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02/12/2021

Large Eddy Simulation of Aerosol Synthesis of Silica Nanoparticles in a Turbulent Flame

Presentation for the UKCTRF Meeting 2021

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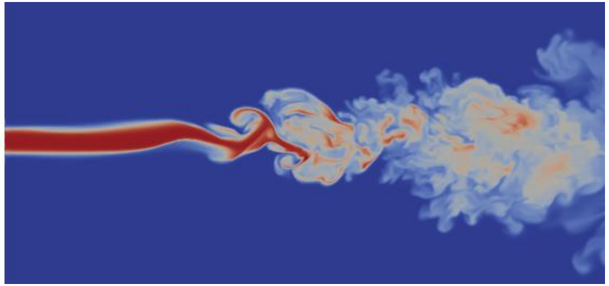
Analysis of turbulent coagulation in a jet with discretised population balance and DNS

- Turbulence-coagulation interaction is studied via Direct Numerical Simulations (**DNS**) in a planar jet.
- Reynolds decomposing the PBE leads to unknown correlations.

Evolution of M1



$$\frac{\partial \bar{n}}{\partial t} + \bar{u}_j \frac{\partial \bar{n}}{\partial x_j} + \frac{\partial\left(\overline{u'_j n'}\right)}{\partial x_j} - \frac{\partial}{\partial x_j}\left(D_p \frac{\partial \bar{n}}{\partial x_j}\right) = \frac{1}{2}\int_0^v \beta(w, v-w)\bar{n}(w)\bar{n}(v-w)dw - \int_0^\infty \beta(v,w)\bar{n}(v)\bar{n}(w)dw$$
$$+\frac{1}{2}\int_0^v \beta(w, v-w)\overline{n'(w)n'(v-w)}dw - \int_0^\infty \beta(v,w)\overline{n'(v)n'(w)}dw$$

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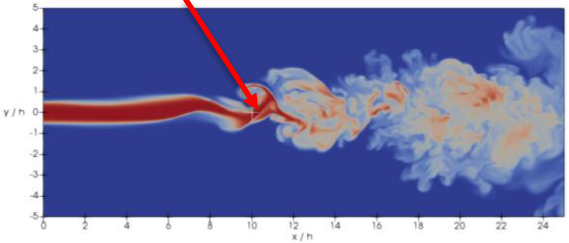
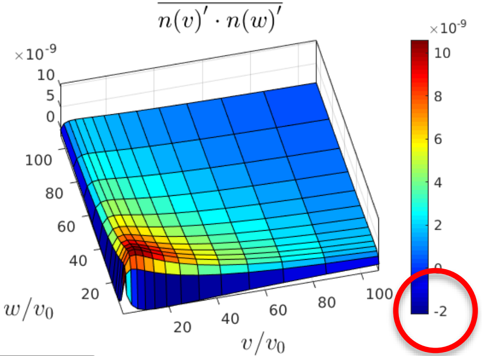
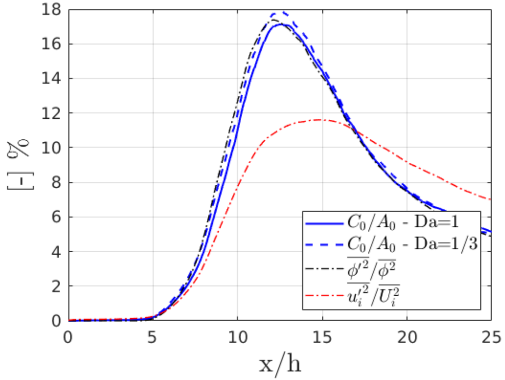
PSD Correlations

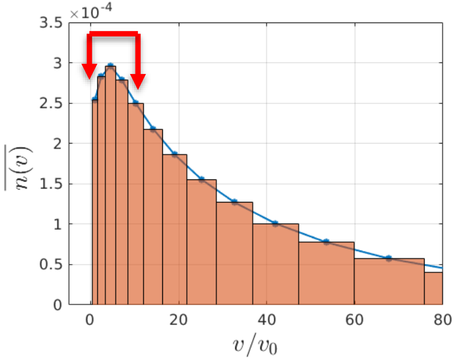
Point (10,0,0) , Da=1





- $\overline{n(v)' \cdot n(w)'}$ were mostly positive
- $\overline{n(v)' \cdot n(w)'} < 0$ close to the jet break-up point
- Were found for distant combinations of particle volumes (e.g., $\overline{n_1' \cdot n_4'}$, $\overline{n_1' \cdot n_5'}$, …)
- Same analysis for the transport equation of moments
- How much is the ratio $\frac{C_0}{A_0}$?
- Can we neglect C_0 ?





