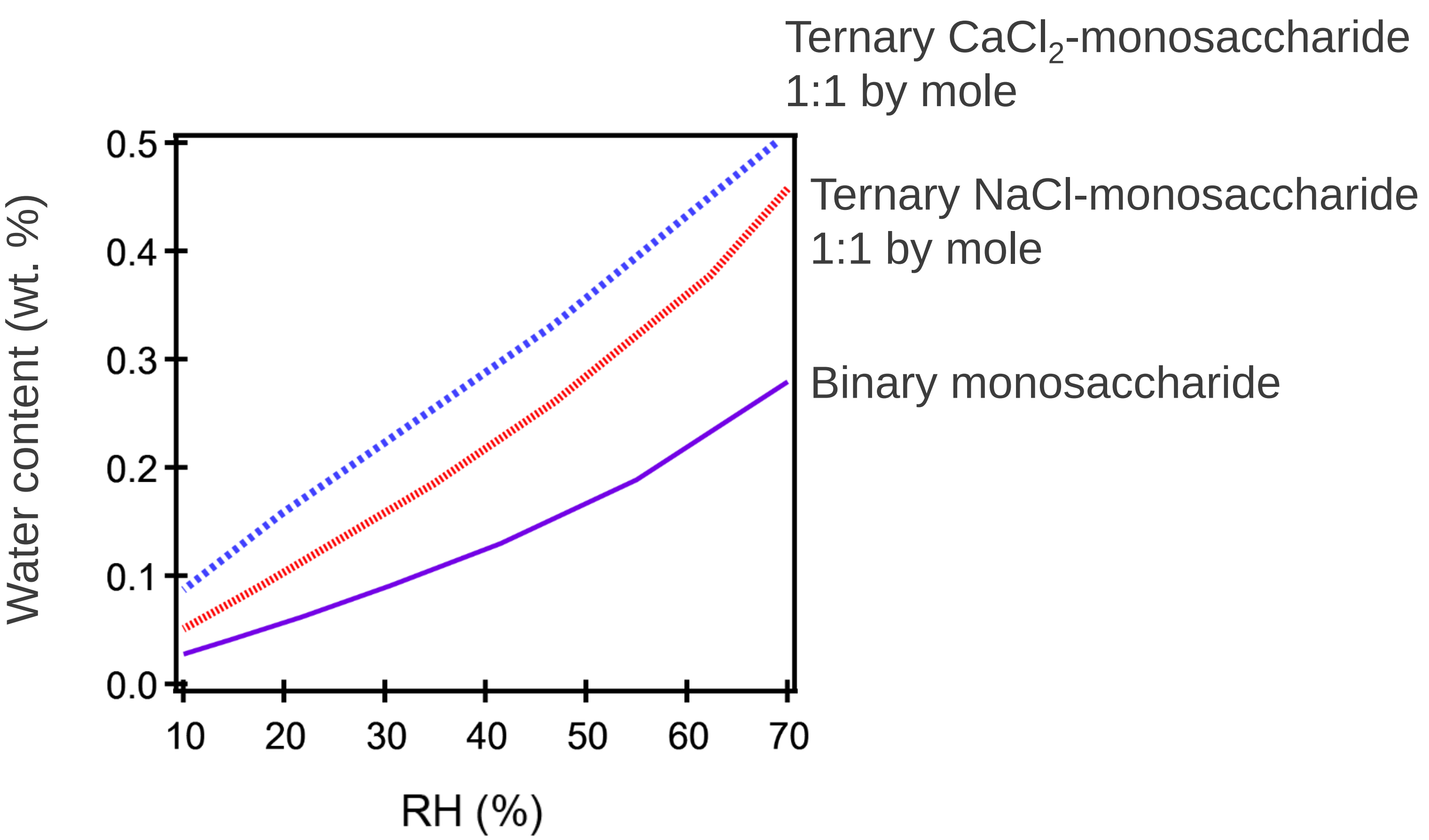
AIOMFAC

Ternary NaCl-organic droplets gradually increase in viscosity with decreasing RH



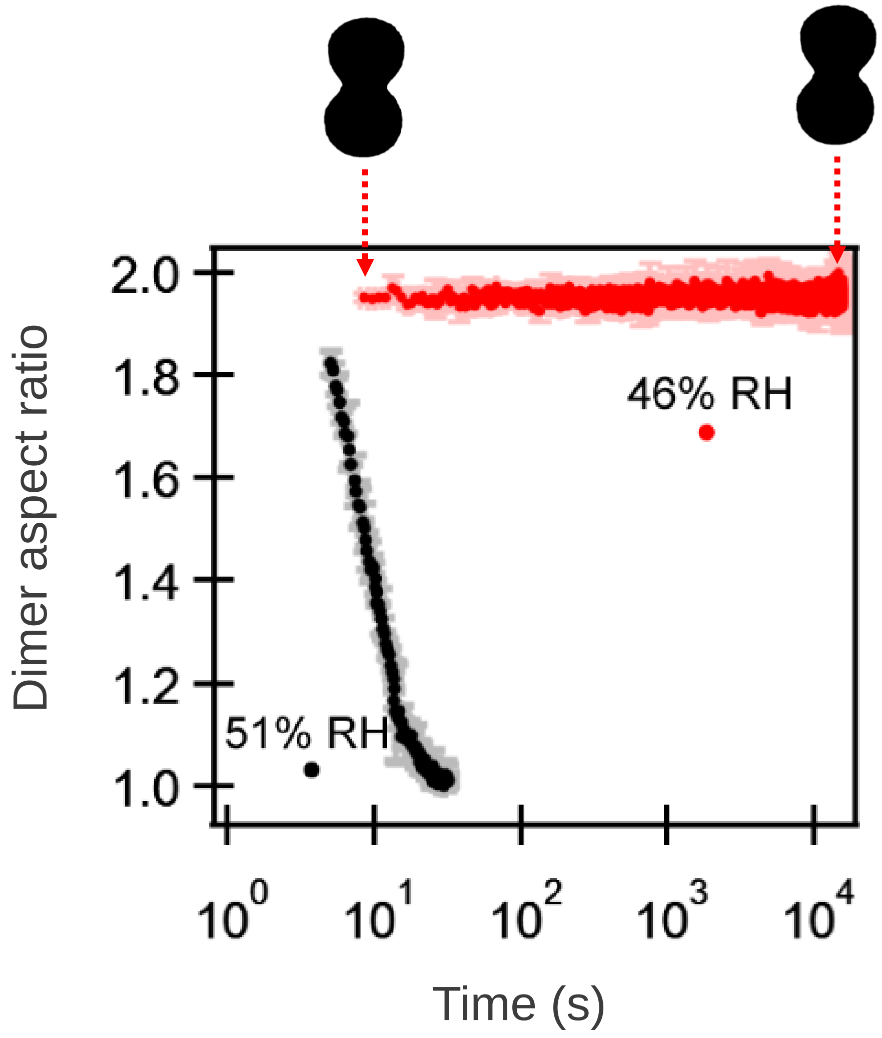
Richards et al. (2020) *Sci. Adv.*

Ternary NaCl-organic droplets gradually increase in coalescence timescale with decreasing RH

