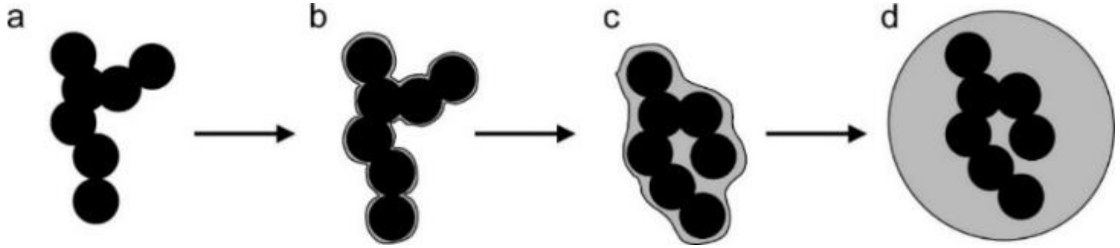
Predicting Supersaturation in a Laminar Flow

Egor Demidov, Alexei Khalizov

New Jersey Institute of Technology, Newark NJ

Background

- Condensation is a major aging pathway for atmospheric aerosols
- Aging alters their climate forcing properties
- Saturator + condenser is a common laboratory technique for simulating condensational aerosol aging



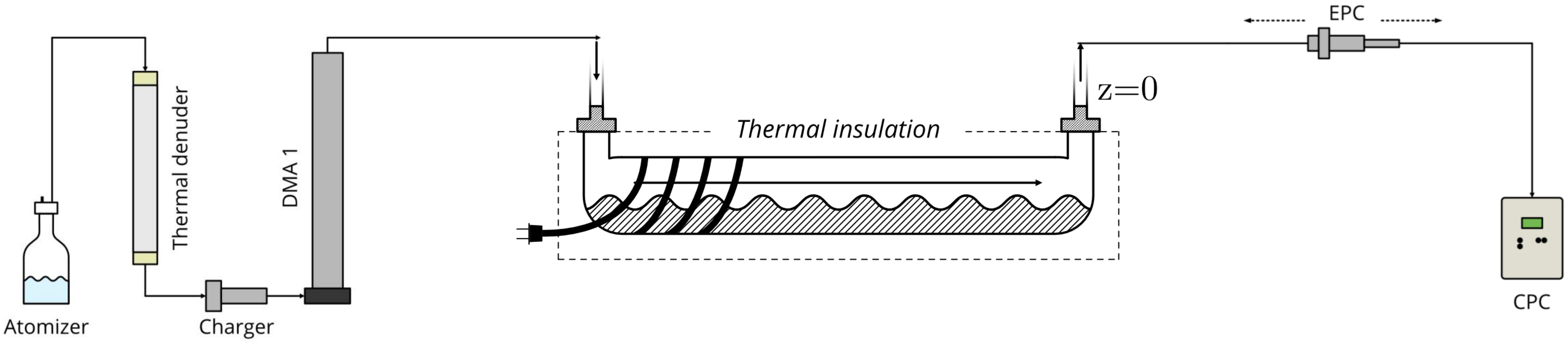
Soot aggregate acquiring coating and restructuring

Project Goal

- In a related project, we are studying experimentally condensation of different vapors on soot. Supersaturation is needed to calculate the amount of condensate.
- The goal of this project was to accurately predict how much material would condense on particles knowing saturator and condenser temperatures
- The objectives were:
    - Design an experiment for measuring particle growth
    - Solve mass and heat balances for vapor concentration and temperature as a function of position
    - Calculate particle growth
    - Compare experimental and modeled results

Experimental Setup

- Aerosol was generated, size-classified, passed through a saturator, condenser, and size was measured at different distances after the saturator
- An Electrostatic Particle Classifier (EPC) was initially installed immediately after the saturator. Then more and more tubing was added before the EPC to measure particle size as a function of distance



Modeling of Particle Growth

- Rate of growth of spherical particles depends on ambient vapor concentration and temperature (Seinfeld & Pandis, 2016)

$$\frac{dR_p}{dt} = \left(C - C_{s,Kelvin}\right) C_{FS} D_i M \frac{1}{\rho R_p}$$