$$\underbrace{-\frac{1}{2}\iint_0^\infty \beta(v,w)\overline{n(v)n(w)}dvdw}_{A_0} = \underbrace{-\frac{1}{2}\iint_0^\infty \beta(v,w)\bar{n}(v)\bar{n}(w)dvdw}_{B_0} \underbrace{-\frac{1}{2}\iint_0^\infty \beta(v,w)\overline{n'(v)n'(w)}dvdw}_{C_0}$$

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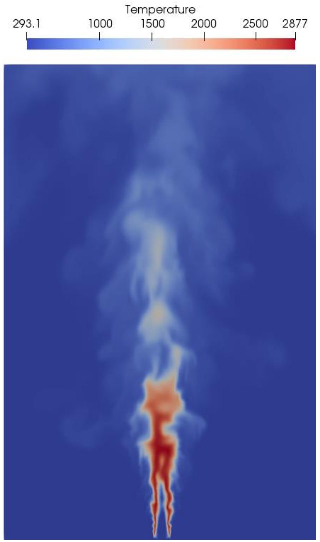

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Application and background

- Flames are used to produce
  SiO_2 nanoparticles
- size between 1 - 100 nm
- Wide range of applications
- Manufacturing of materials with enhanced properties
  - Nanocomposites
  - Photonics / Biomaterials
  - Toothpaste /Flowaid /Cosmetics

Picture borrowed from Dr. Frank Ernst’s lecture notes

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How are they made?

- The flame is the reactor!
- This route has received increased attention over the last few decades.
- Highly reactive environment. Rapid synthesis. O(100) msec
- Processes can easily be scaled-up (diffusion flames).
- Does not require the multiple steps and cleaning of liquid by-products like wet chemistry.
- Particle collection is easier from gas than liquid streams.

Objective => to increase the production rate of nanoparticles
=> control their properties

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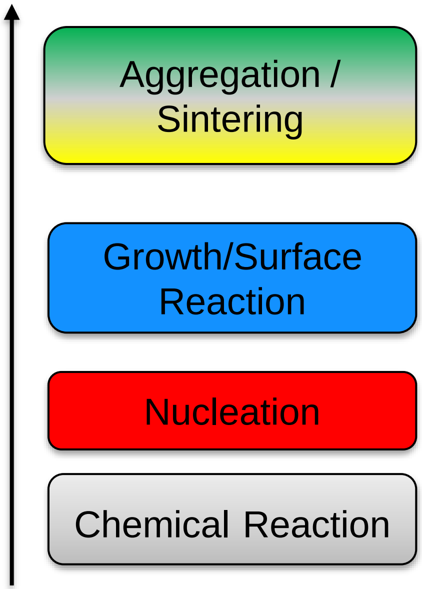
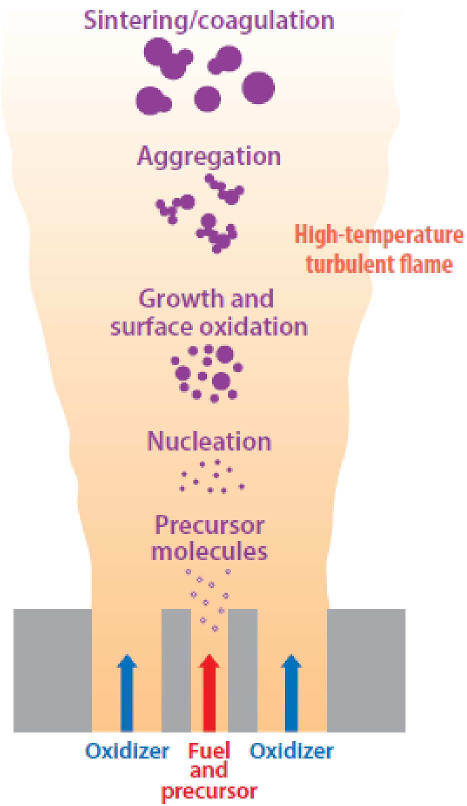
Flame synthesis of nanoparticles





Schematic borrowed from (Raman & Fox, 2016)

Raman V, Fox RO. Modeling of fine-particle formation in turbulent flames. Annual Review of Fluid Mechanics. 2016 Jan 3;48:159-90.