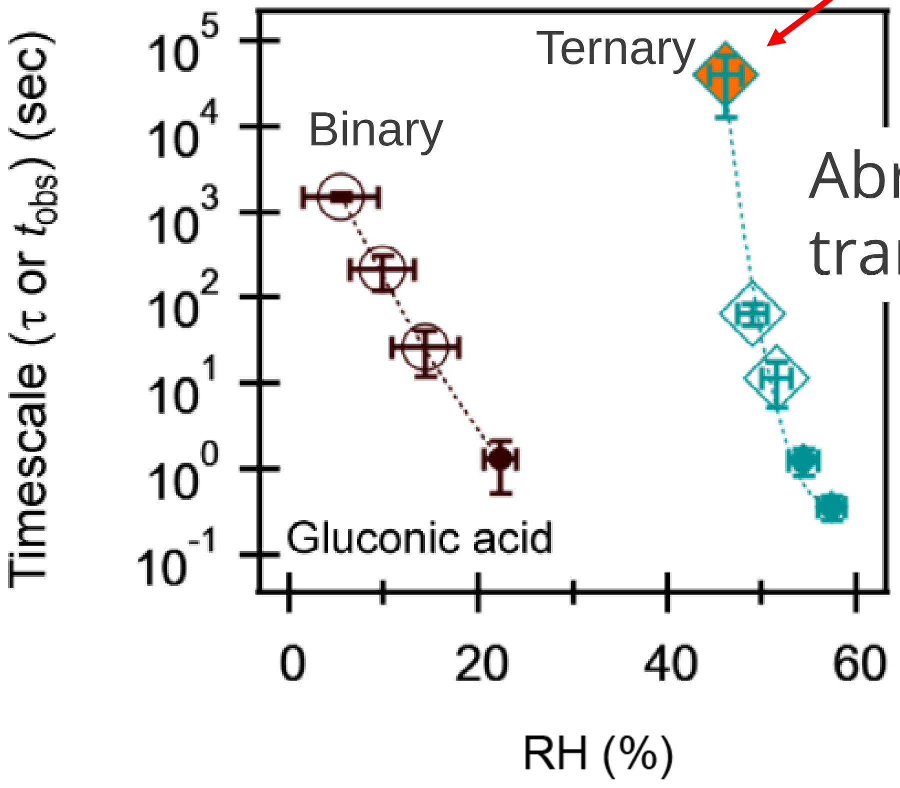


AIOMFAC

Ternary $CaCl_2$-organic droplets transition to rigid micro-structures



1:1 (by mole) $CaCl_2$: gluconic acid



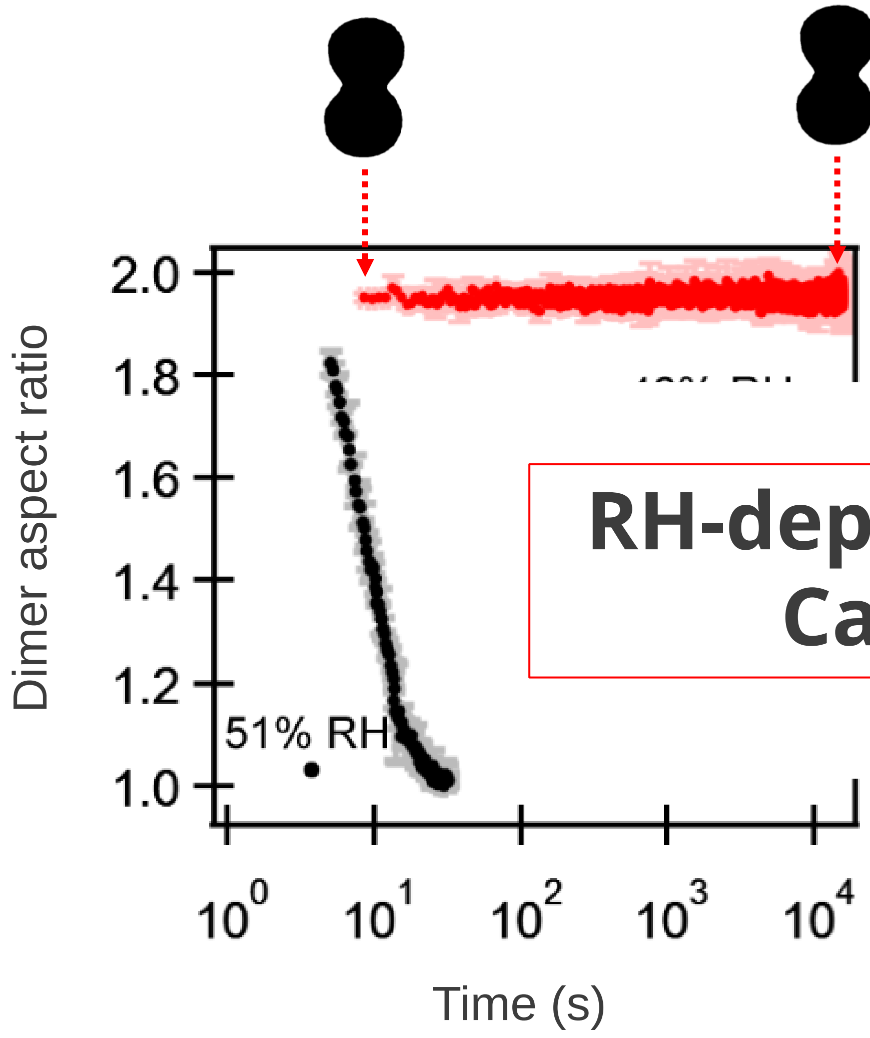
Rigid. No coalescence

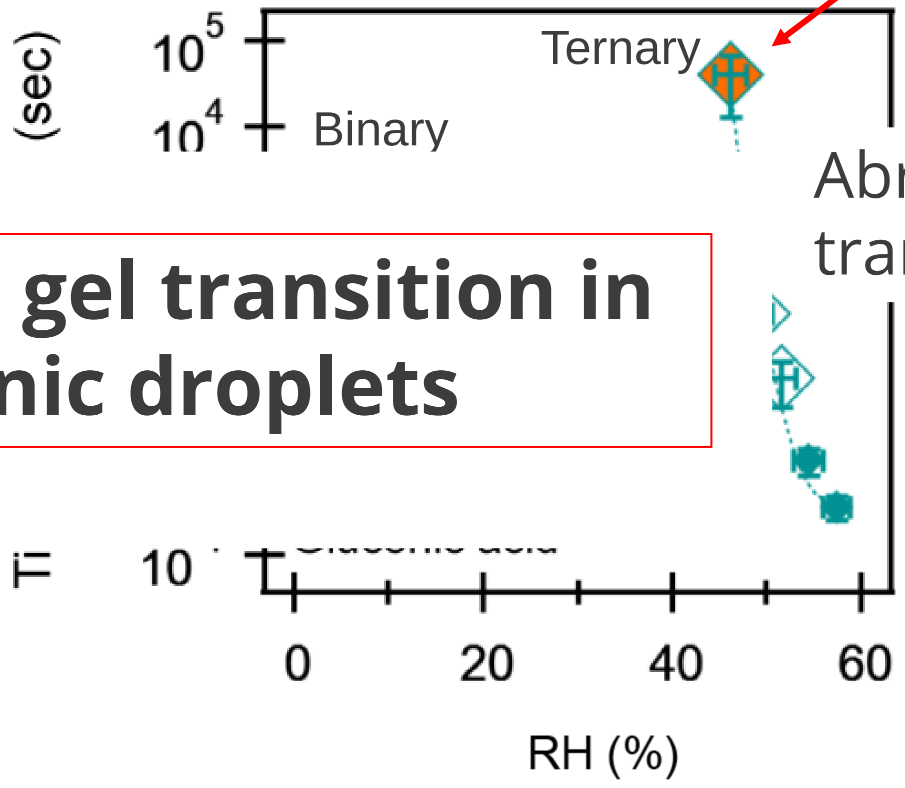
Abrupt transformation

Richards et al. (2020) *Science Advances*

Ternary $CaCl_2$-organic droplets transition to rigid micro-structures

1:1 (by mole) $CaCl_2$: gluconic acid





Rigid. No coalescence

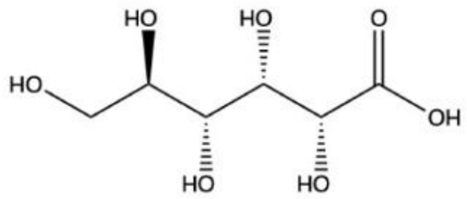
Abrupt transformation

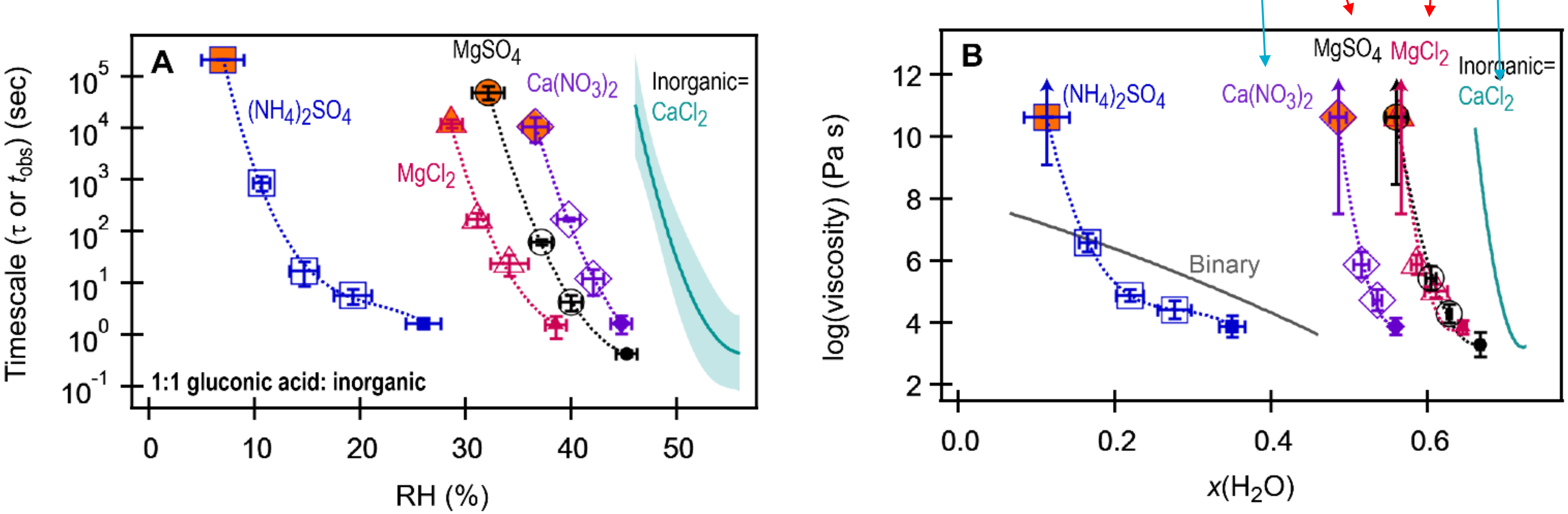
RH-dependent gel transition in Ca^{2+}-organic droplets

Richards et al. (2020) *Science Advances*

Gelation of gluconic acid was observed with a range of divalent ions (in ternary droplets)

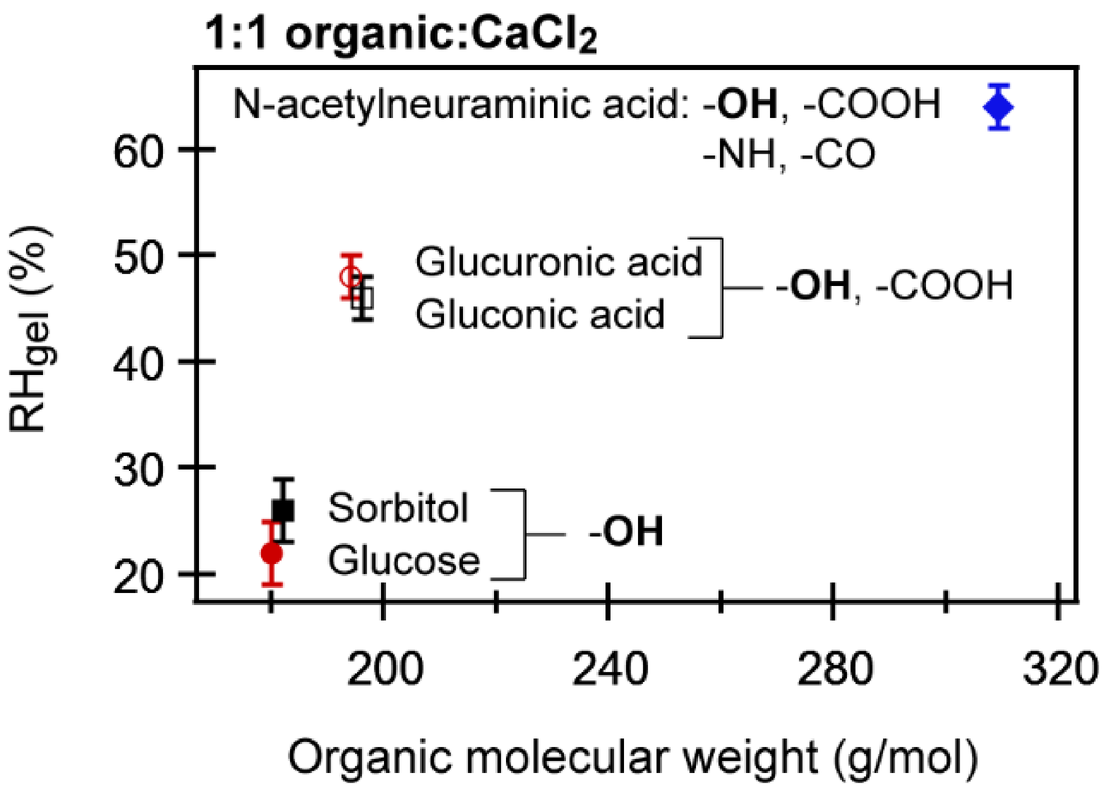
D-gluconic acid:

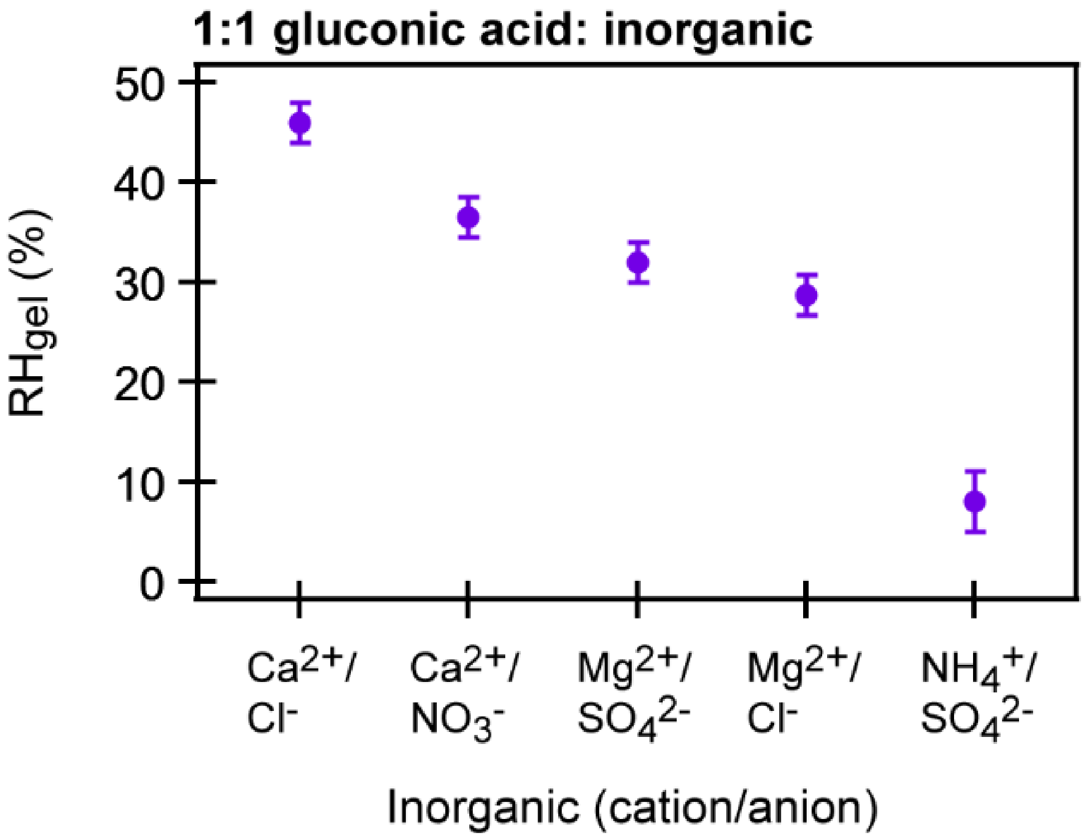




Richards et al. (2020) *Sci. Adv.*

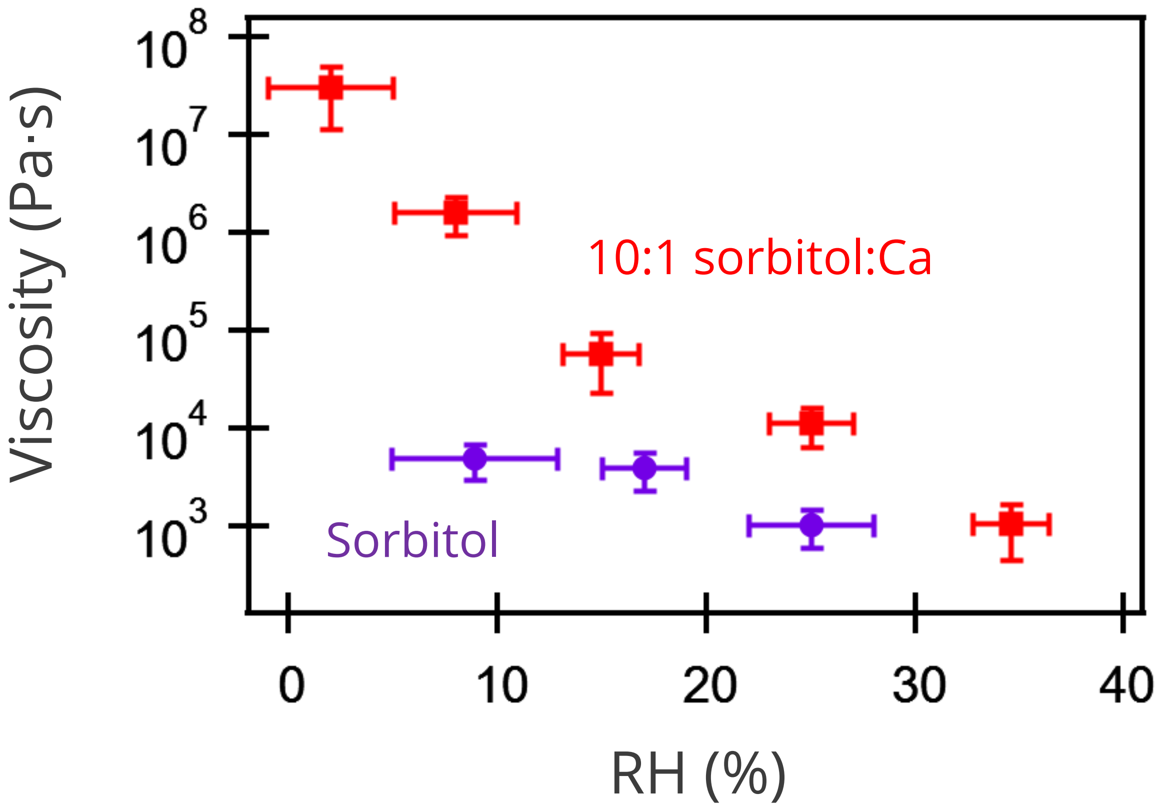
Gel formation is related to organic molecular functionality as well as ion speciation