Where C is ambient vapor concentration, $C_{s,Kelvin}$ is Kelvin-corrected vapor concentration near the surface of a particle, C_{FS} is a transition correction factor of choice (Fuchs & Sutugin, 1971 used here), D_i is diffusivity, M is molar mass of condensing material, ρ is density of condensing material, and R_p is particle radius

- Vapor concentration as a function of particle position in the condenser needs to be determined to calculate growth

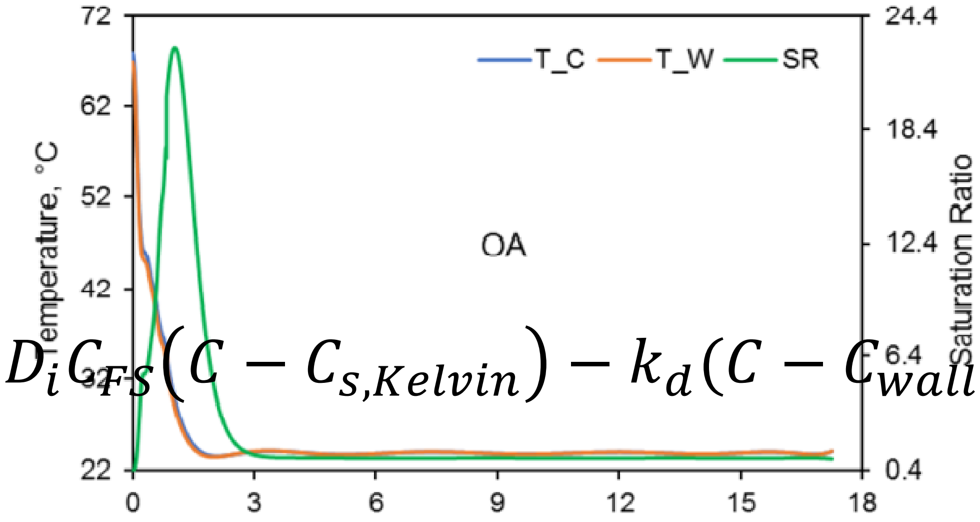
Seinfeld, J. H., & Pandis, S. N. (2016). Atmospheric Chemistry and Physics: From Air Pollution to Climate Change

Fuchs, N. A., & Sutugin, A. G. (1971). HIGH-DISPERSED AEROSOLS. In G. M. Hidy & J. R. Brock (Eds.), Topics in Current Aerosol Research (p. 1). Pergamon

1D Model

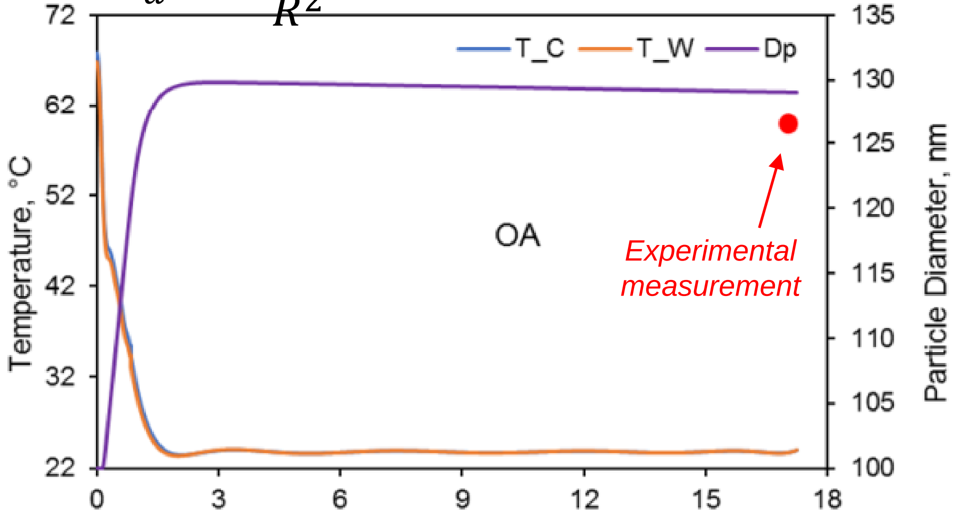
- Chen et al., 2018 used a 1D model to calculate vapor concentration and supersaturation (ζ)
- The model is primed with wall and centerline temperatures and assumes vapor is distributed uniformly across the tube

