NJIT New Jersey's Science & Technology University

Soot Restructuring in Condensation-Evaporation Cycles

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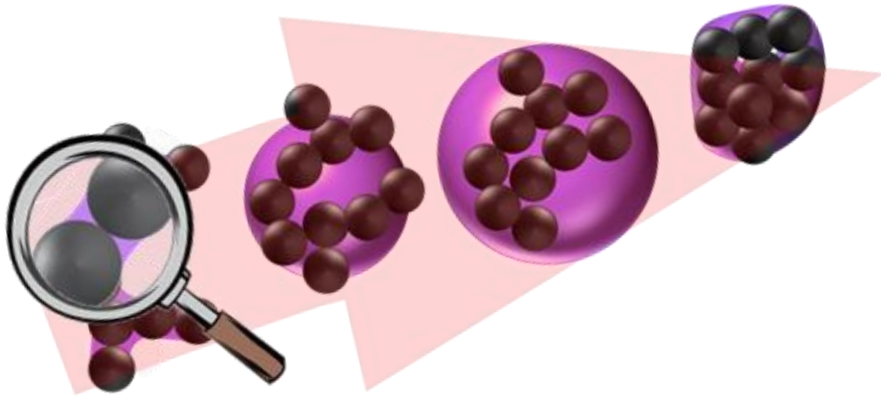
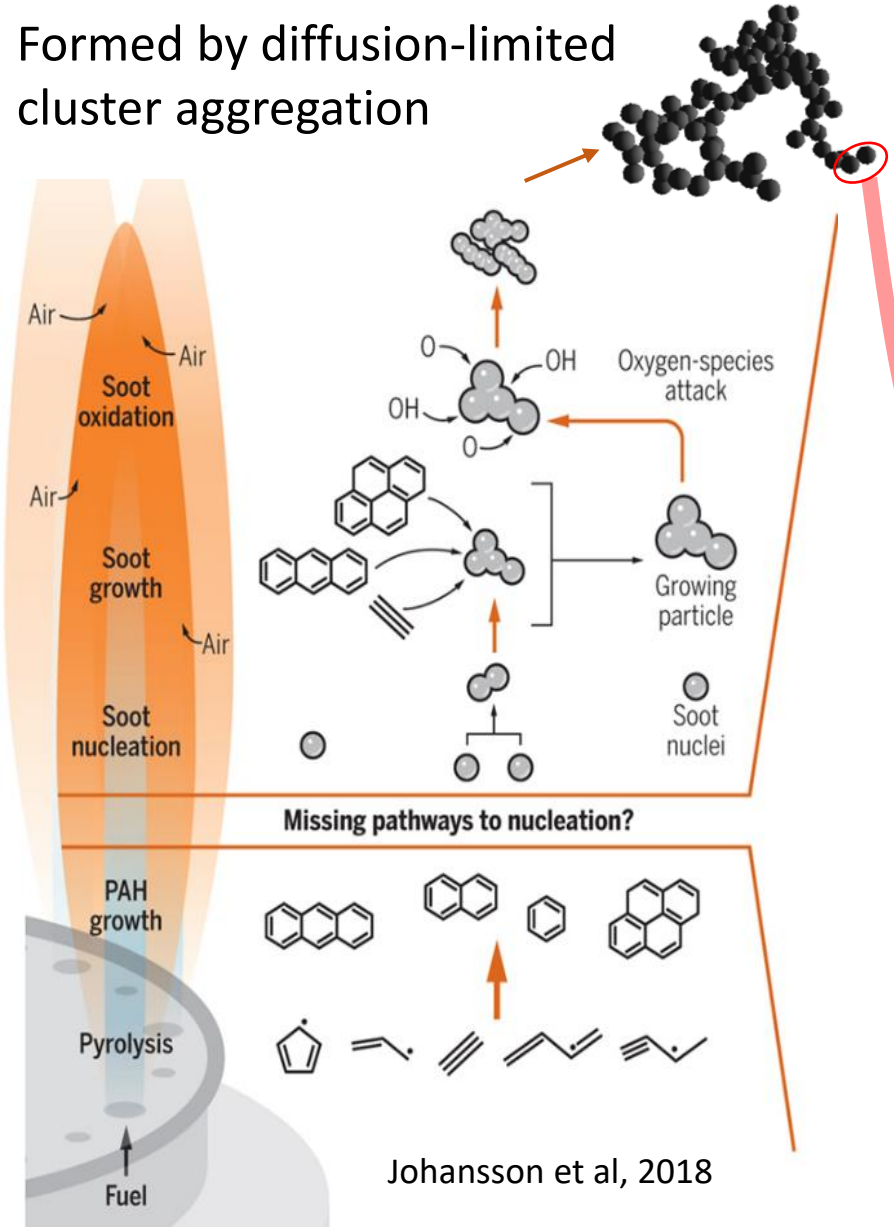


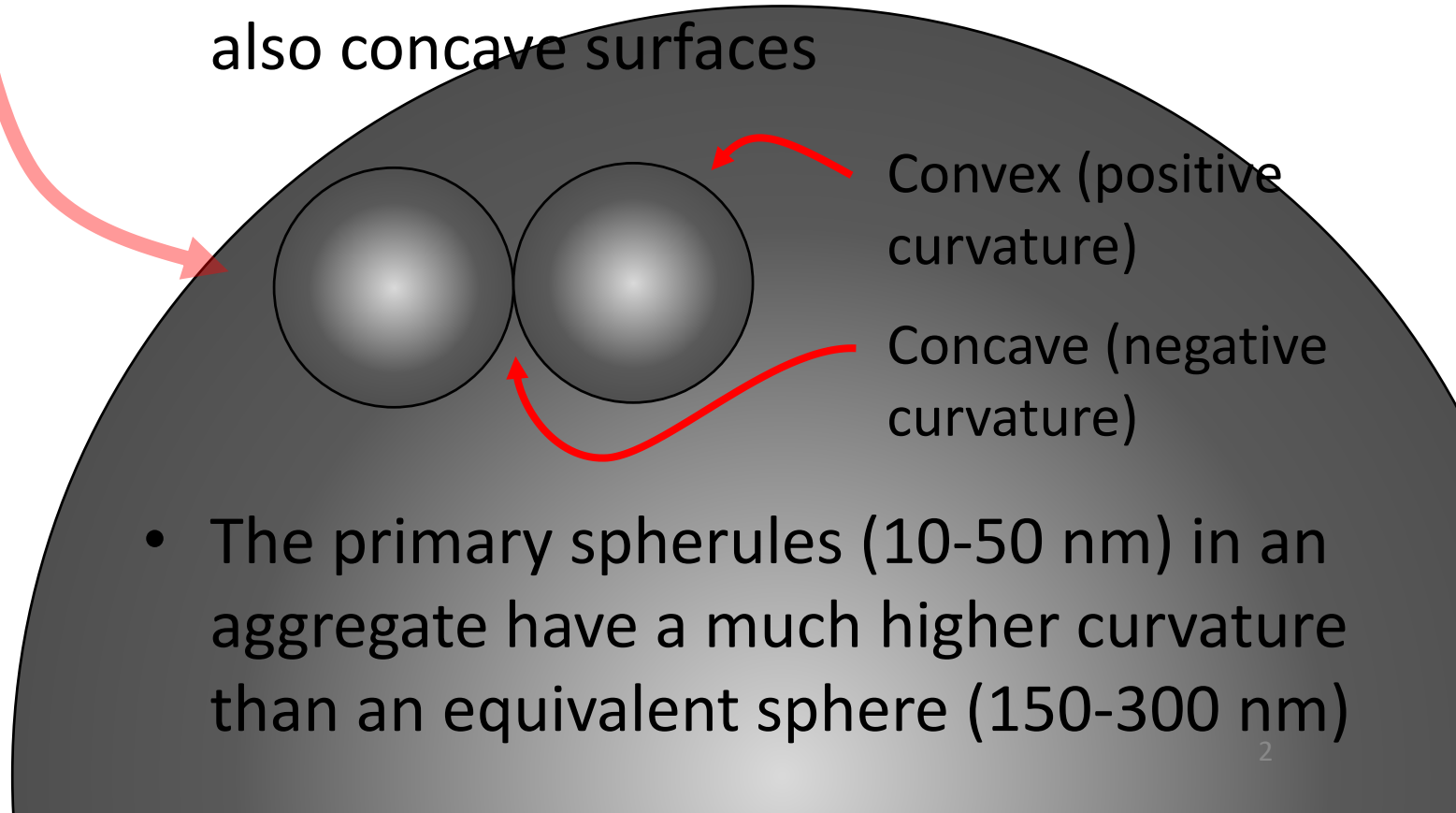
Soot particles are lacey aggregates

Formed by diffusion-limited cluster aggregation



Johansson et al, 2018

- A fractal aggregate has a ~50% larger surface than an equivalent sphere
- The aggregate has not only convex but also concave surfaces