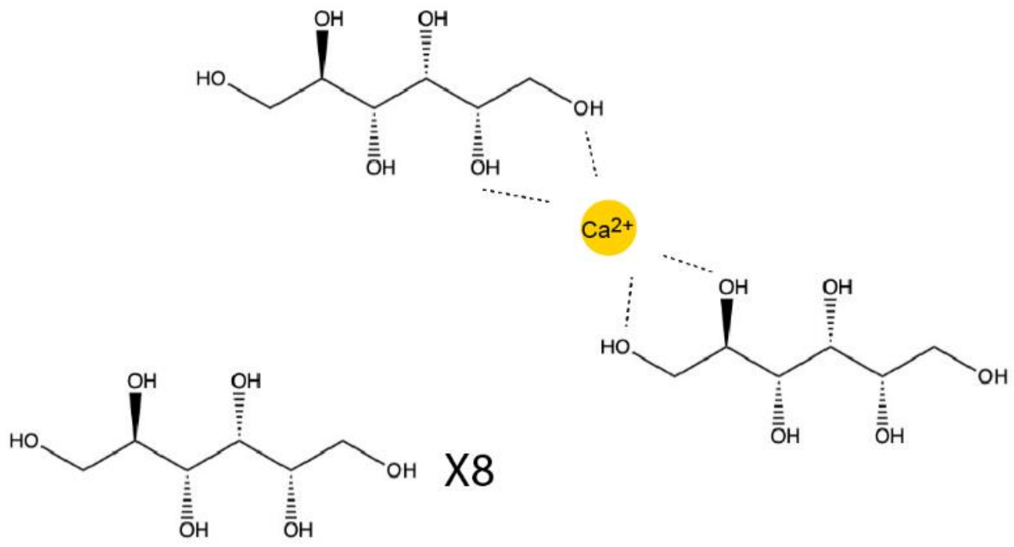


Richards et al. (2020) *Sci. Adv.*

Ca^{2+} induced thickening at 10:1 ratio of sorbitol:Ca^{2+}



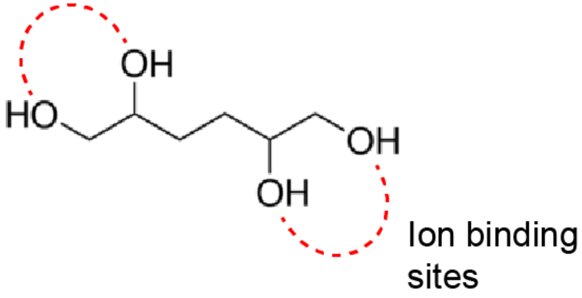
Short-range coupling increasing the effective MW

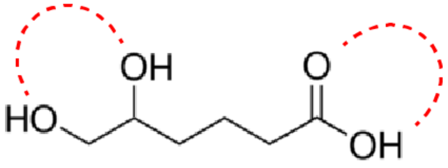


Richards et al. (2020) *Sci. Adv.*

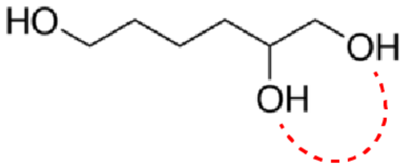
Two or more ion binding sites are likely necessary for long-range networks
One binding site may facilitate ion-induced thickening

Gelation potential

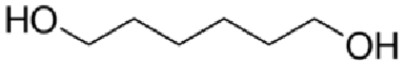




Increase in viscosity predicted



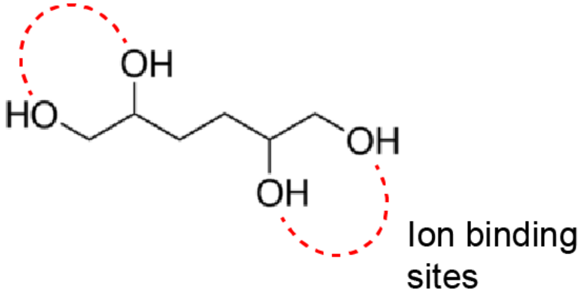
No significant ion influence predicted

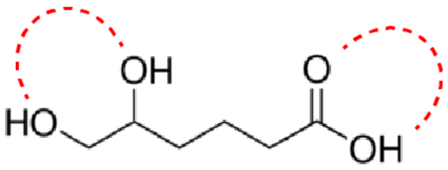


Richards et al., (2020) *Sci. Adv.*

Two or more ion binding sites are likely necessary for long-range networks
One binding site may facilitate ion-induced thickening

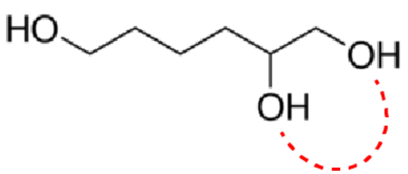
Gelation potential

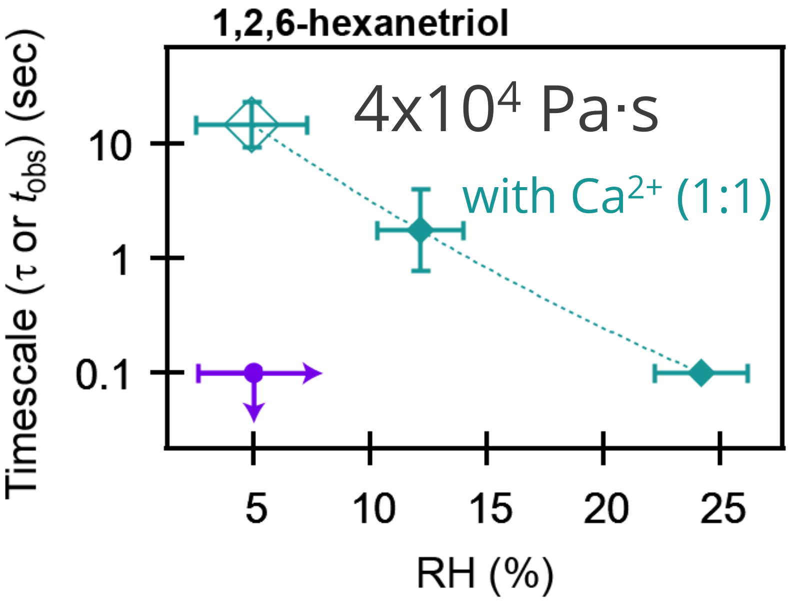




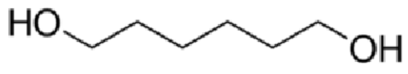
Richards et al., (2020) *Sci. Adv.*

Increase in viscosity predicted





No significant ion influence predicted

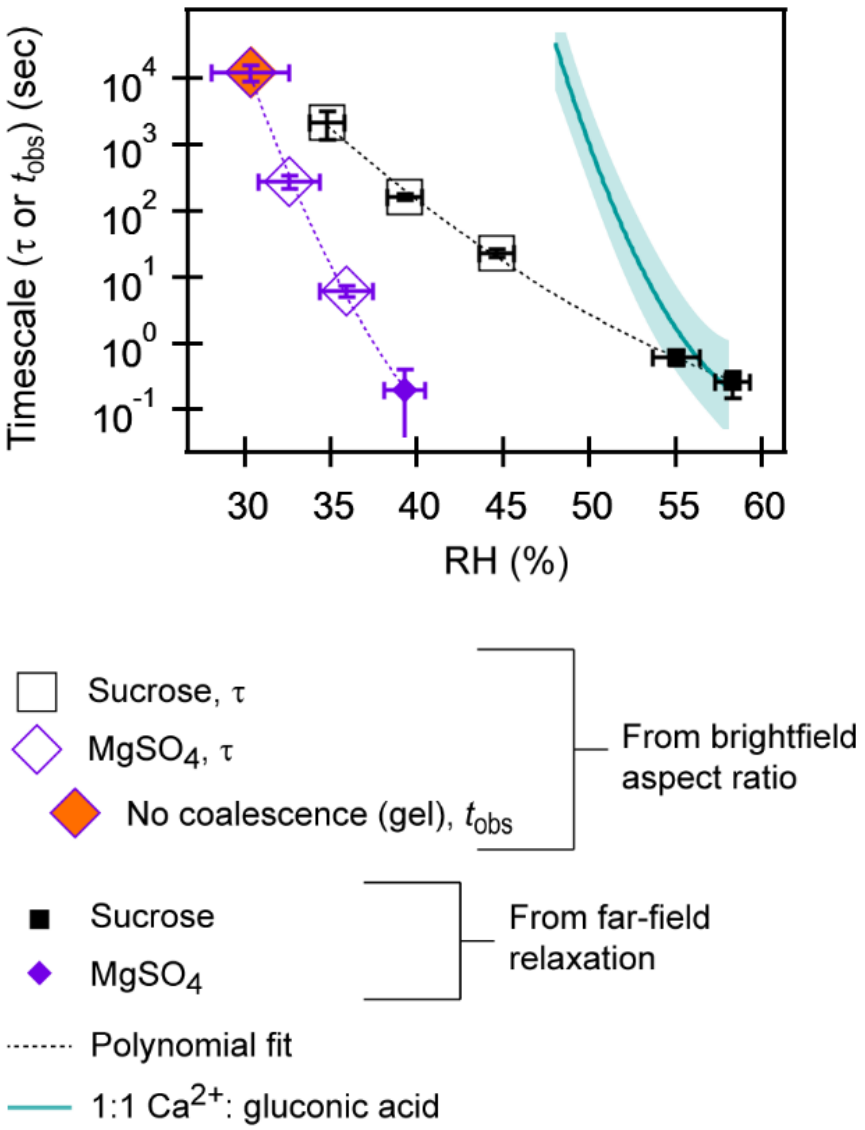


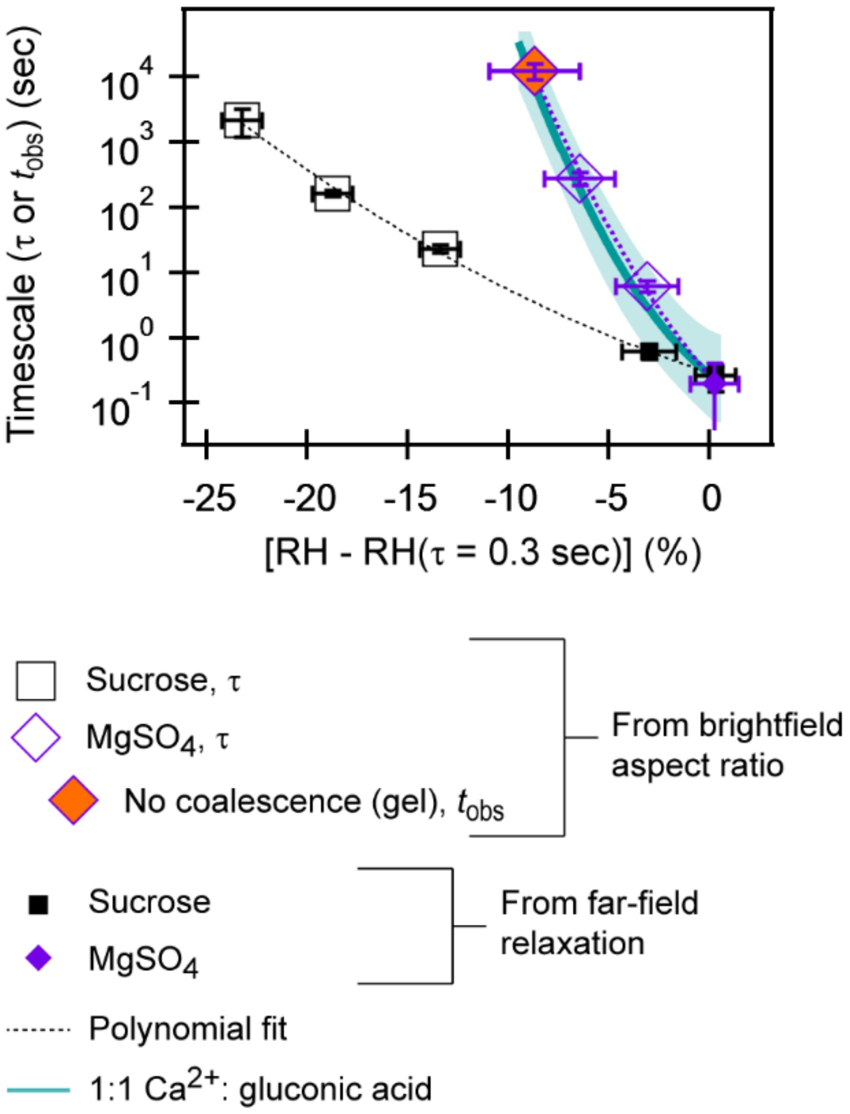
Ca^{2+} does increase the viscosity relative to 1,2,6-hexanetriol alone