$$\frac{dC}{dt} = -4\pi n R_p D_i C_{FS}\left(C - C_{s,Kelvin}\right) - k_d\left(C - C_{wall}\right)$$



Saturation ratio, oleic acid

$$k_d = \frac{3.65 D_i}{R^2}$$



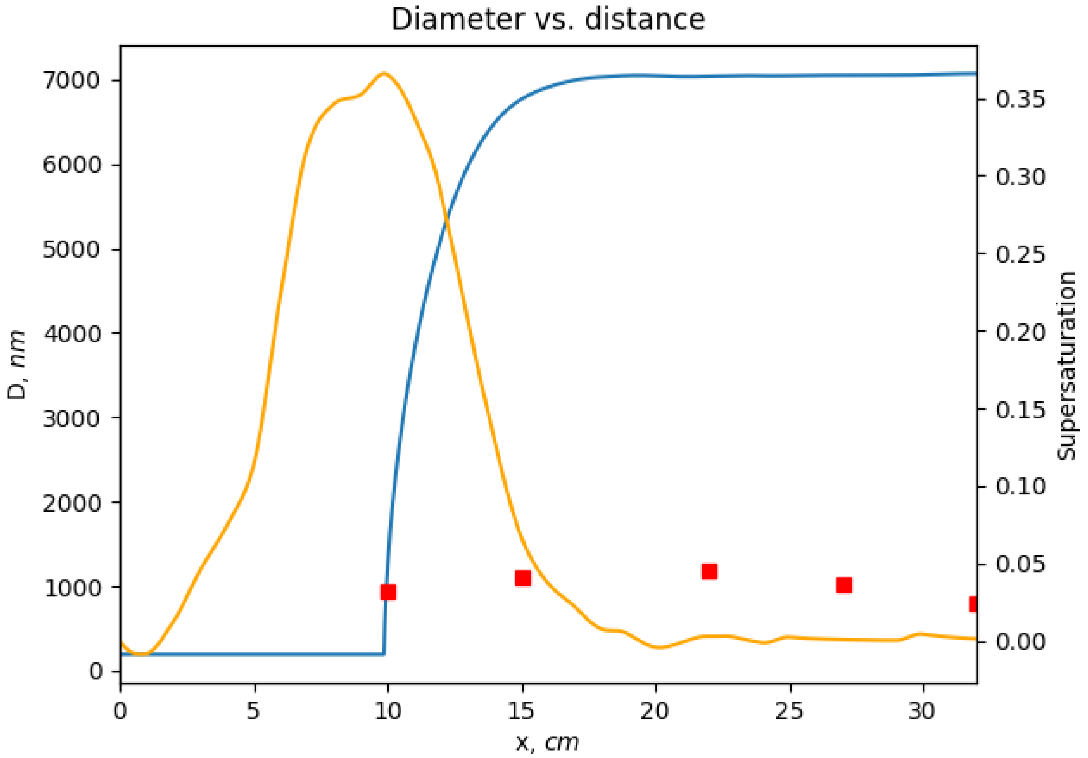
Particle diameter, 100 nm PSL

Chen, C., Enekwizu, O. Y., Fan, X., Dobrzanski, C. D., Ivanova, E. V., Ma, Y., Gor, G. Y., & Khalizov, A. F. (2018). Single Parameter for Predicting the Morphology of Atmospheric Black Carbon.

Hanson, D. R., & Eisele, F. (2000). Diffusion of H2SO4 in Humidified Nitrogen: Hydrated H2SO4.