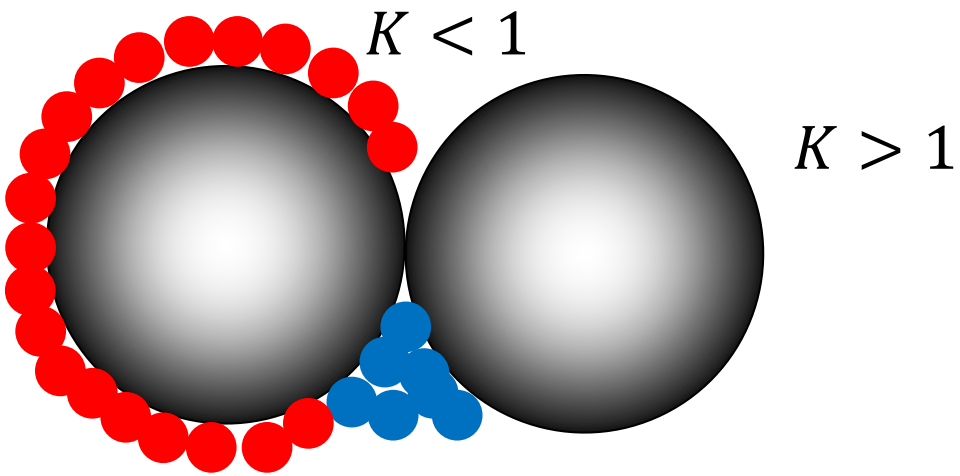
- The primary spherules (10-50 nm) in an aggregate have a much higher curvature than an equivalent sphere (150-300 nm)

Negative curvature allows capillary condensation

$$Rate \propto A \times n_{sat} \times (S - K)$$

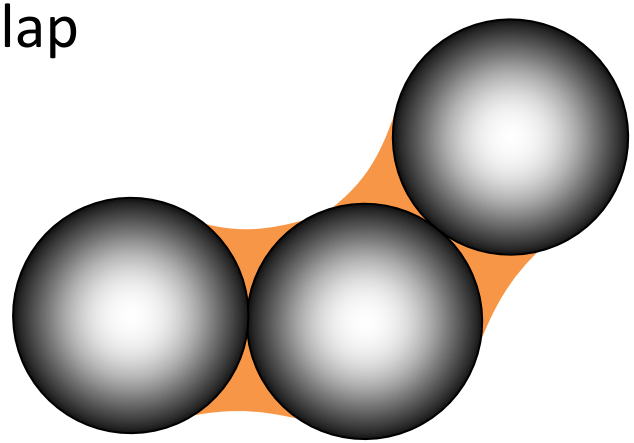
supersaturated

subsaturated



subsaturated

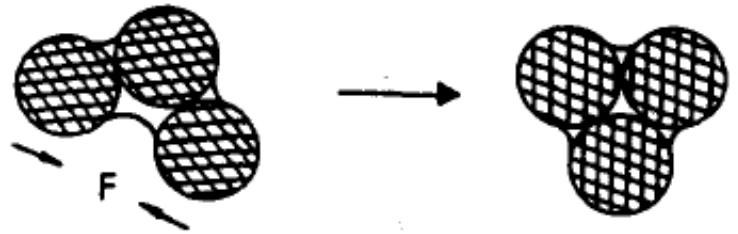
- Supersaturated vapor condenses without preference
- Subsaturated vapor undergoes capillary condensation
- The presence of even a small amount of condensate in the junctions may promote restructuring when menisci overlap

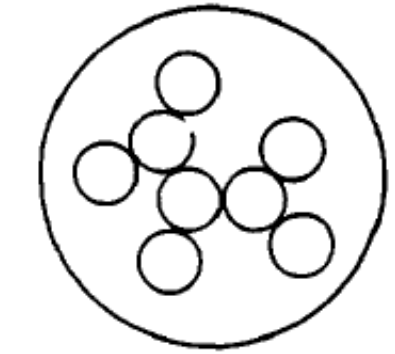


Chen et al., A single parameter for predicting the morphology of atmospheric black carbon, *Environ. Sci. Technol.*, **2018**, 52 (24) 14169-14179

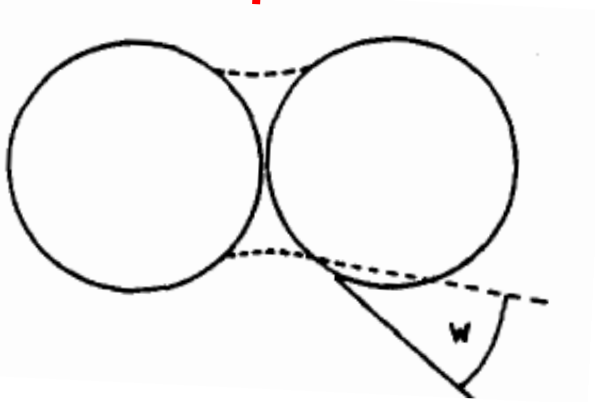
Droplet growth and evaporation: how much does each contribute to restructuring?

Condensation (S > 1)

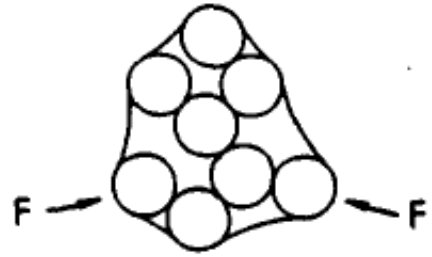




Capillary force from liquid menisci



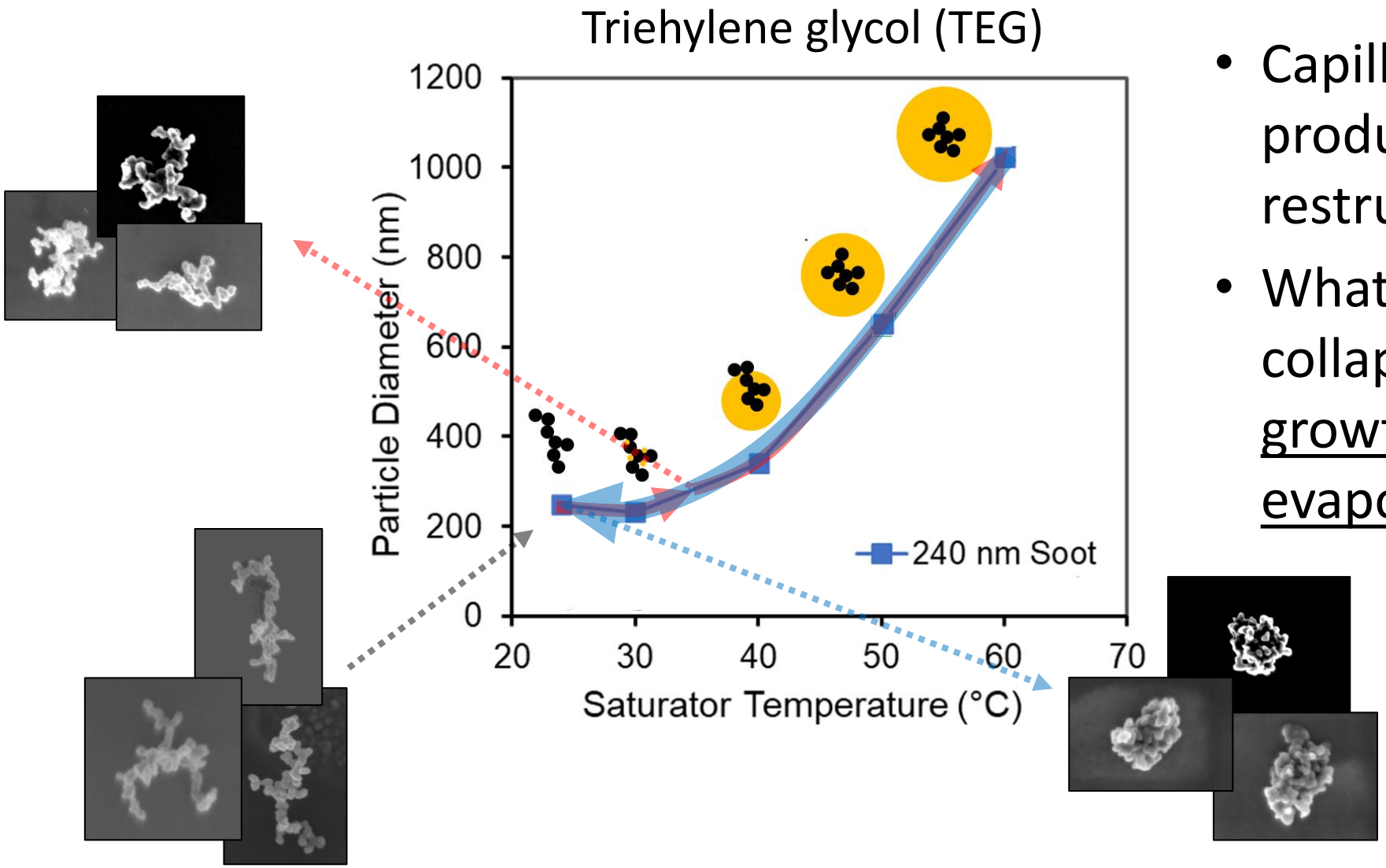
Capillary **condensation** (S < 1)



Evaporation (S < 1)

Kütz and Schmidt-Ott, Characterization of agglomerates by condensation-induced restructuring, *Journal of Aerosol Science* ***23(Suppl 1),*** 357-360, 1992.