Under arid conditions:
$4x10^4$ Pa·s with Ca^{2+},
2.6 Pa·s for pure hexanetriol*

*As reported by Sigma

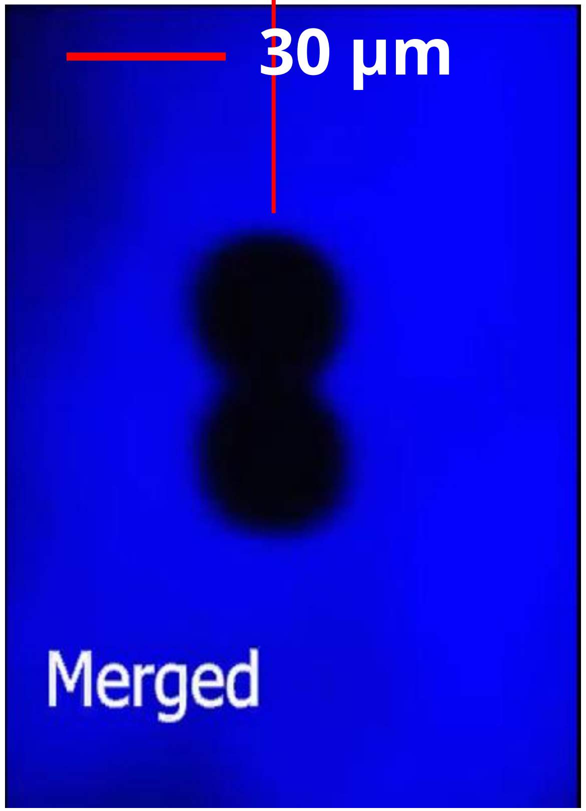
Rheological trends



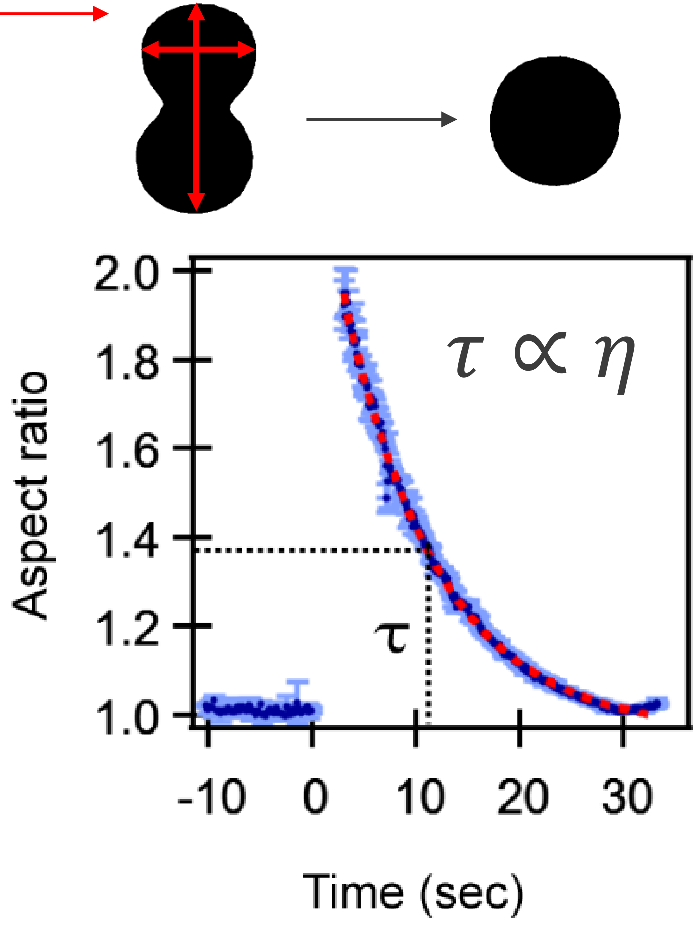


Optical microscopy was used to monitor merged dimer micro-rheology as a function of time

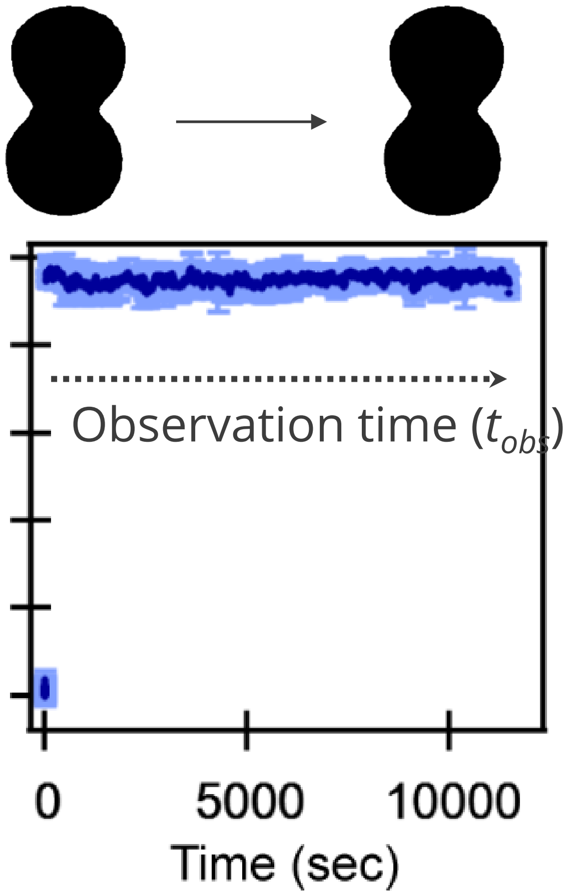
Binarization



Viscous fluids:



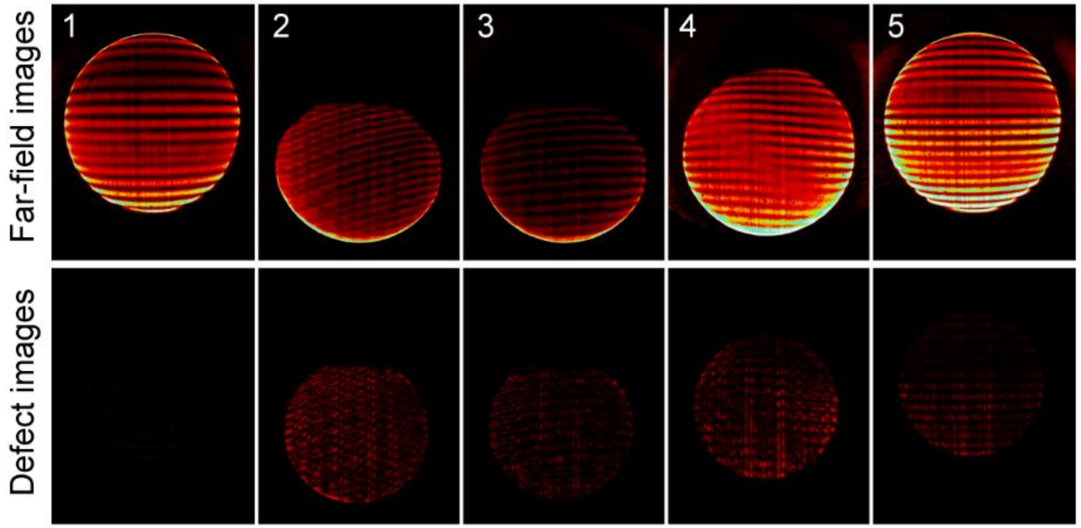
Microgel:

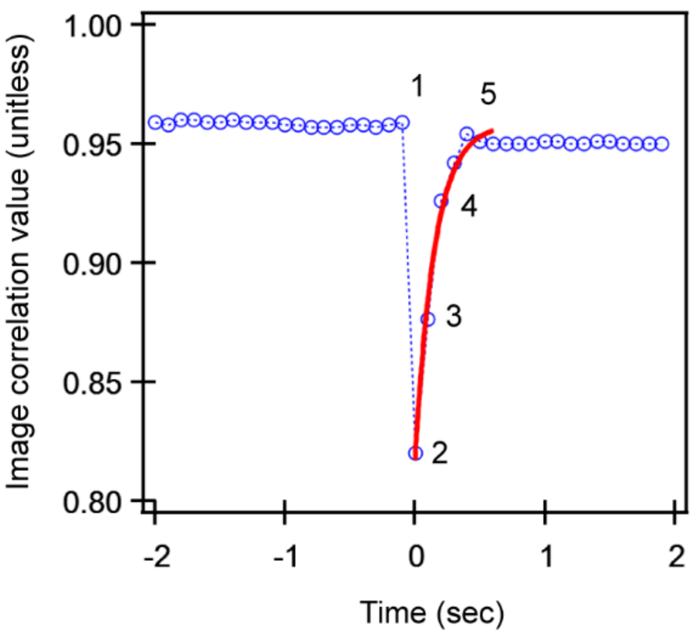


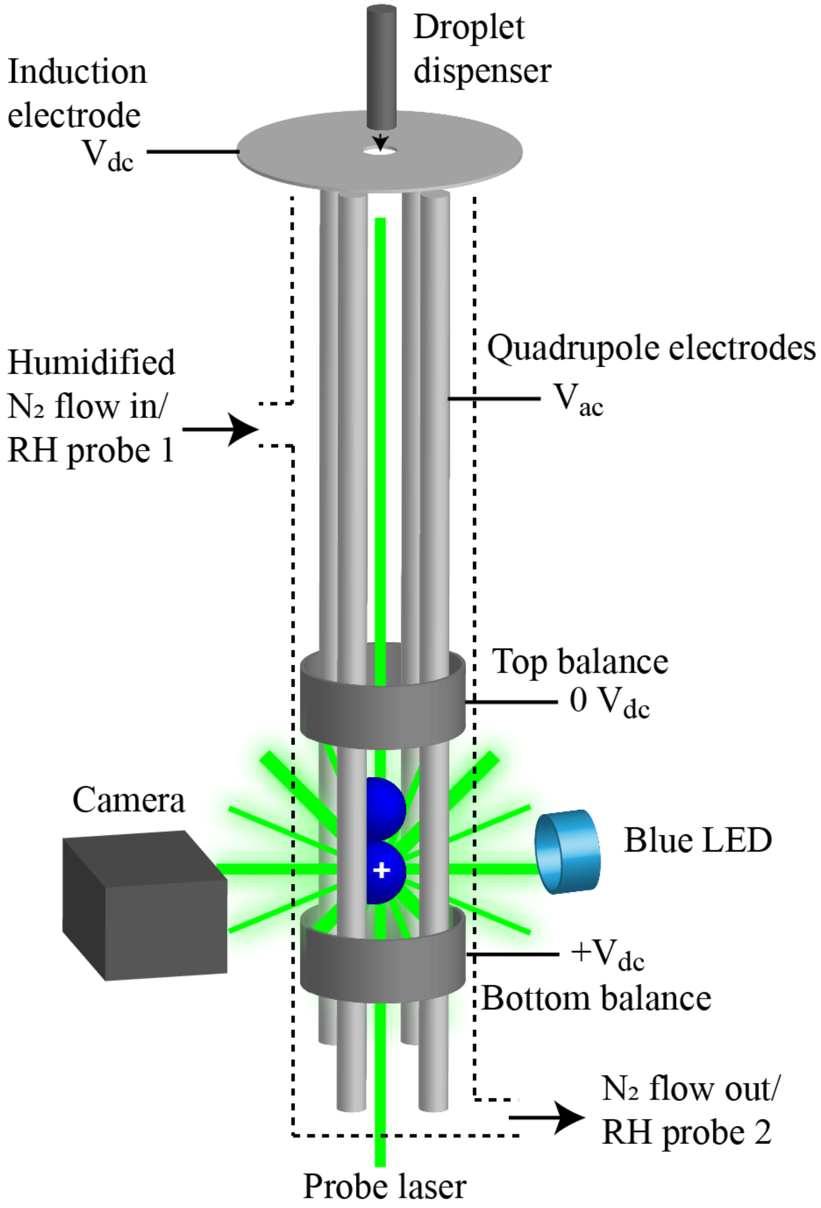
$MgSO_{4(aq)}$
~30% RH

Richards et al., 2019, in review

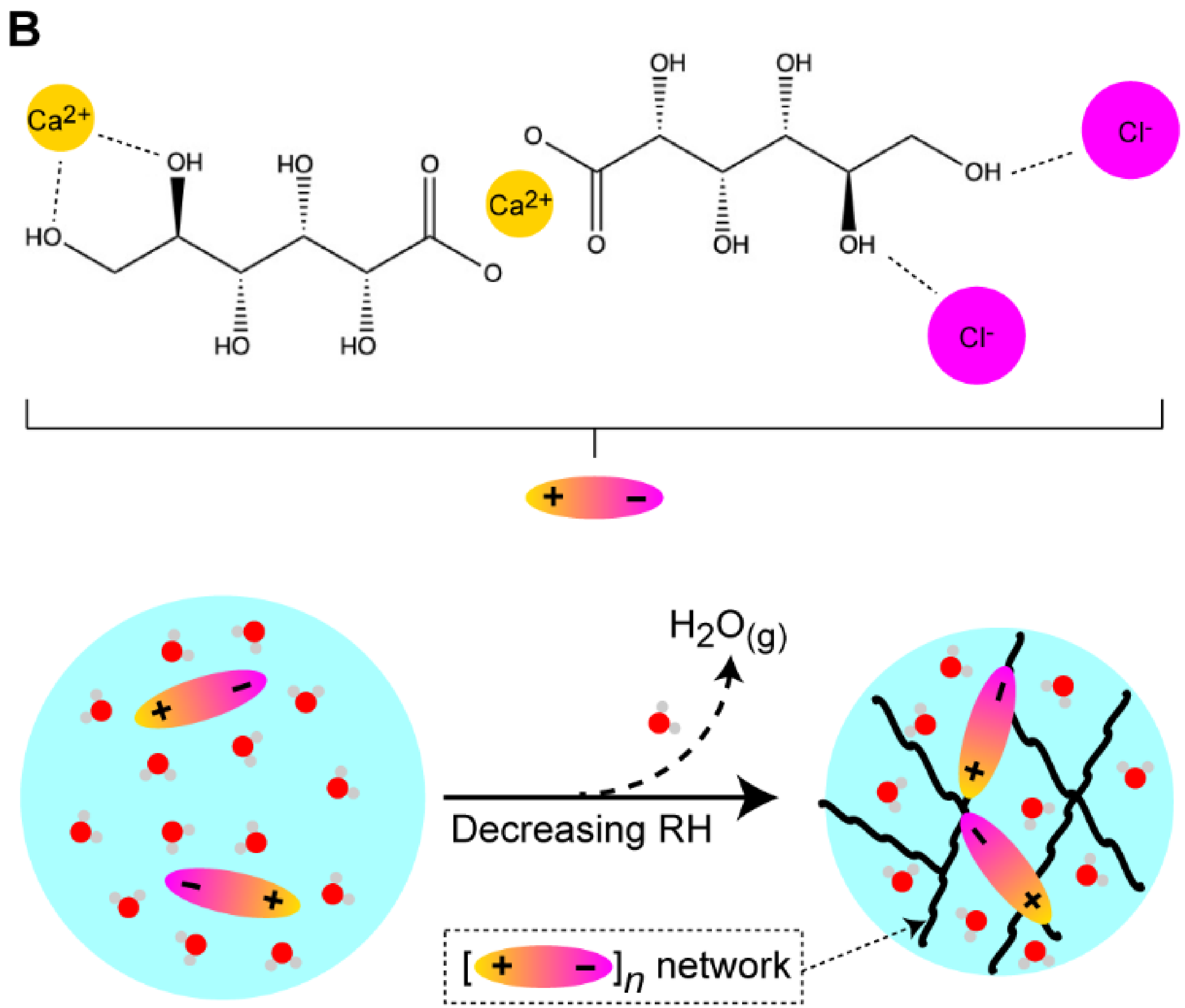
Laser scatter imaging







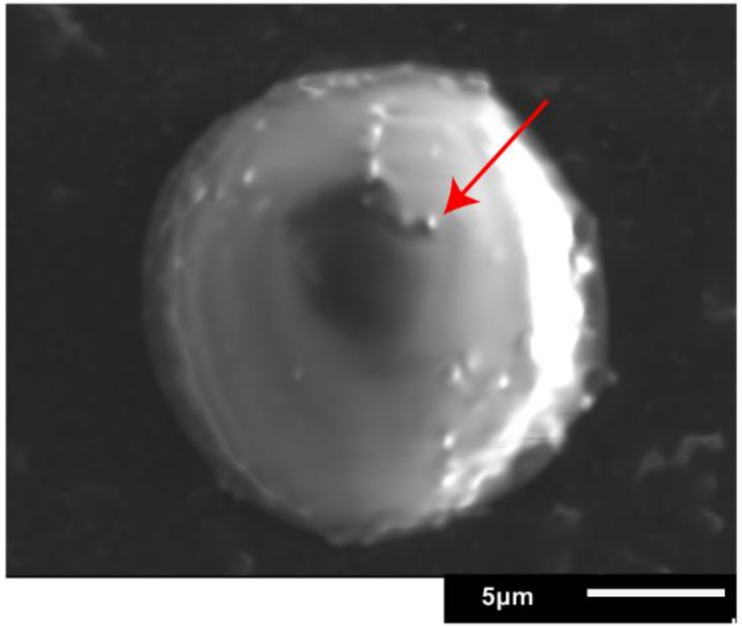
Gelation with carboxylic acids

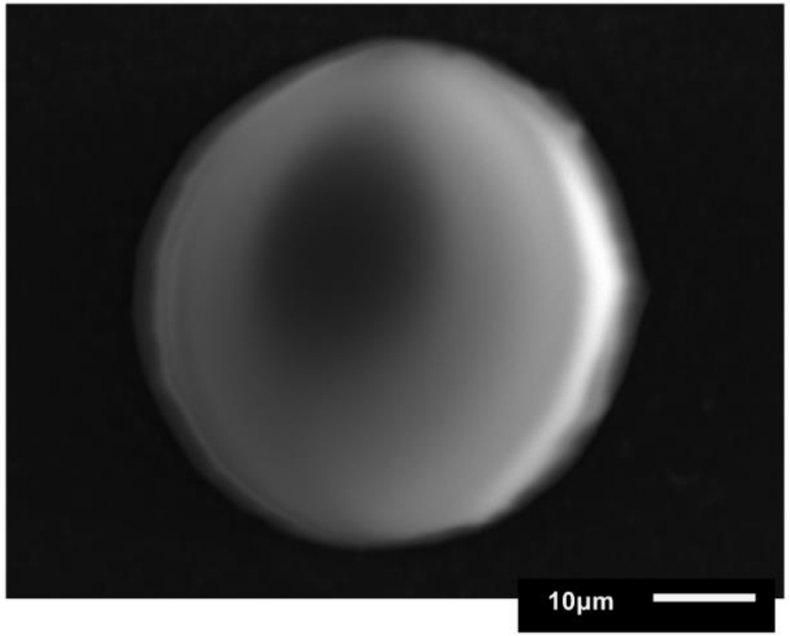


Gelation in the presence of NaCl$_{(s)}$

1:1:1 (by mole) $NaCl:CaCl_2$:sorbitol

B





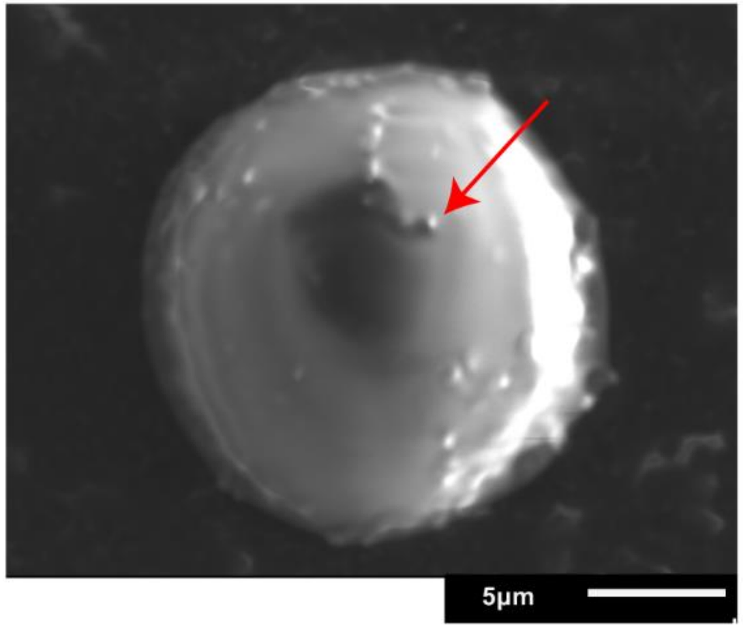
Non-Newtonian flow: viscosity is not constant with applied force

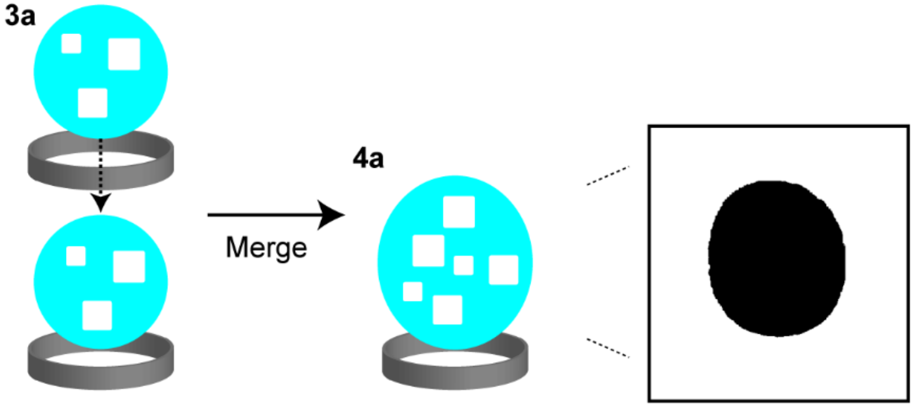
Example at right: a saltwater-beach sand slurry exhibiting shear-induced thickening

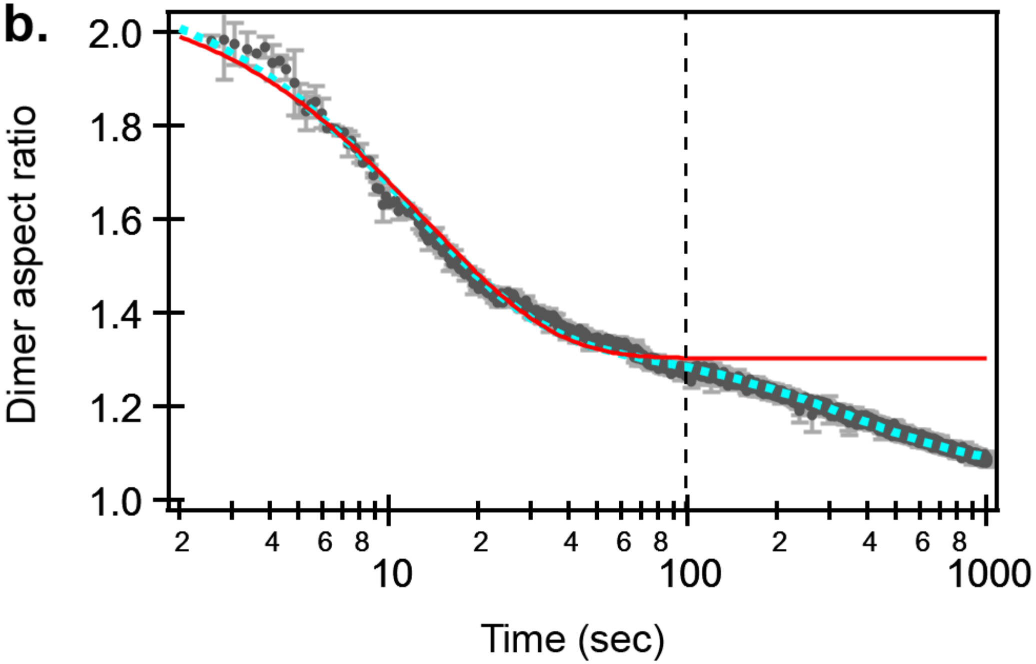
Why would we care if atmospheric aerosol exhibit non-Newtonian flow?