Failure of 1D Model

- The 1D Model significantly overestimated particle growth and vapor supersaturation with water
- Attempts were made to improve the model:
    - Delayed start time for growth with water vapor (to account for hydrophobicity of soot)
    - Latent heat released by condensing water
    - Changing flow velocity due to cooling and loss of mass
- Possible reasons why closure between experiments and model wasn't attained:
    - The model relies on experimentally obtained gas temperature, which is hard to measure in a 5 mm ID tube
    - Temperature and concentration are not evenly distributed radially in a laminar flow



Water condensing on 240 nm soot, saturator at 80° C

2D Model

- Heat conduction and mass diffusion are modelled by solving two partial differential equations:

$$\frac{\partial T}{\partial t} + \vec{v} \cdot \nabla \mathrm{T} = \alpha_t \nabla^2 T$$

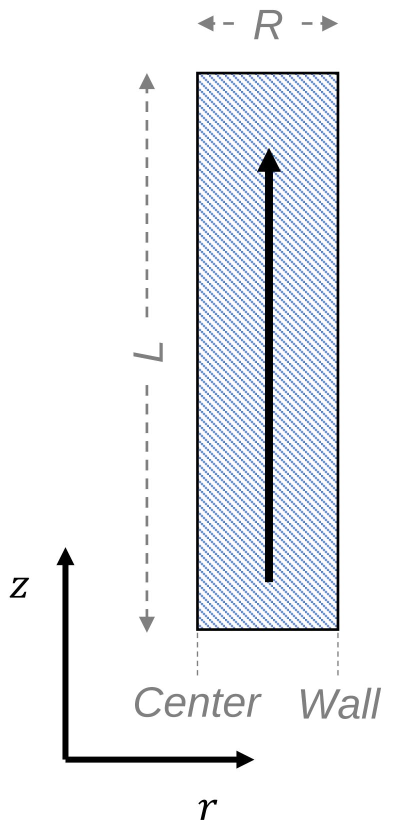
$$\frac{\partial C}{\partial t} + \vec{v} \cdot \nabla C = D_i \nabla^2 C$$

- The model is primed with wall temperature. Saturated vapor near the wall is assumed.
- For steady-state, laminar flow in cylindrical coordinates:

$$\frac{\partial T}{\partial z}\left[1 - \frac{r^2}{R^2}\right] U = \alpha_t \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right)$$

$$\frac{\partial C}{\partial z}\left[1 - \frac{r^2}{R^2}\right] U = D_i \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right)$$

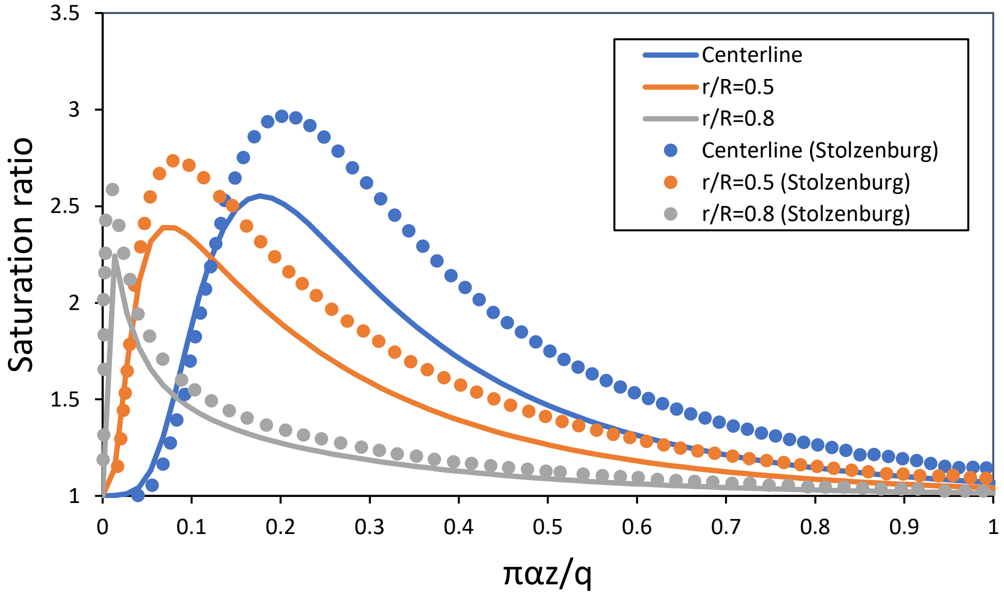
- Finite element method was used to solve the PDEs