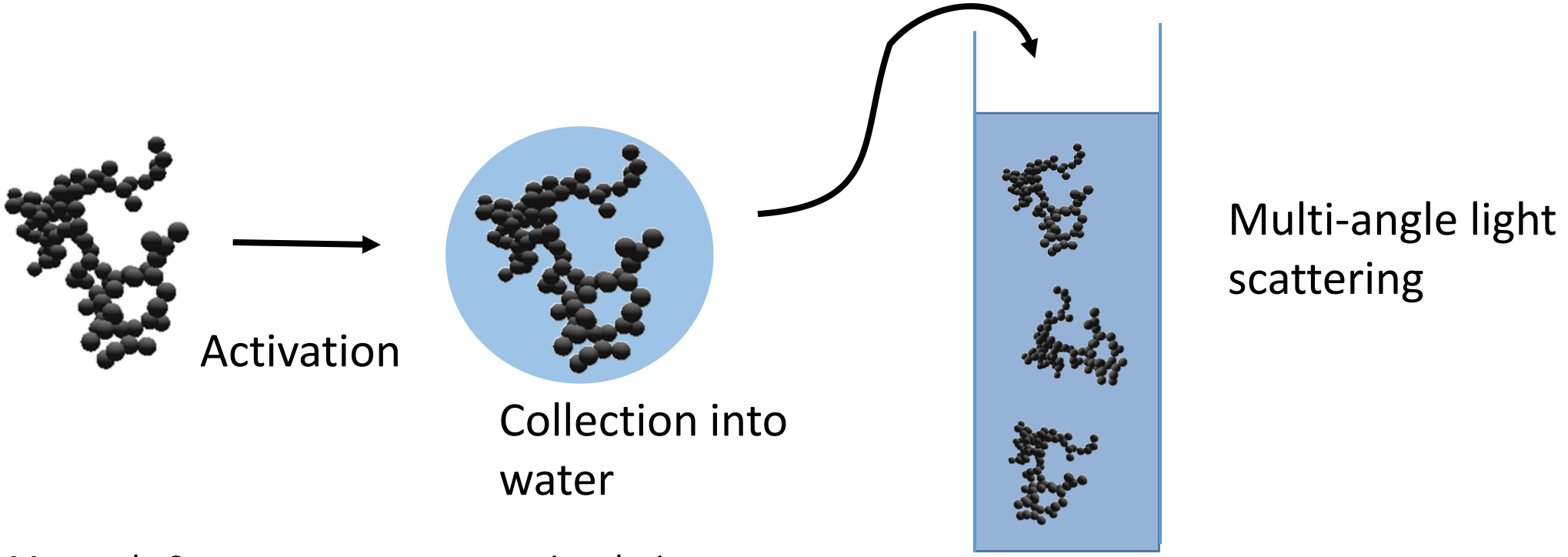
Encapsulation is needed for complete compaction



- Capillary condensation produces partial restructuring
- What causes complete collapse: condensational growth or condensate evaporation?

Enekwizu, et al. Vapor Condensation and Coating Evaporation Are Both Responsible for Soot Aggregate Restructuring. *Environ. Sci. Technol.* **2021**, 55, 13, 8622–8630

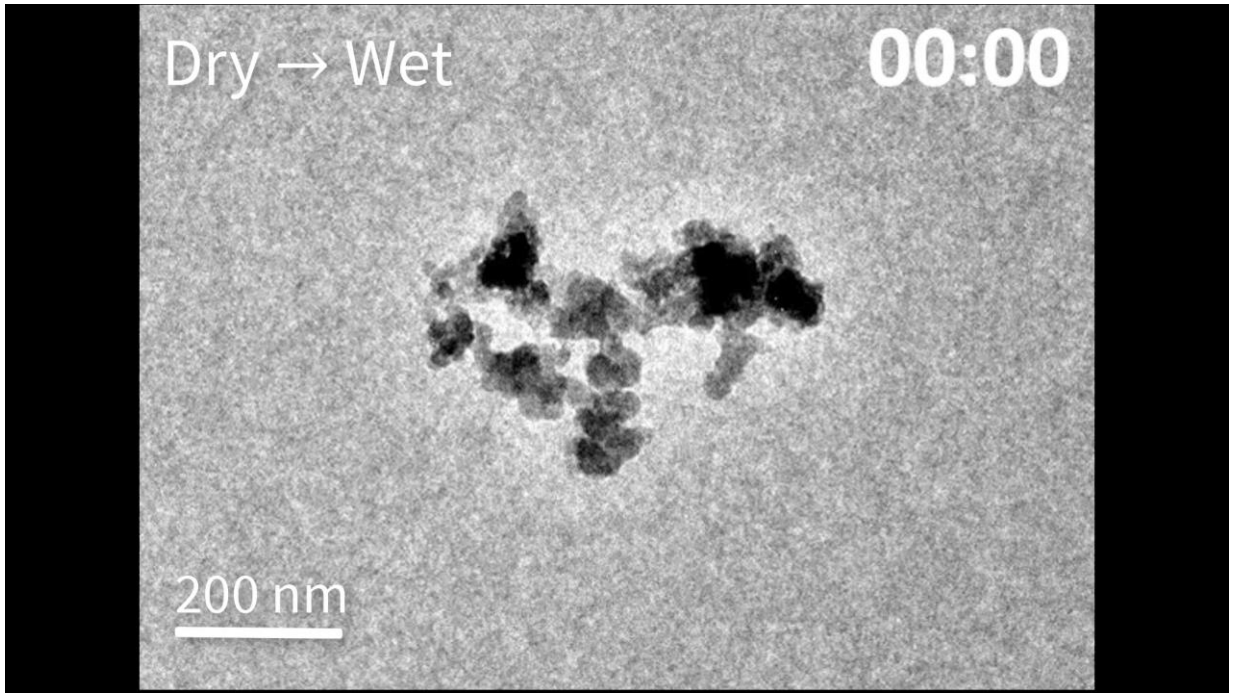
Only the evaporation causes restructuring during water processing

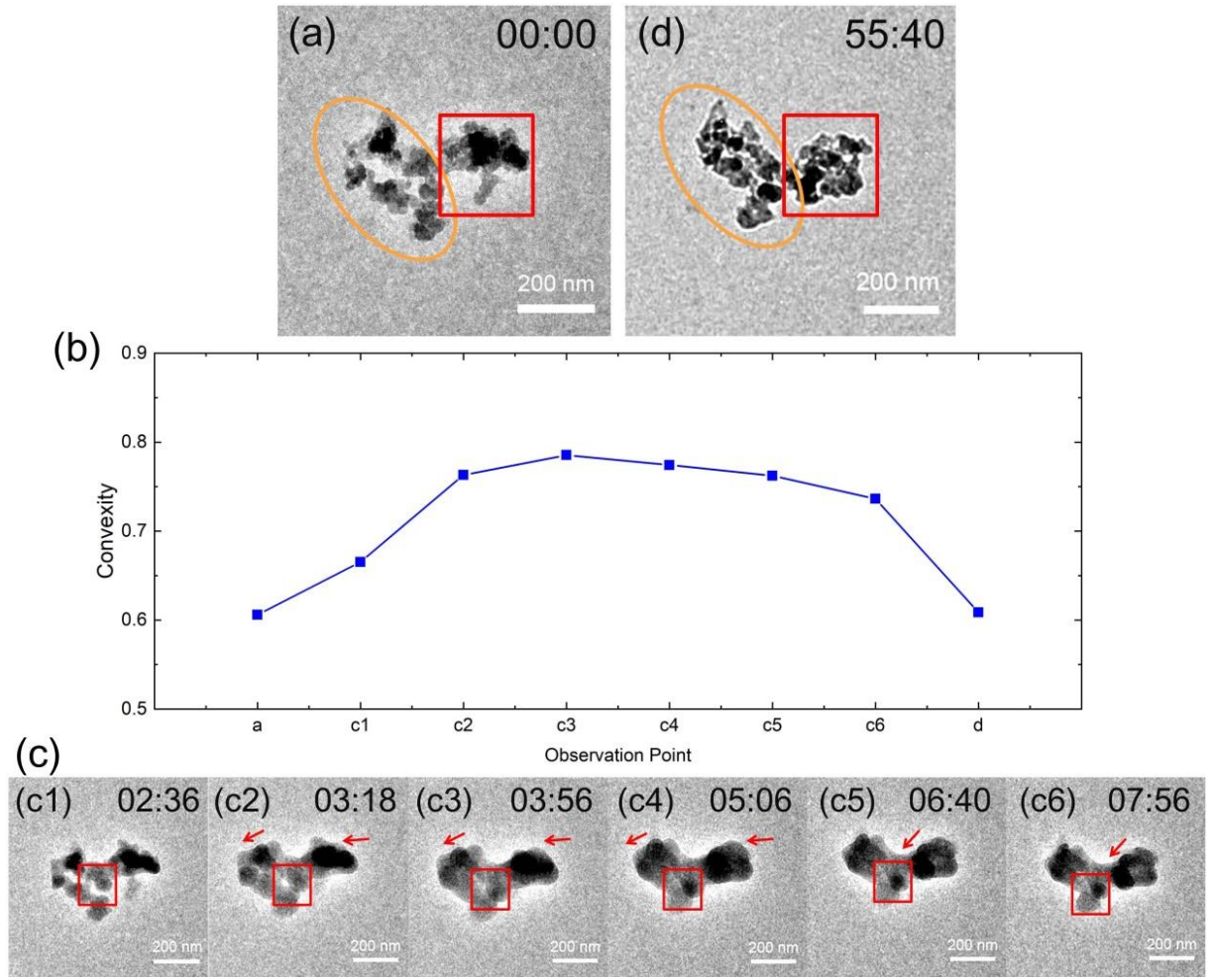


Ma, et al., Soot aggregate restructuring during water processing, *J. Aerosol Sci.*, ***66,*** 209-219, 2013

Does this be apply to all condensates?