Non-Newtonian flow is indicative of a non-uniform or two-phase system

Example: a partially-effloresced slurry of NaCl solid in a sorbitol-$CaCl_2$ viscous liquid

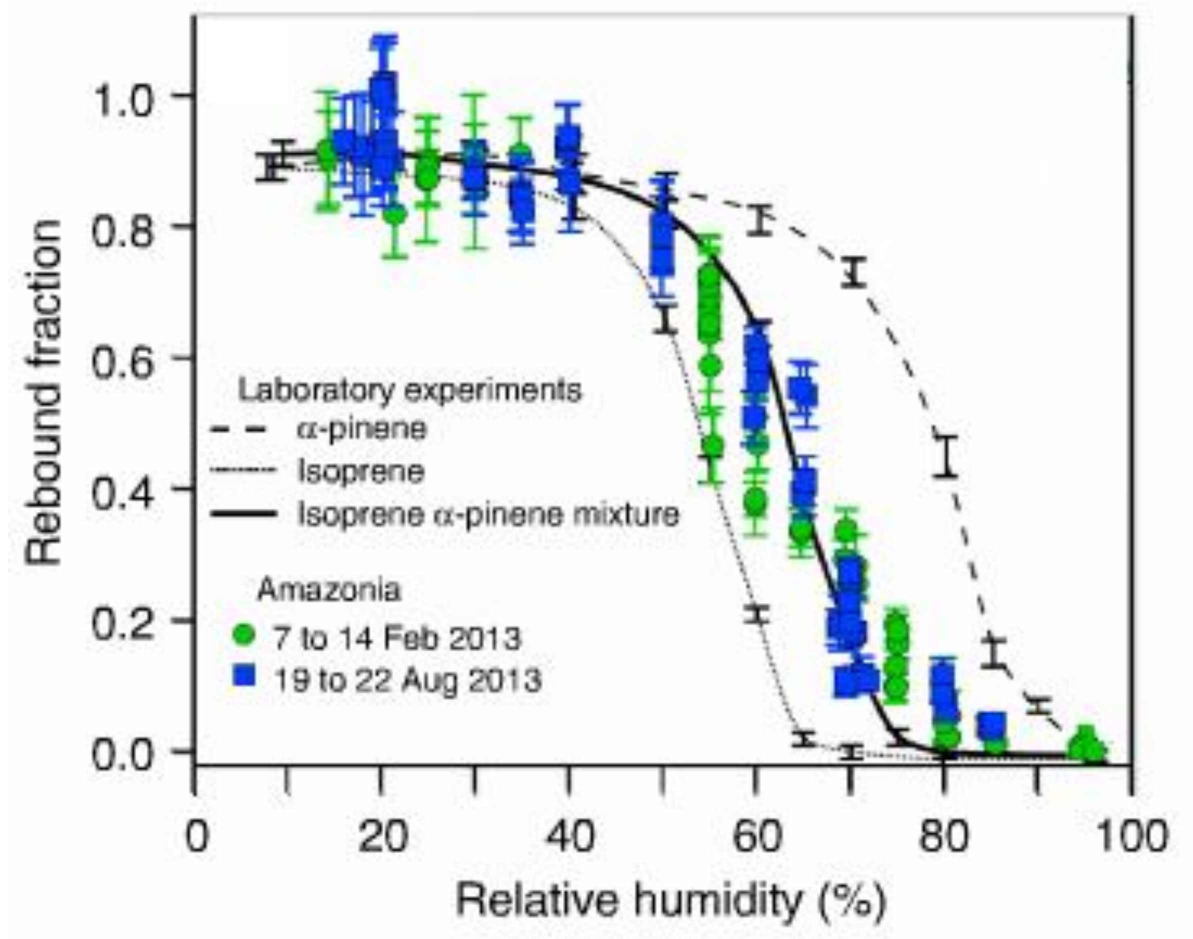






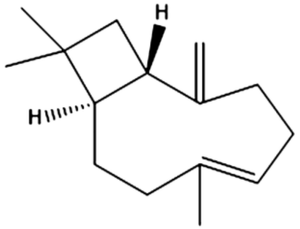
Consensus: Viscosity of organic aerosol increases with decreasing RH

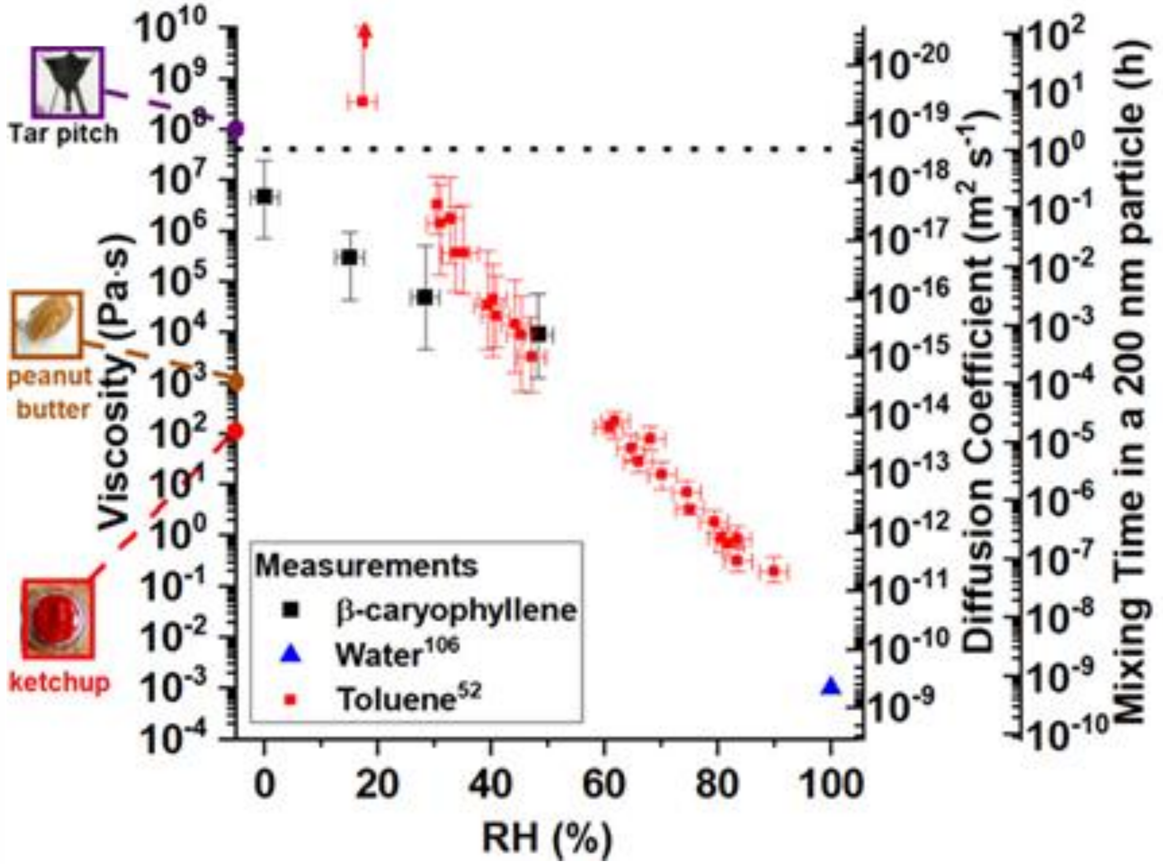
Field studies coupled with lab-generated proxies



Bateman et al., *Nature Geosci.*, 2016

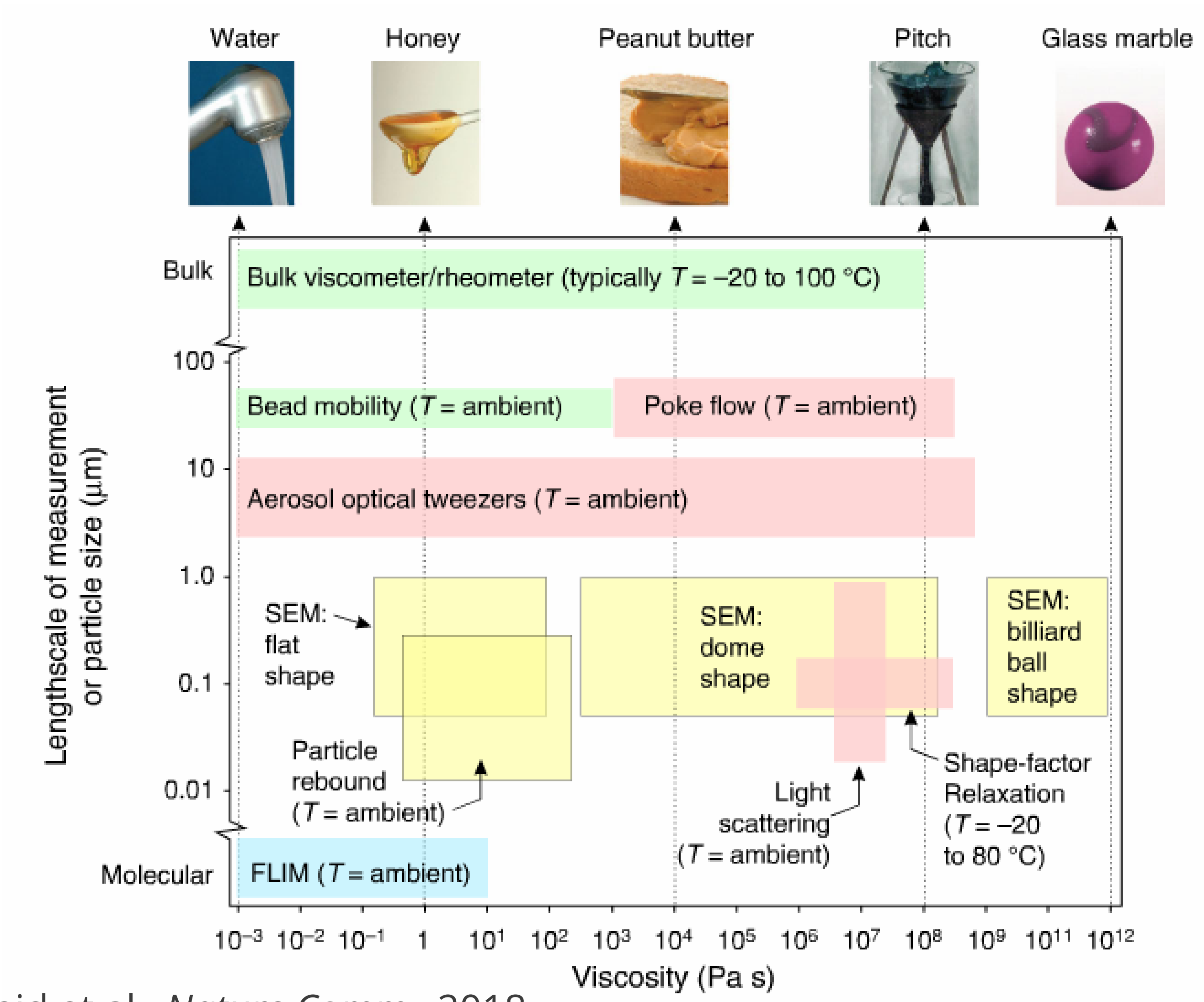
Poke-flow method for viscosity of β-Caryophyllene SOA





Maclean…Shiraiwa…Nizkorodov, Bertram (2021) *ACS Earth Space Che*

Many techniques have been developed to explore viscosity of atmospherically-relevant organic aerosol



Reid et al., *Nature Comm.*, 2018

Recall:

Relating viscosity (η) to diffusion constants (D):

$$\eta \propto \frac{1}{D}$$

Relating diffusion constants (D) to diffusional mixing time (τ_{mix}):

$$\tau_{mix} \propto \frac{1}{D}$$

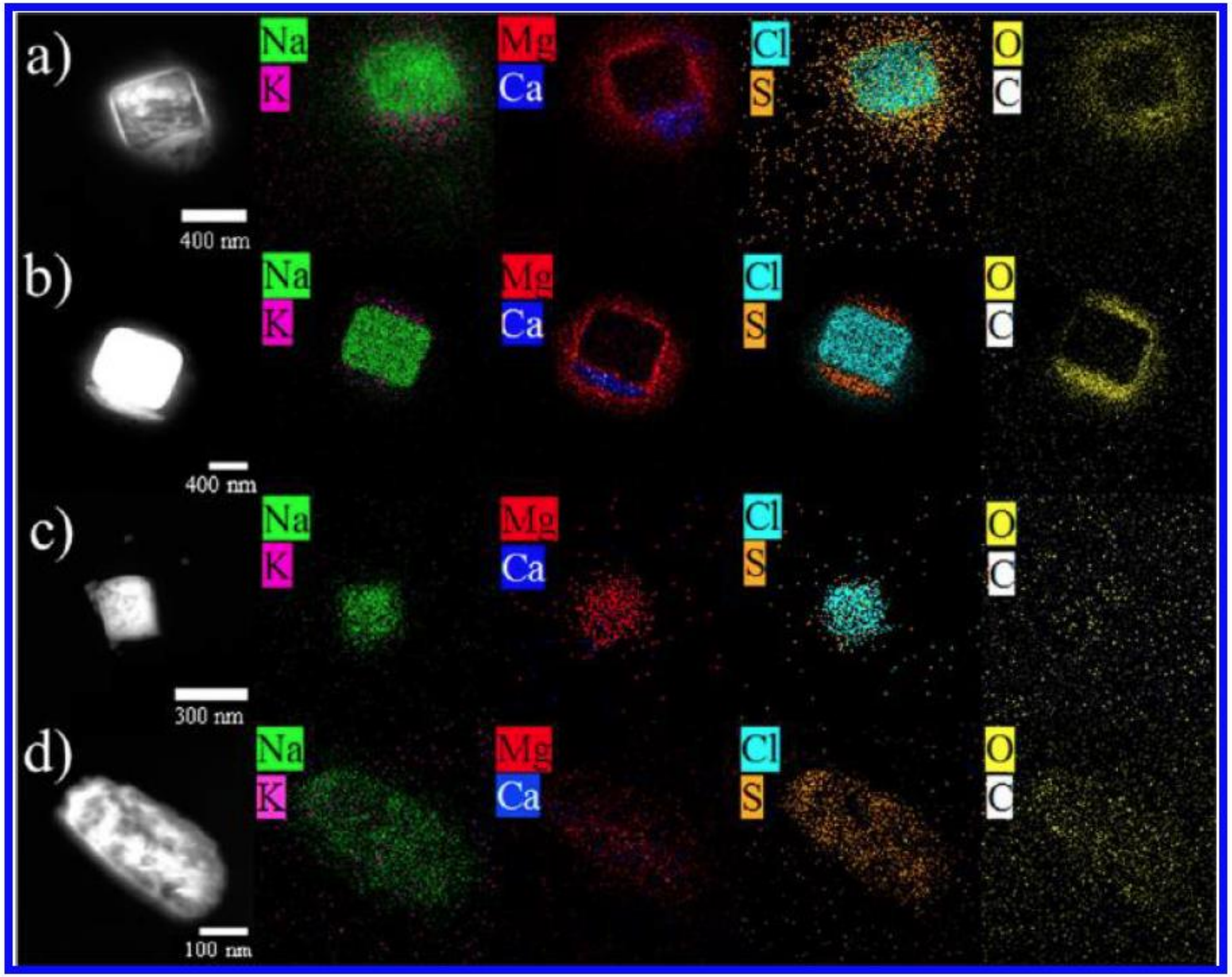
$$\tau_{mix} \propto \eta$$

Is supramolecular chemistry influencing aerosol phase in the atmosphere?

Searching for clues…

Sea spray aerosol:

Ca, Mg can be present with organics in amorphous regions of aerosol (but not always)

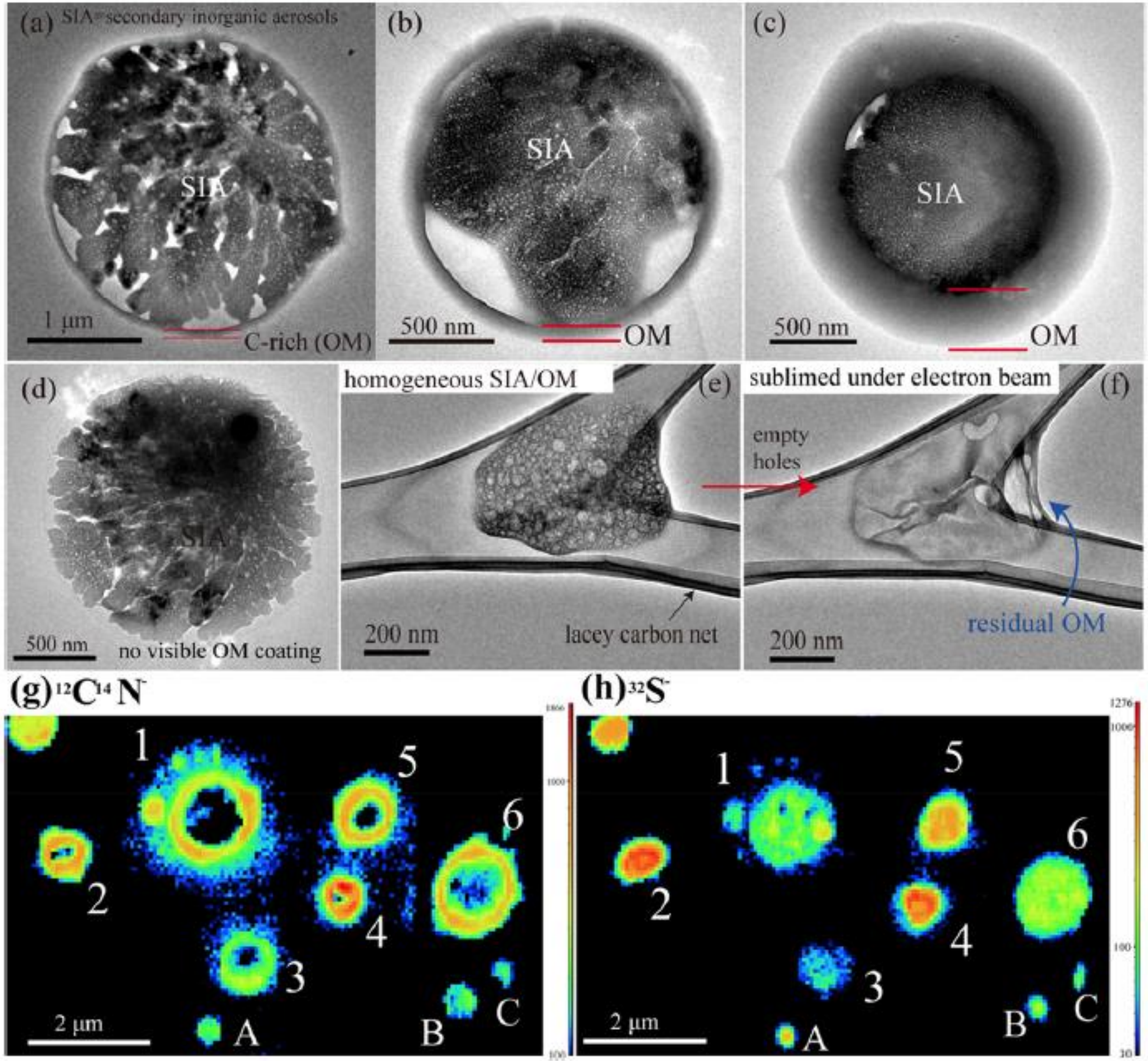


TEM images (dark field) and elemental maps of common particle types observed below 1 μm: (a) SS-OC with Ca and S not isolated to any specific region within the particle, (b) SS-OC with Ca−S rod structure (CaSO4), (c) SS-OC with S and other cations distributed homogeneously throughout the particle, and (d) an OC particle which also contains inorganic elements including Na, Mg, Ca, and S but not Cl. From Ault…Grassian (2013) ES&T

Searching for clues…

Urban and rural aerosol:

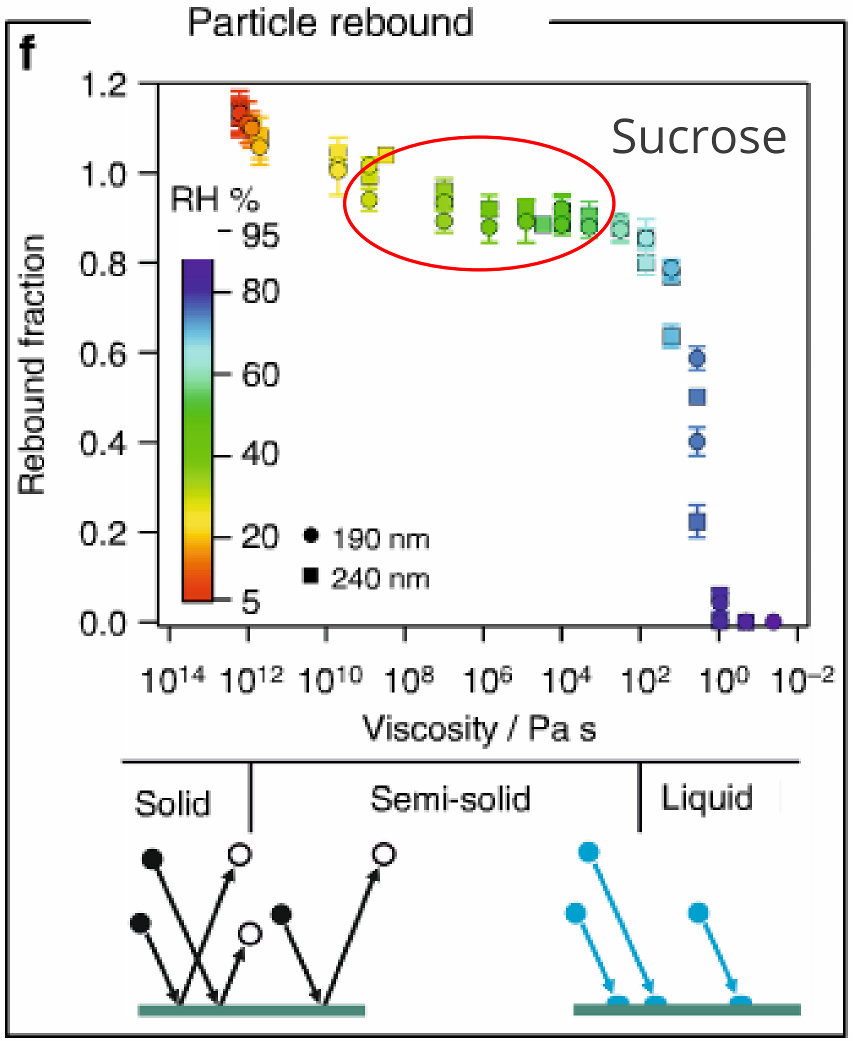
Sulfate can be homogeneously mixed with organic in aerosol (or phase separate)



Microscopic Evidence for Phase Separation of Organic Speci Inorganic Salts in Fine Ambient Aerosol Particles

Weijun Li,* Lei Liu, Jian Zhang, Liang Xu, Yuanyuan Wang, Yele Sun, and Zongbo Shi*

Particle rebound is the most common field-based technique to *qualitatively* infer phase state

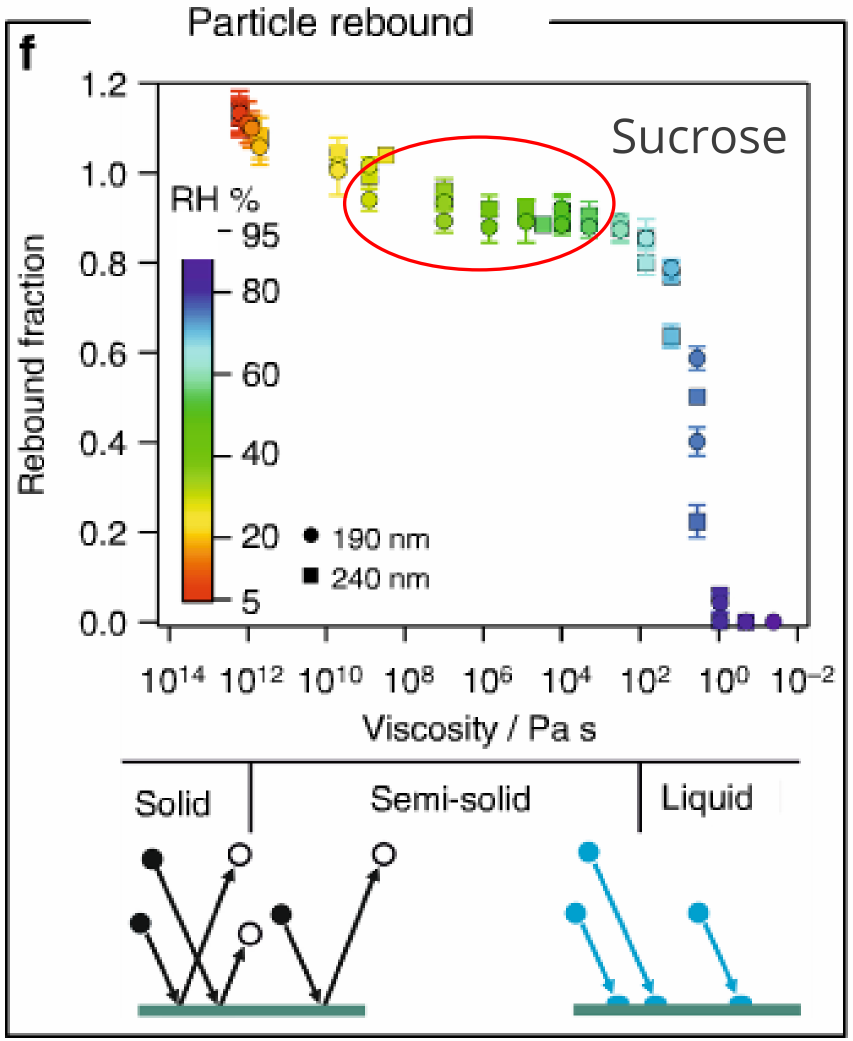


Bateman…Martin, *JCPA*, 2015

Particle rebound:
identifies liquids vs. non-liquids

Large uncertainty exists regarding the viscosity of ambient atmospheric aerosol particles!