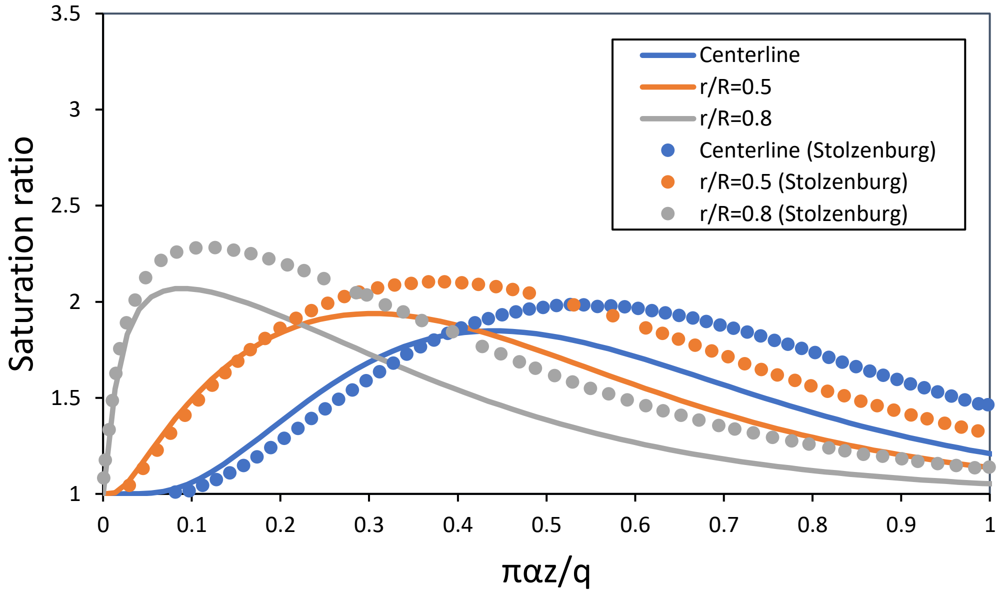
Spatial domain

Model verification

- The model has been verified against Hering & Stolzenburg, 2005
- The slight mismatch between absolute values was likely caused by the authors using a different Antoine equation (not reported in the paper)



Cold-to-hot transition



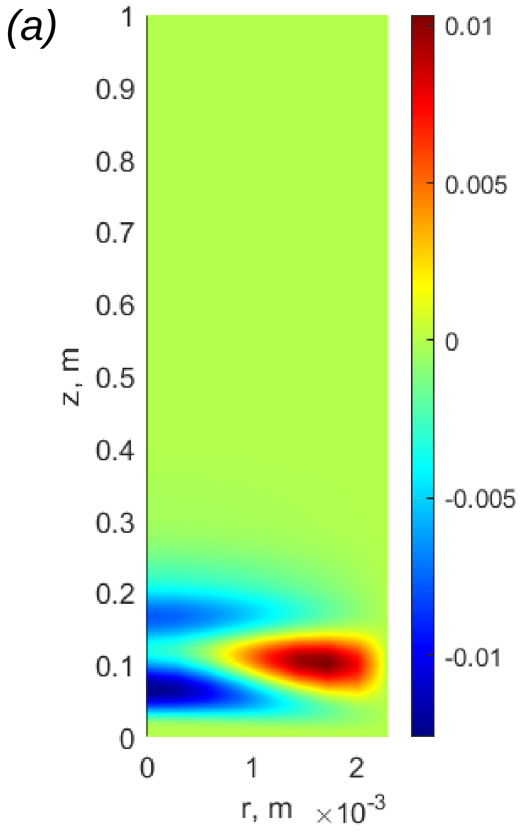
Hot-to-cold transition

Hering, S. V., & Stolzenburg, M. R. (2005). A Method for Particle Size Amplification by Water Condensation in a Laminar, Thermally Diffusive Flow. Aerosol Science and Technology, 39(5), 428–436. https://doi.org/10.1080/027868290953416