How to determine morphology of aggregates while they are still encapsulated?



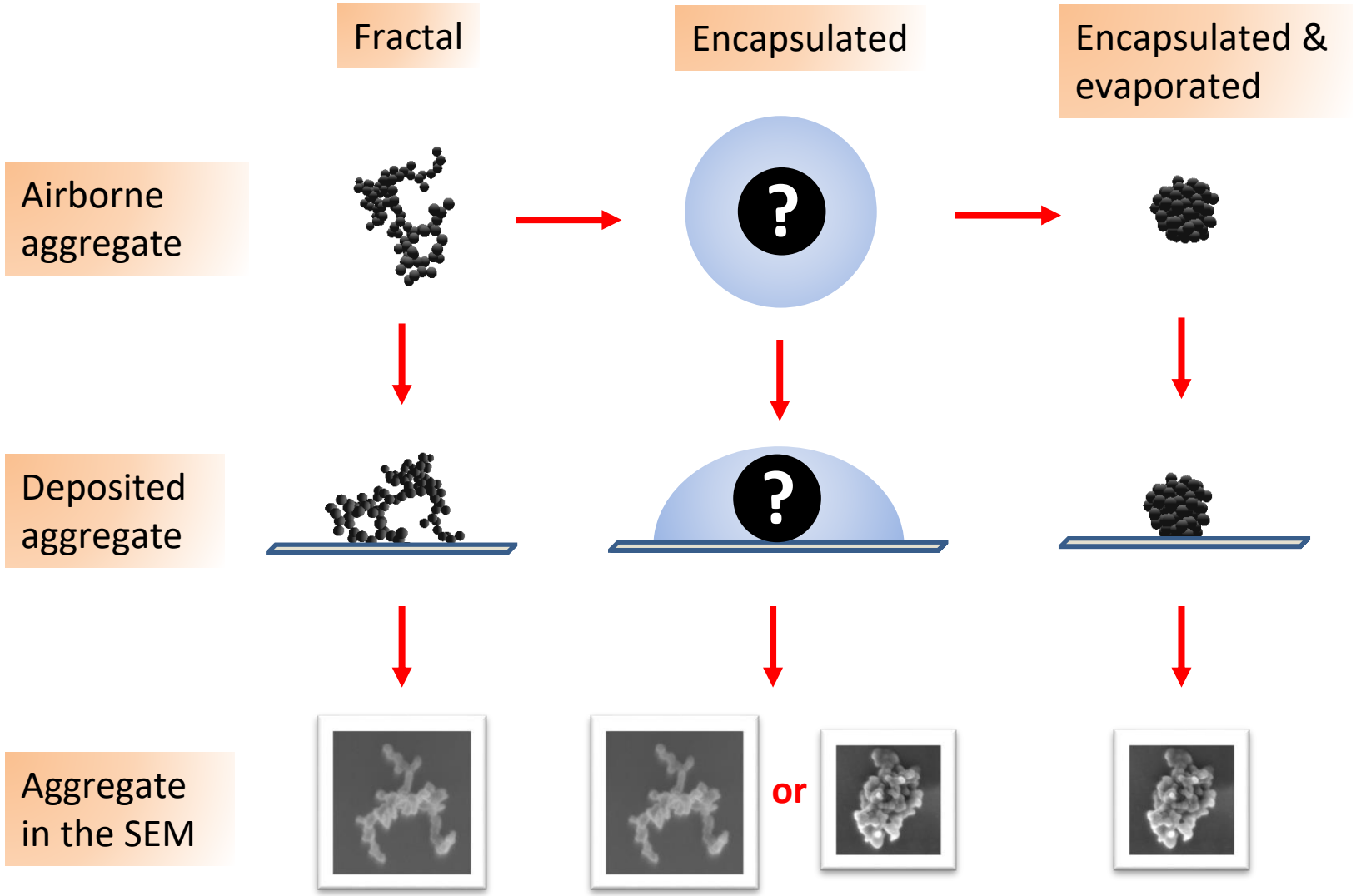


Chen et al., The impact of sampling medium and environment on particle morphology, *Atmosphere*, **2017**, 8 (9), 162

Chen et al., Drastically different restructuring of airborne and surface-anchored soot aggregates. *J. Aerosol Sci.* **2023**, 168, 106103

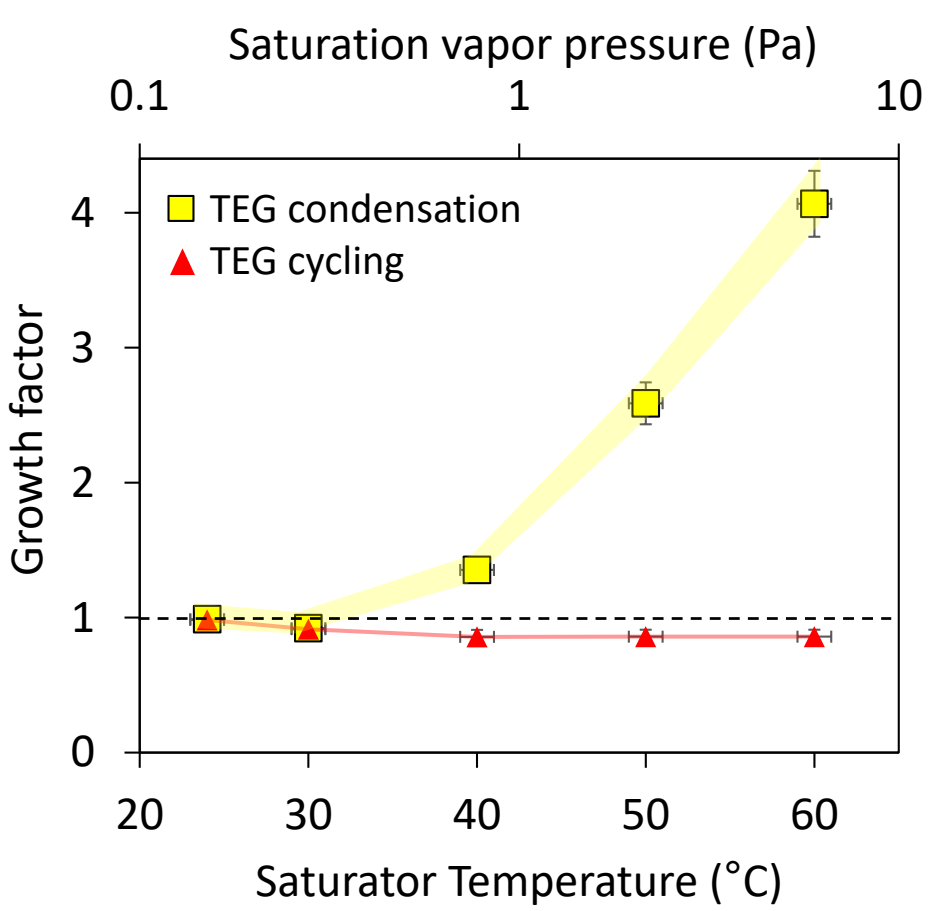
Fix 'em on a surface!