Particle rebound is the most common field-based technique to *qualitatively* infer phase state



Bateman…Martin, *JCPA*, 2015

Particle rebound:
identifies liquids vs. non-liquids

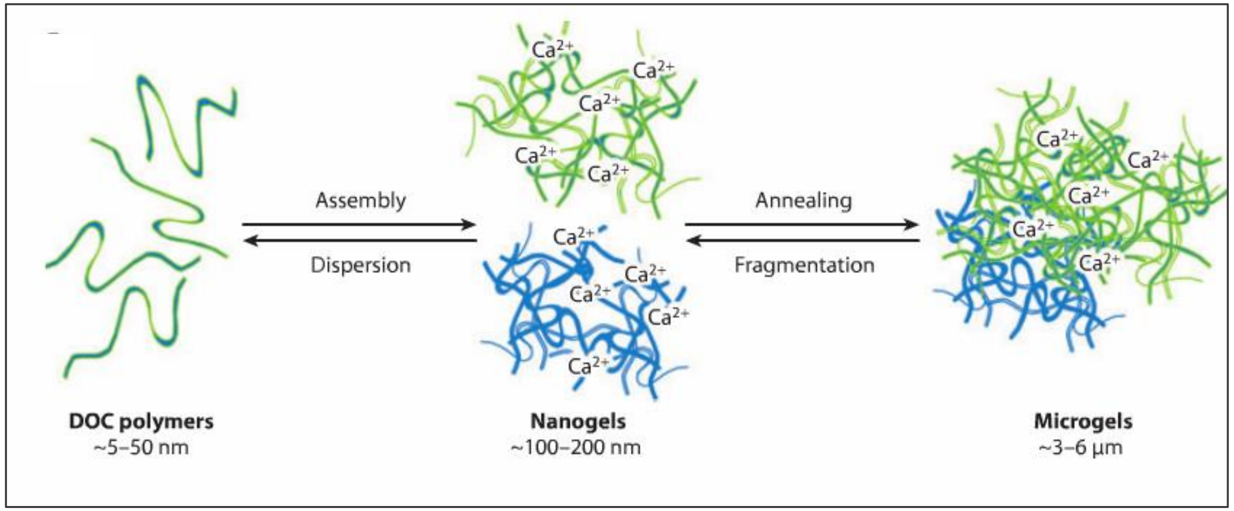
Fundamental laboratory studies are necessary to develop predictive models for aerosol viscosity

Koop et al., *PCCP*, 2011

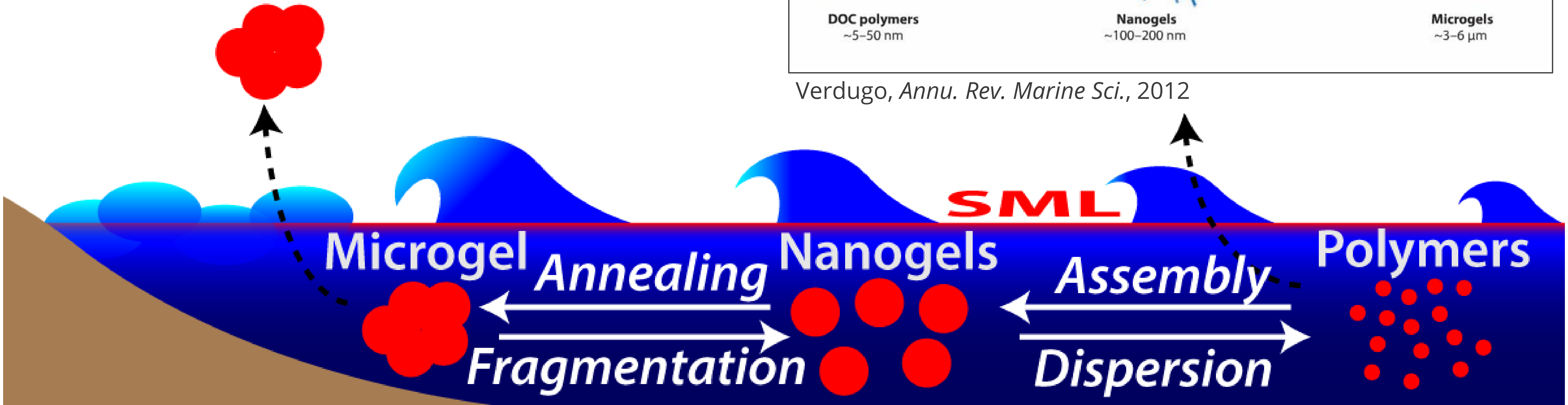
Marine microgels have been observed in the Arctic atmosphere

Orellana et al., *PNAS*, 2011

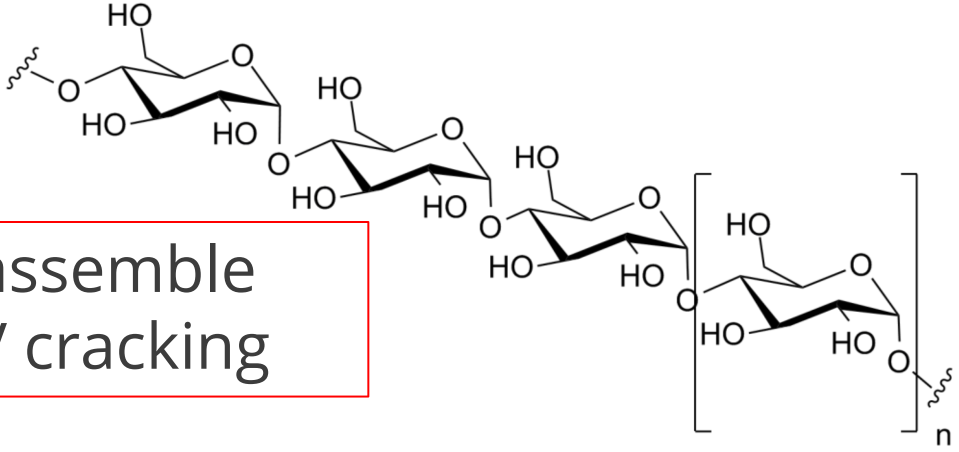
Process begins with large macromolecules (polysaccharides)



Verdugo, *Annu. Rev. Marine Sci.*, 2012

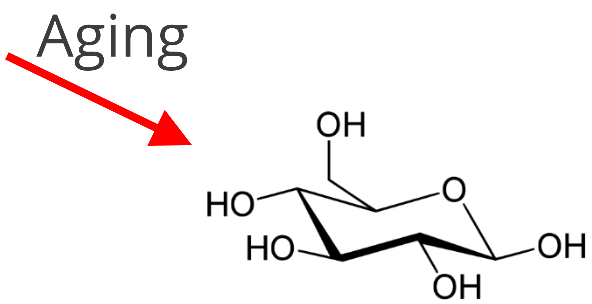


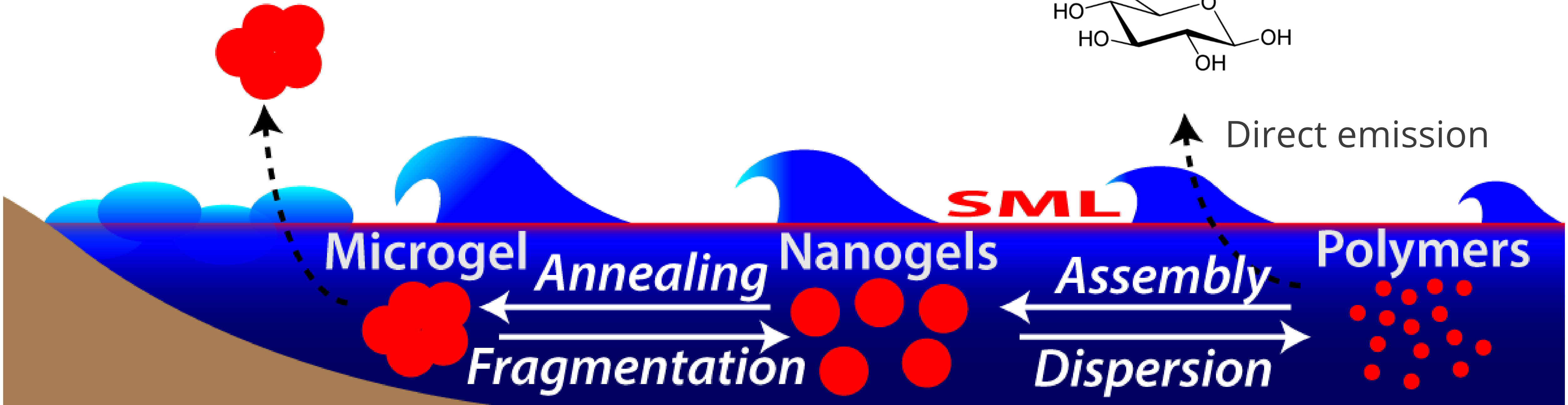
Marine microgels have been observed in the Arctic atmosphere



Expected to disassemble due to aging, UV cracking

Orellana et al., 2003

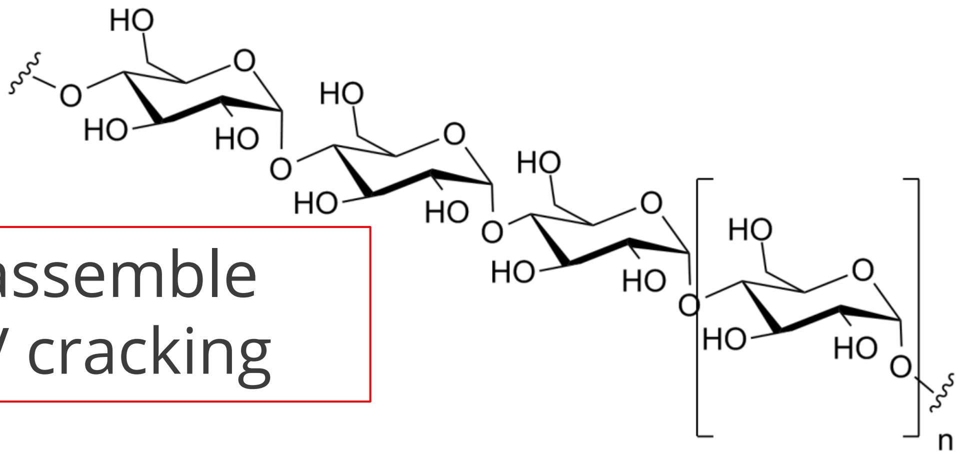




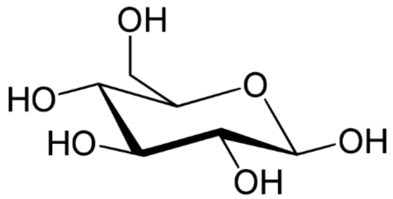
Monosaccharides and small oxygenated organics are abundant in sea spray aerosol

Expected to disassemble due to aging, UV cracking

Orellana et al., 2003



Aging



Monosaccharides do not form gels in bulk solution