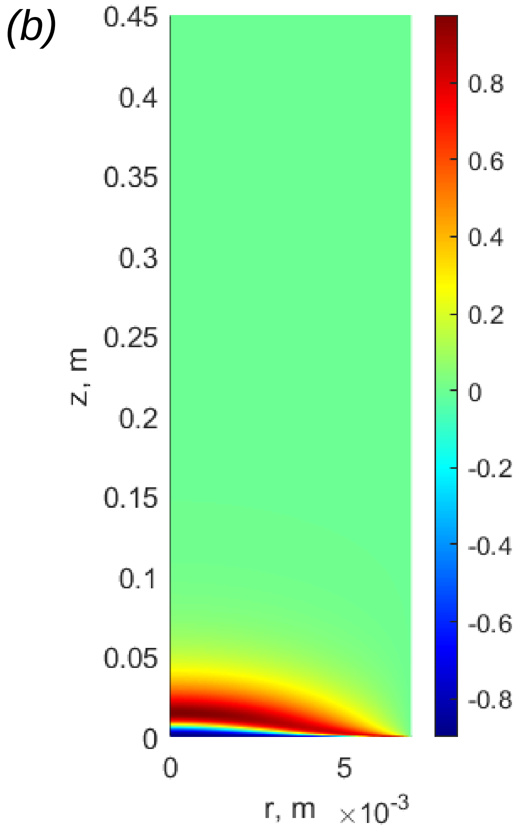
Modeled Supersaturation

$$SS = \frac{CR_gT}{P_{sat}(T)} - 1$$

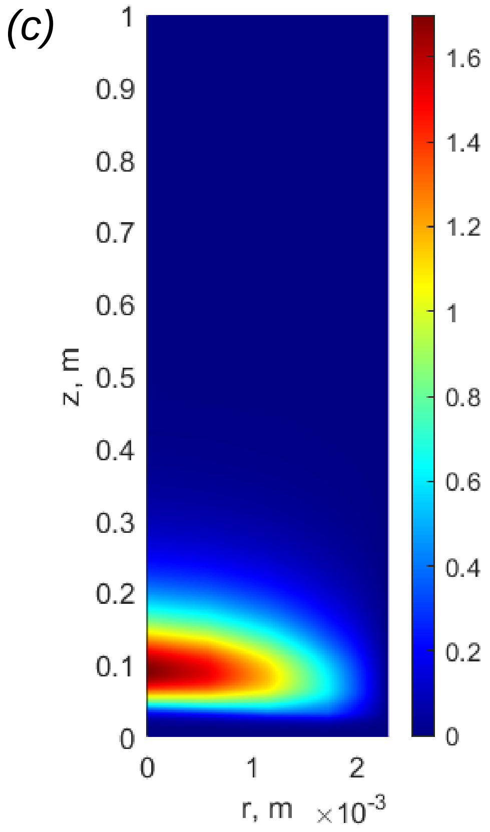
Supersaturation



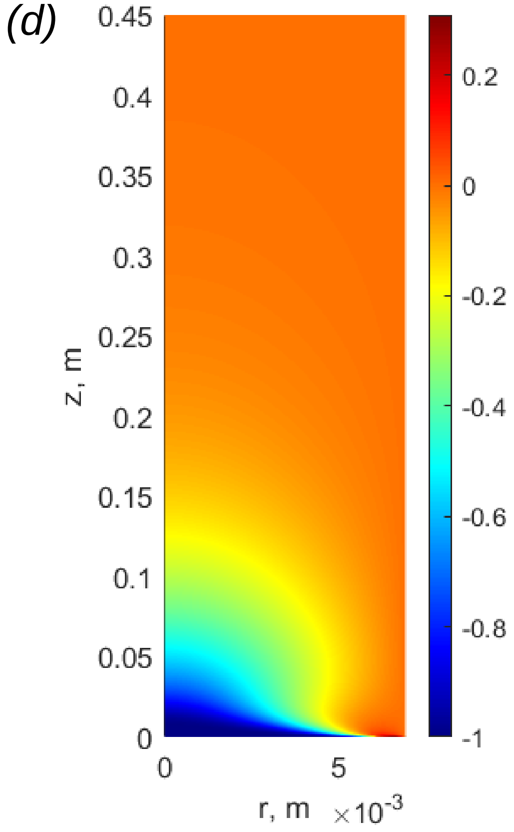
Water
hot → cold
(exit)



Water
cold → hot
(entrance)



TEG
hot → cold
(exit)



TEG
cold → hot
(entrance)

What determines the difference in supersaturation location?

- Behavior of supersaturation depends on Lewis number (Le)

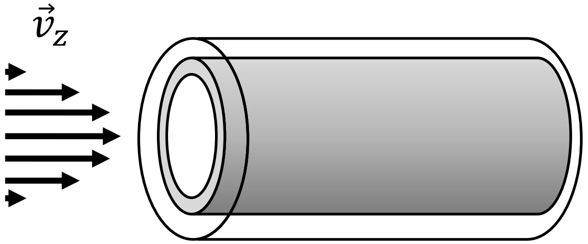
$$Le = \frac{\alpha_t}{D_i}$$

$$\alpha_t = \frac{k}{\rho C_p} \text{ (thermal diffusivity)}$$

- Lewis number depends on condensing material and diffusion medium (air in our case)

Triethylene Glycol ($Le > 1$)	**Water ($Le < 1$)**
Supersaturation is higher	Supersaturation is lower
Supersaturation occurs mostly at hot → cold transition	Supersaturation occurs mostly at cold → hot transition