How to “freeze” encapsulated aggregates

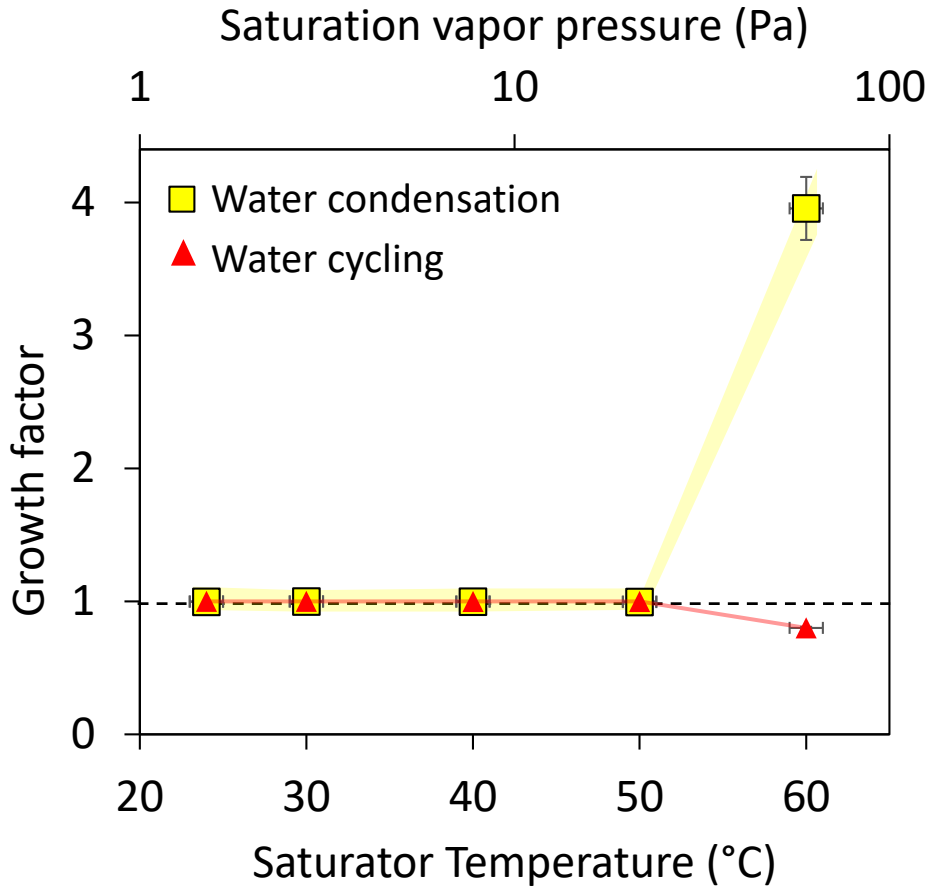


Encapsulation of airborne aggregates

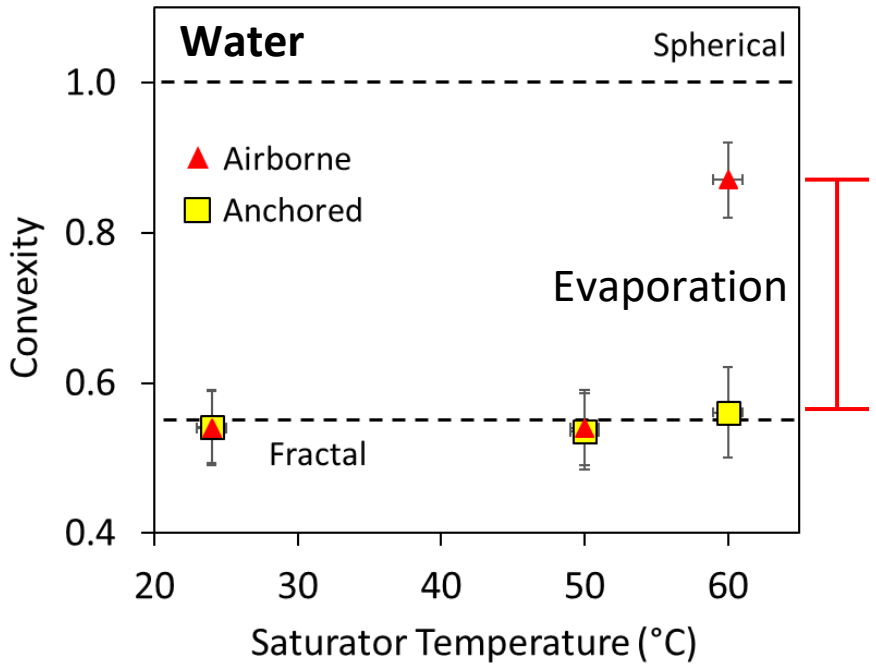
Triethylene glycol (TEG)
(wetting fluid)

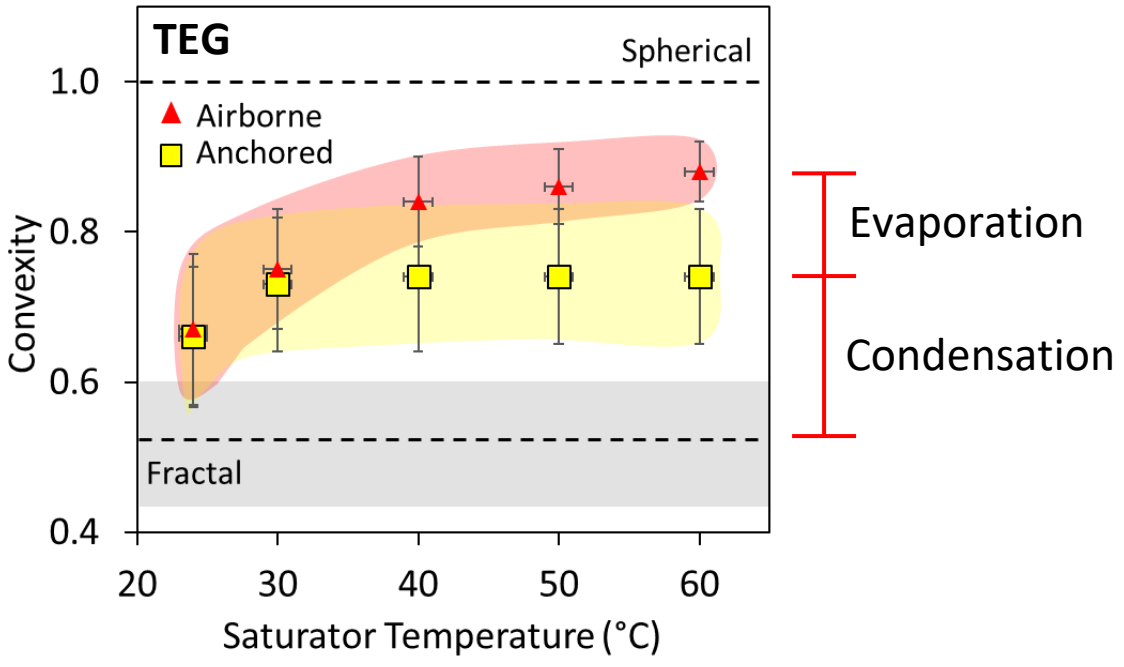


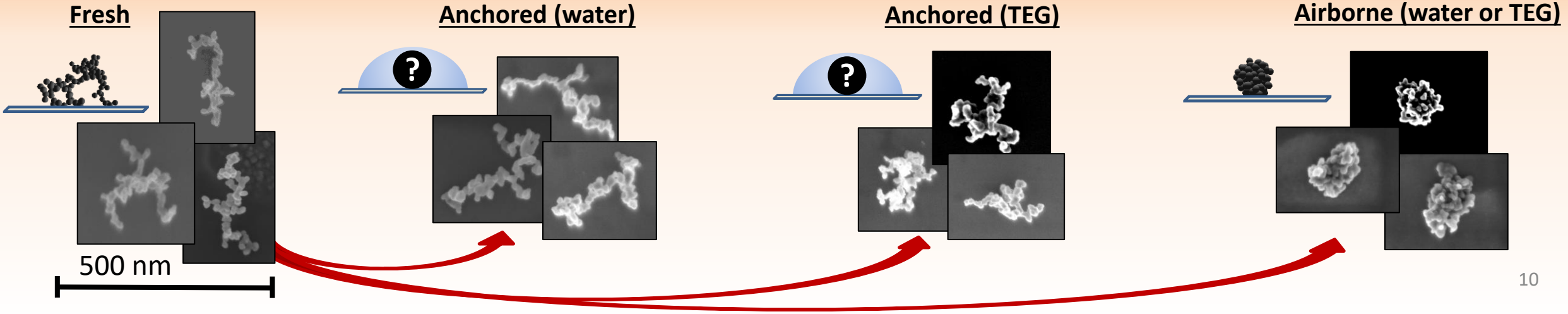
Water
(non-wetting fluid)