Modeled vs. Measured Particle Growth

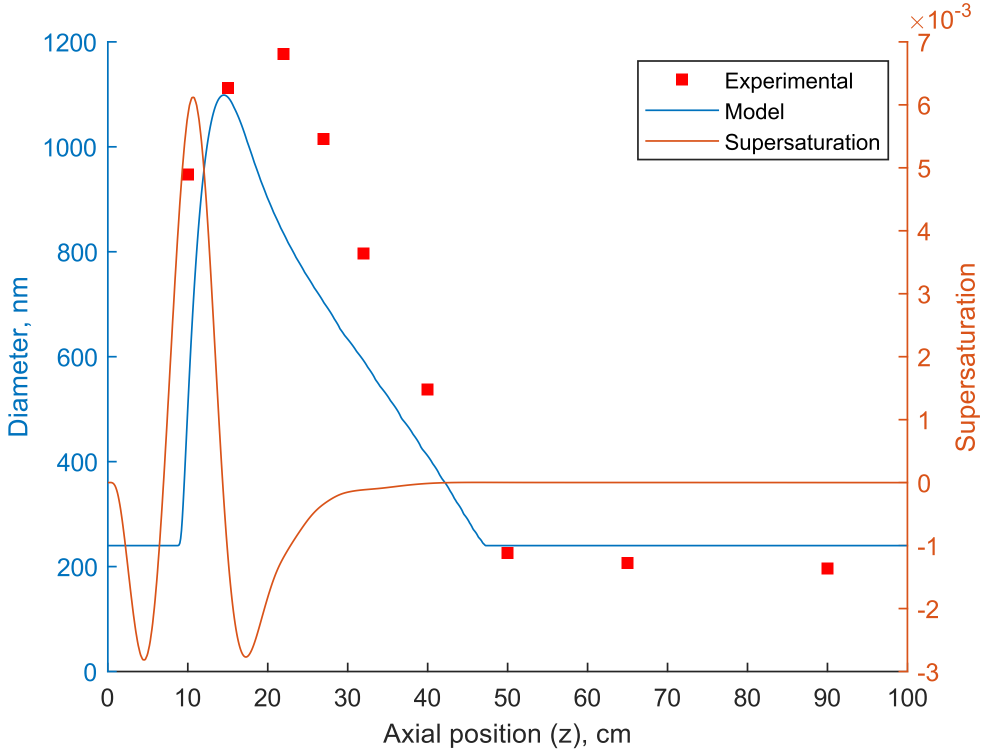


Thin shell

- Growth was calculated assuming even mass distribution over equal-width concentric shells and non-mixing layers
- Let N be the total number of shells

$$D = \frac{1}{N^2} \sum_{n=1}^{N} D_n(2n-1)$$

- D is the mean particle diameter at position z



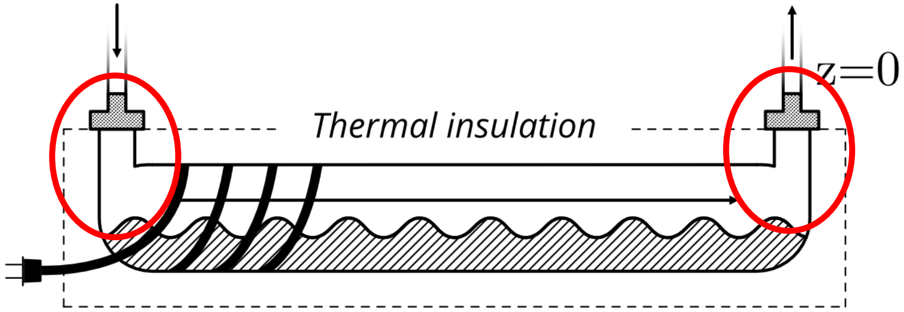
Sample growth curve, 240 nm soot, water

Conclusions

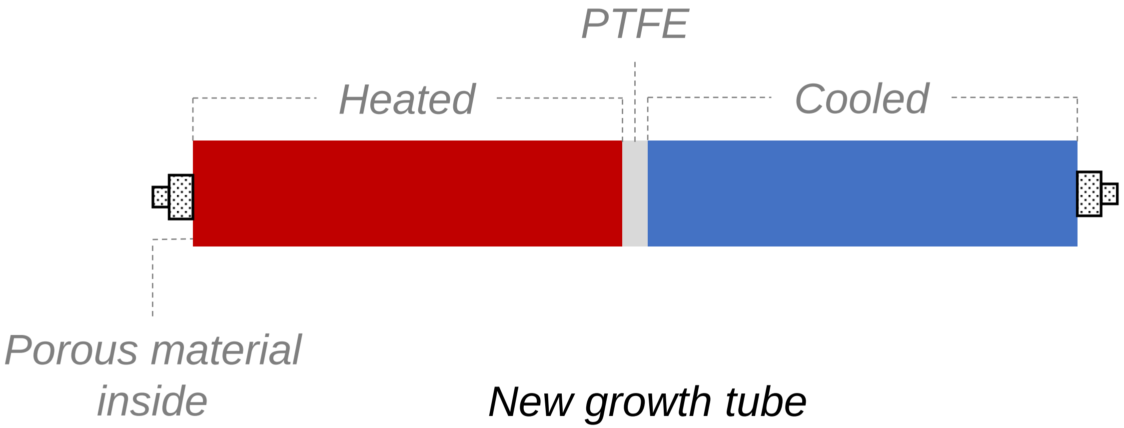
- Any laboratory aging setup will contain both transitions:
  cold → hot → cold
- However, both transitions need not be considered in most cases – one of them is usually insignificant
- Transition with the highest impact can be determined by calculating a single parameter - Le
- In this study, the amount of condensate was calculated and was close to experimental results

Future work

- Existing saturator contains areas where temperature is poorly defined
- A new growth tube is being built
- Will explore condensation of three fluids (DOS, TEG, water)



Existing saturator



New growth tube

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