Imaging of “frozen” encapsulated aggregates

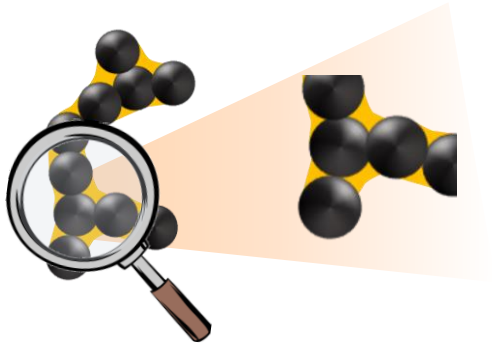




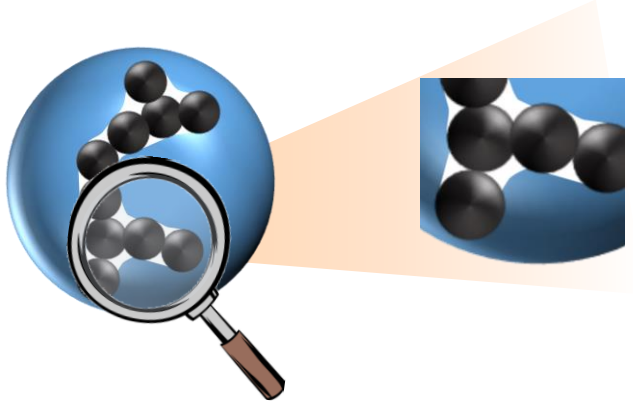


What happens during encapsulation

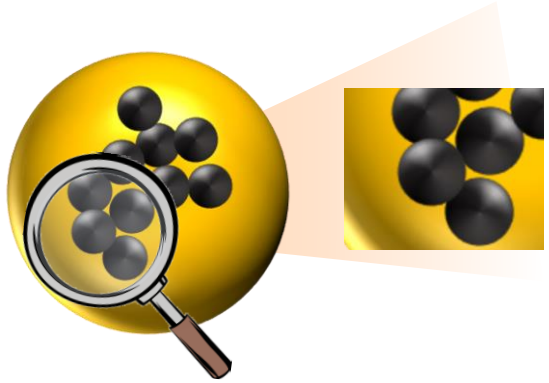
Wetting fluids



Non-wetting fluids



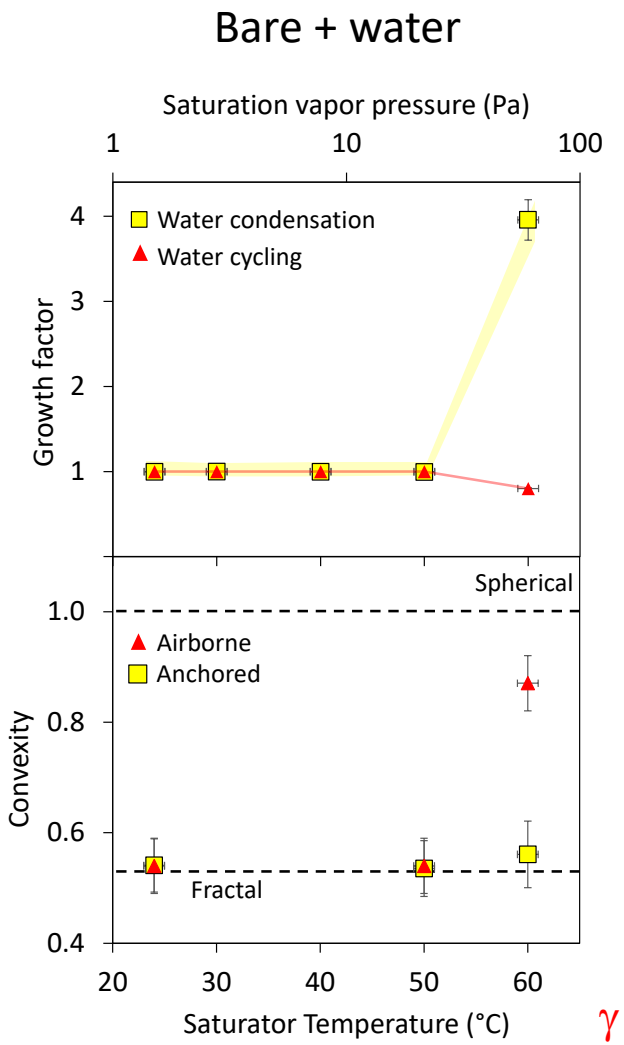
…but nature abhors a vacuum?!



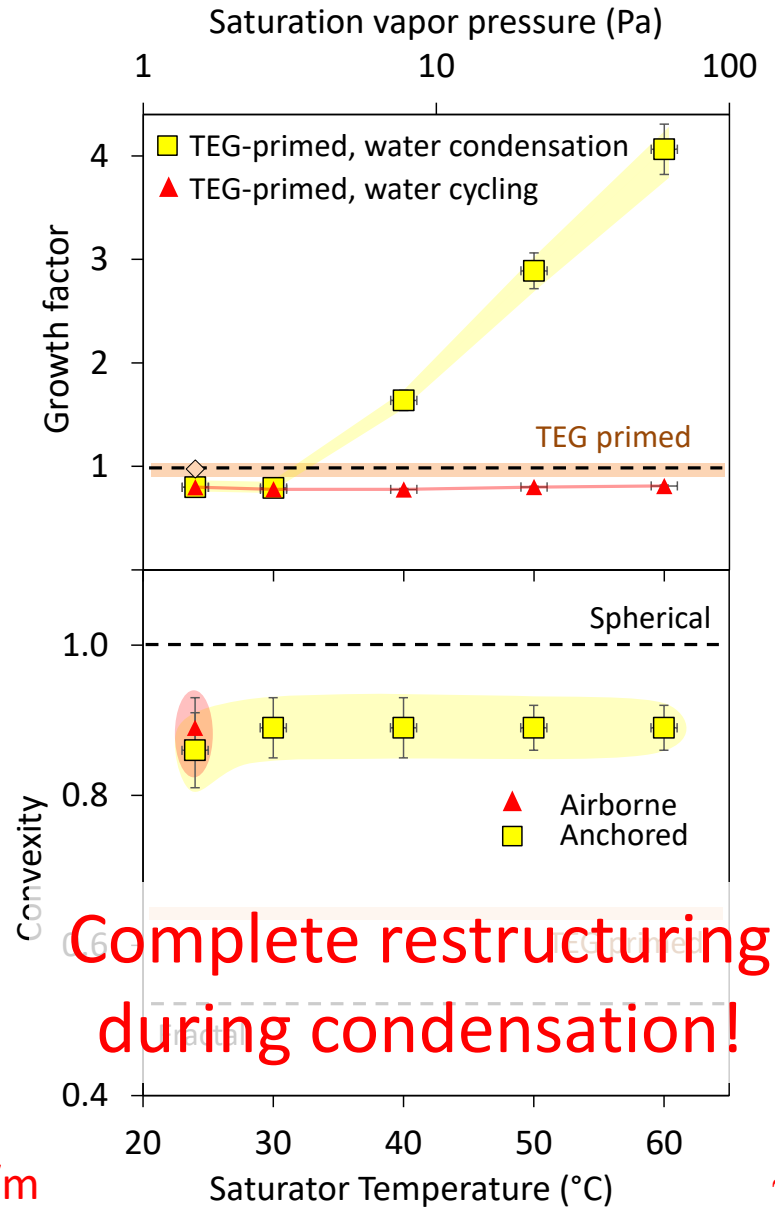
- Holding water inside a 1.5 nm slit graphite pore requires 3500 atm!

  Pršlja et al., Adsorption of water, methanol, and their mixtures in slit graphite pores, J. Chem. Phys., **2019**, 150(2), 024705
- Laplace pressure for a 1 μm droplet is only 1.4 atm
- For methanol in same pore, the pressure is 0.0036 atm
- For a water-methanol mixture with a bulk x_{MeOH} = 0.115, the pressure is 0.056 atm
- Can we try something similar with soot aggregates?

Water-processing of **TEG**-primed aggregates

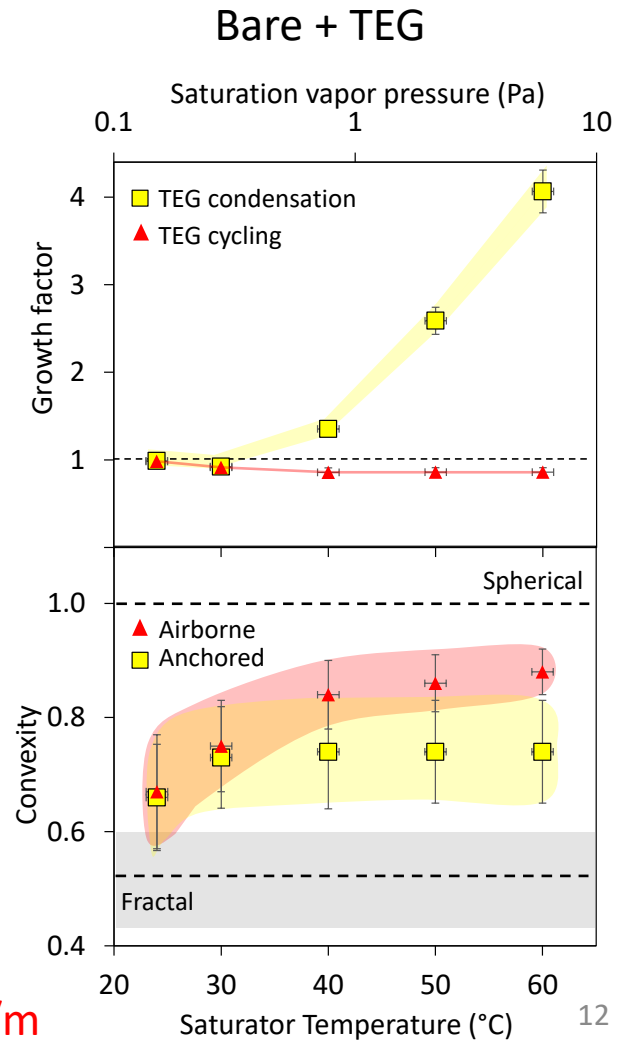


γ = 72 nN/m



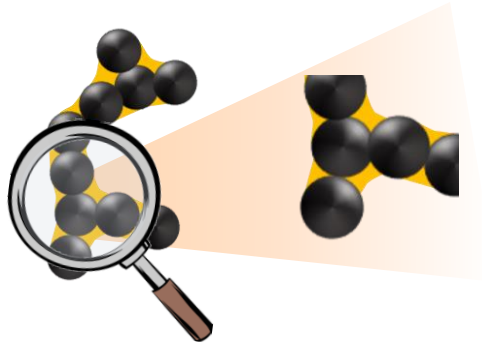
Complete restructuring during condensation!

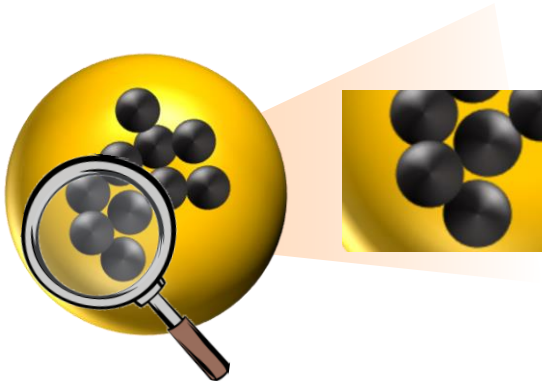
γ = 46.5 nN/m

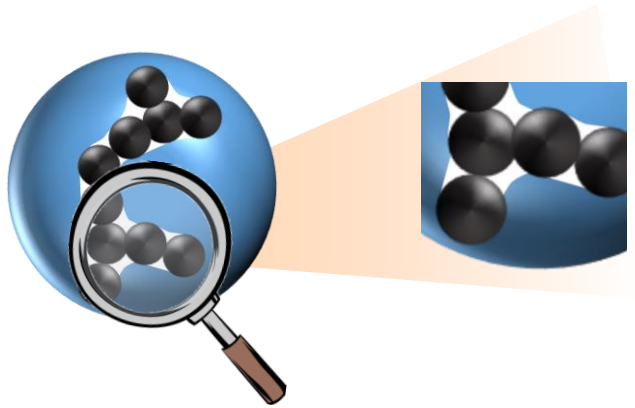


Conclusions

- Vapors of wetting fluids undergo capillary condensation even below the saturation point, promoting initial restructuring
- Additional restructuring of encapsulated aggregates is possible during evaporation, driven by the surface tension of the shrinking droplet
- Non-wetting fluids (water) do not penetrate junctions even in a fully encapsulated aggregate
- Water with a small amount of surfactant can produce compete restructuring already upon condensation
- Cloud activation of lightly-coated soot may be an important compaction route in the atmosphere







Priming affects where the collapse would occur

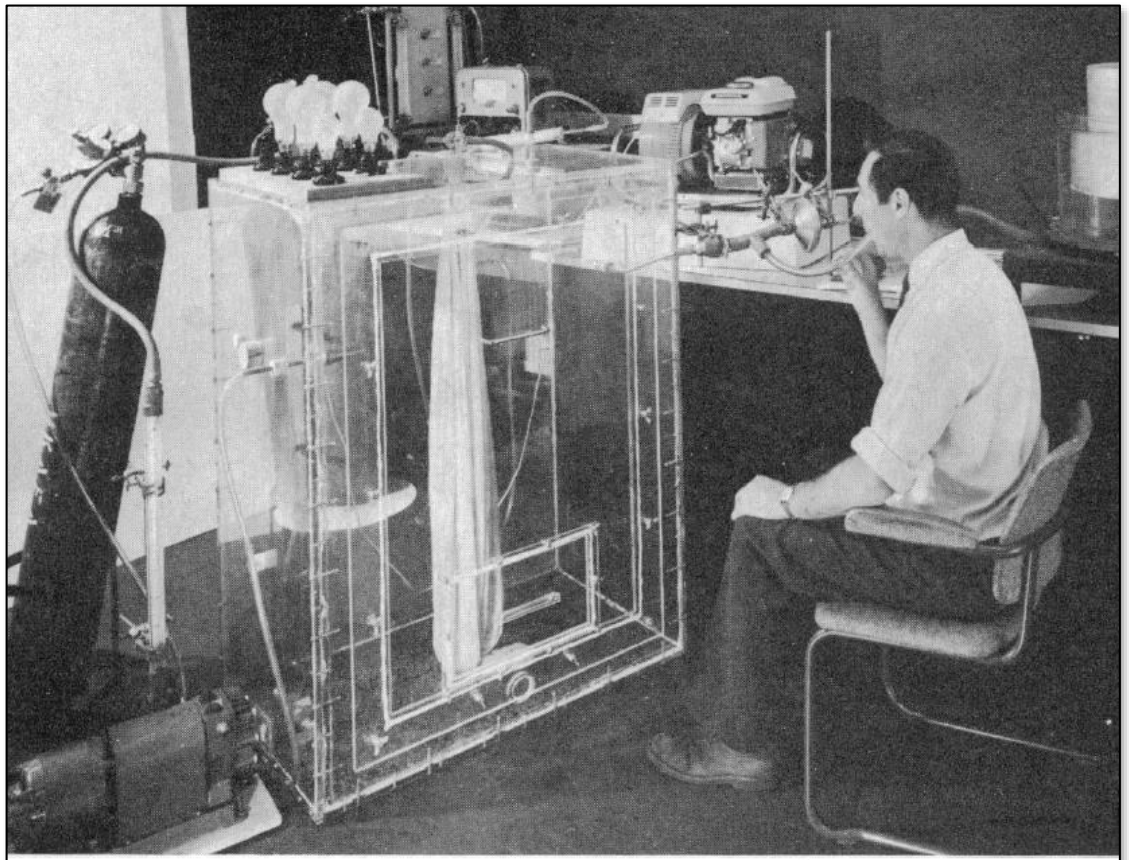
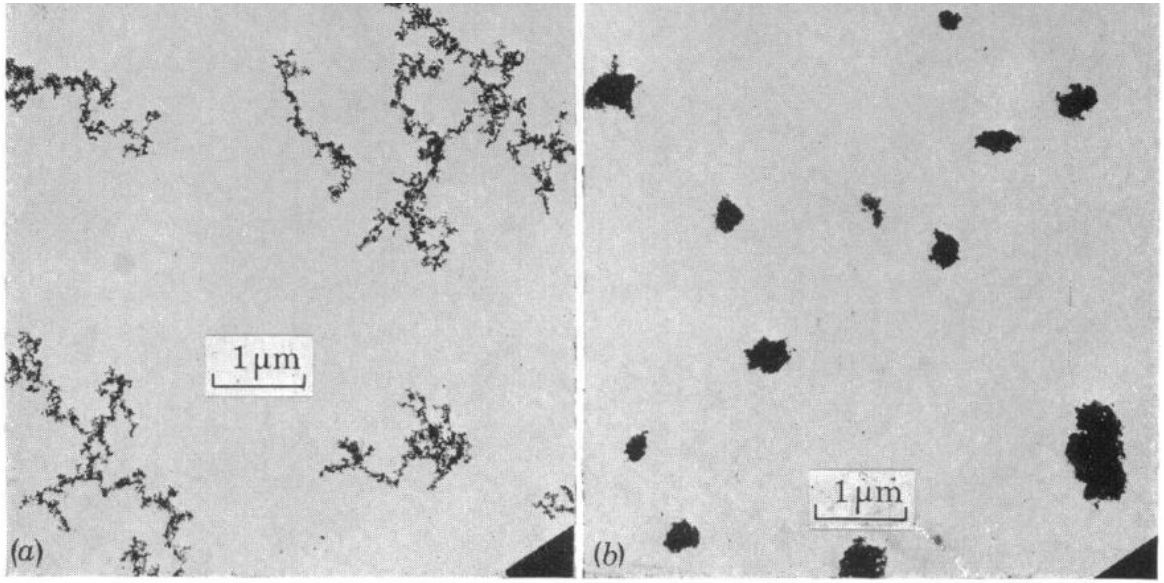


FIGURE 1. A volunteer inhaling exhaust aerosol.

Chamberlain et al., Proceedings of the Royal Society of London. Series B, Biological Sciences 1975, 192(1106), 77-110



before **after**

Bare: upon exhaling

Primed: upon inhaling, in the lungs

Acknowledgements

9CA.9 Ella Ivanova: Capillary condensation...

9CA.10 Egor Demidov: Discrete element method...

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AAAR 2023

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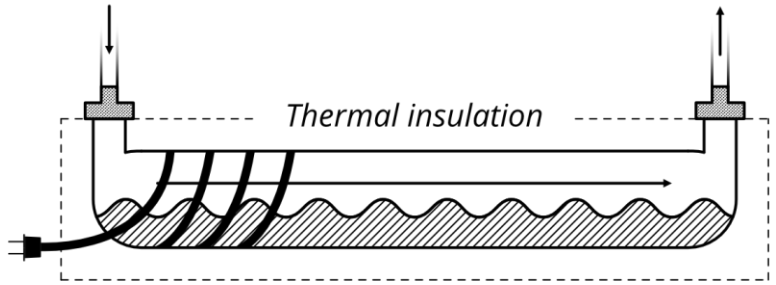
Dr. Ogo Enekwizu
(PD @ BNL)

(PD @ UC Riverside)
Dr. Ella Ivanova

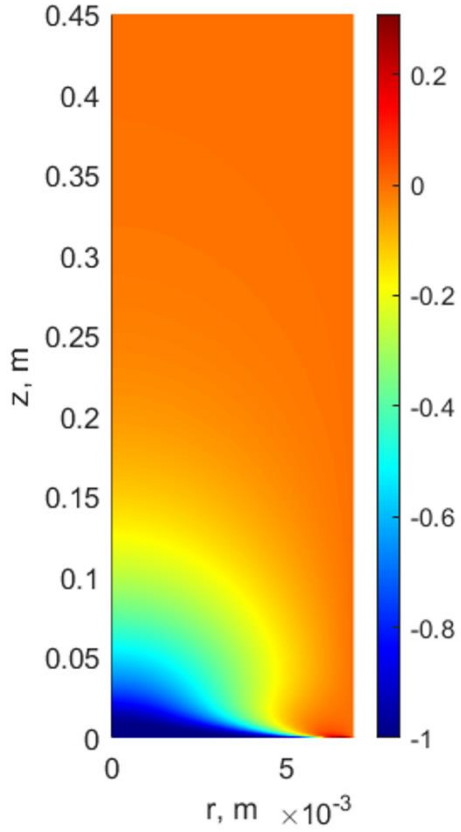
Appendix

Modeled vapor supersaturation

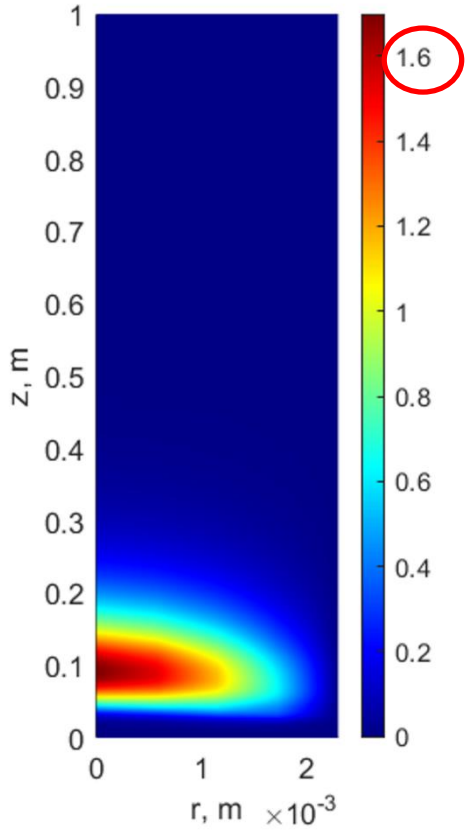
$$\frac{\partial C}{\partial t} = \nabla \cdot (D_i \nabla C) \qquad \frac{\partial T}{\partial t} = \nabla \cdot (\alpha_t \nabla T)$$



TEG

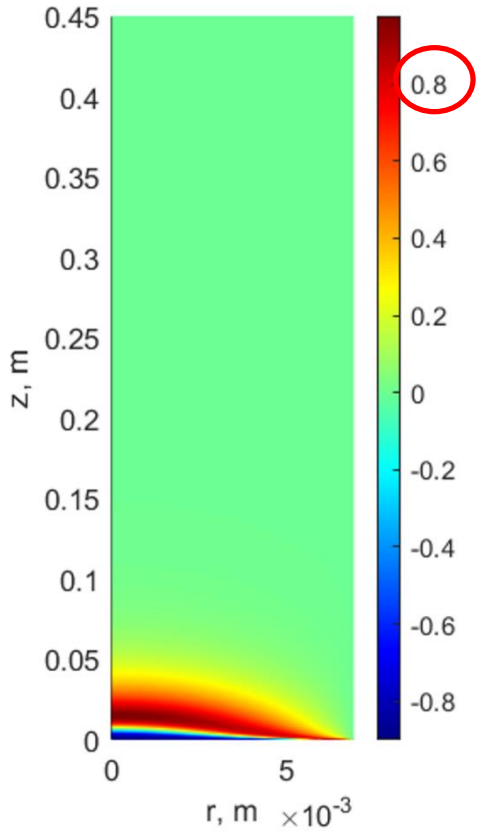


Entrance
(cold → hot)

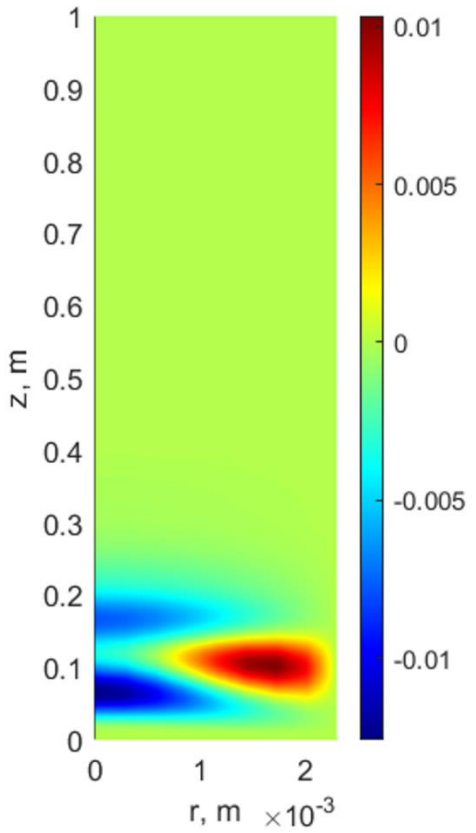


Exit
(hot → cold)

Water

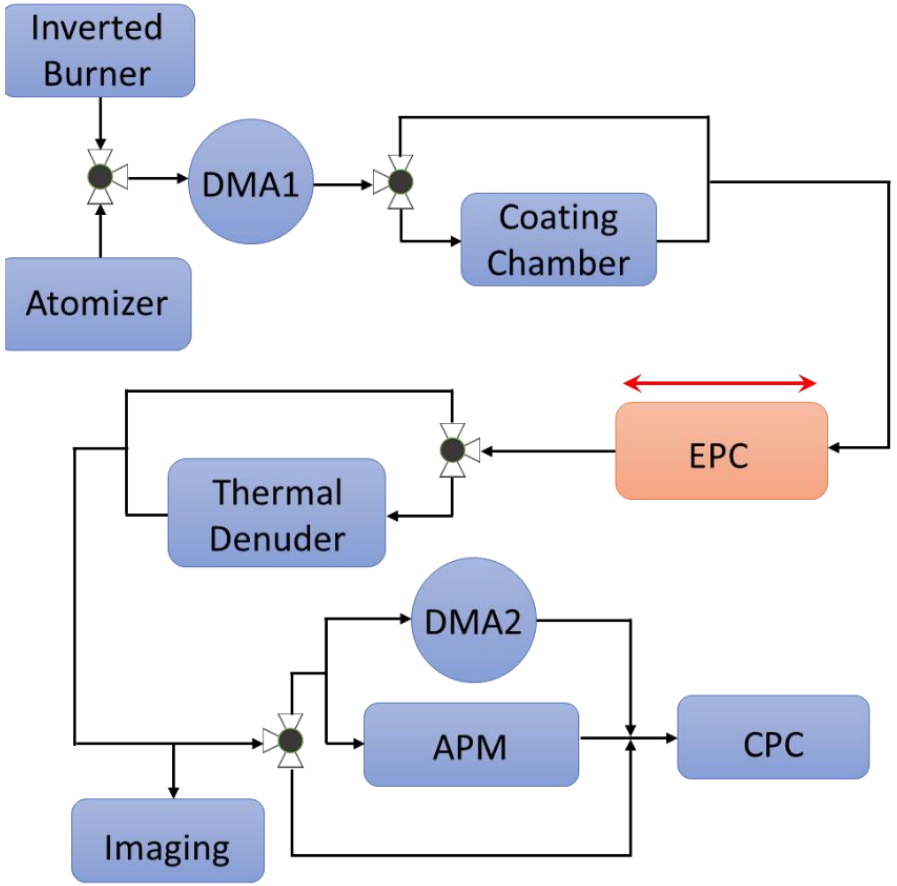


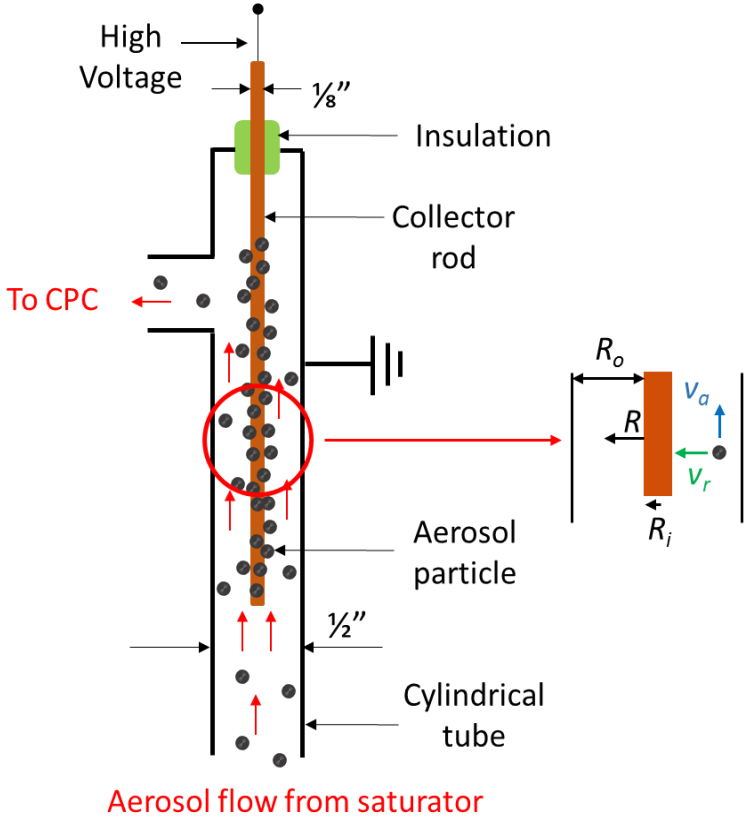
Entrance
(cold → hot)



Exit
(hot → cold)

Did we lose coating before it could be measured?





Water-processing of H_2SO_4-primed aggregates