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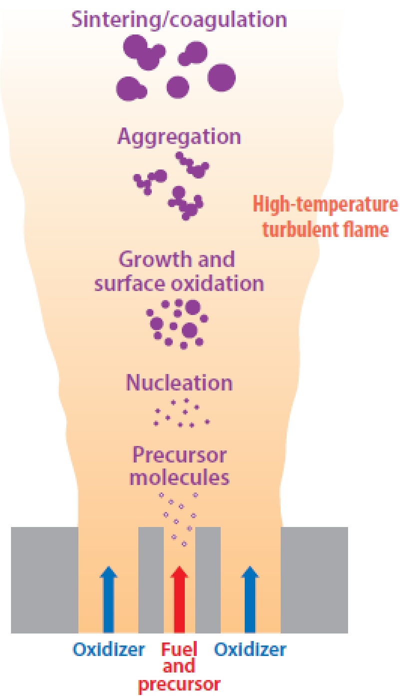
Flame synthesis of nanoparticles

Chemical Reaction

- Gas phase chemical reactions
- Vapor product (precursor)
- Precursor decomposition to monomer species

$$HMDSO + OH \rightarrow 2\,SiO + 6\,CH_3 + H$$
$$SiO + H_2O \rightarrow \mathbf{SiO_{2\,(g)}} + H2$$

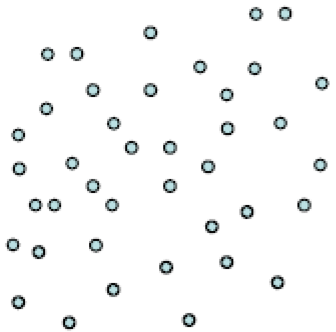


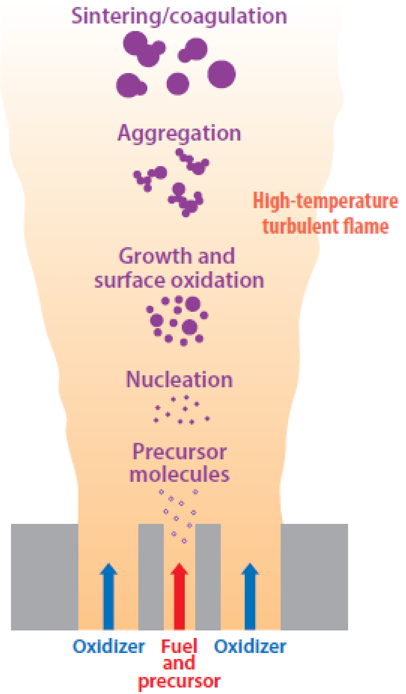
Schematic borrowed from (Raman & Fox, 2016)

Flame synthesis of nanoparticles

Chemical Reaction | Nucleation

- **Nucleation** = Formation of initial clusters
- Two scenarios:
  1. *Classical Nucleation Theory (CNT)*
     condensation ⇔ evaporation in equilibrium
  2. *Instantaneous Nucleation Assumption*
     monomers are thermodynamically stable and serve as critical clusters (nuclei)





Schematic borrowed from (Raman & Fox, 2016)

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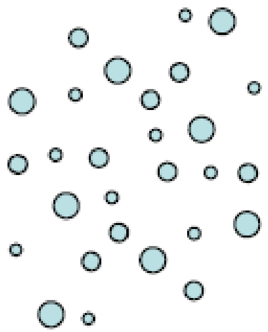
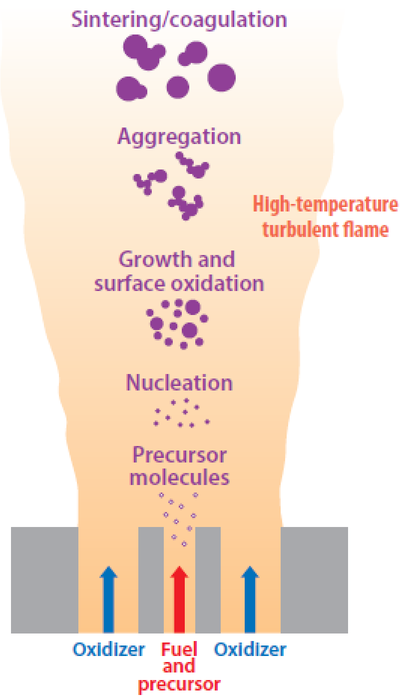
Flame synthesis of nanoparticles

Chemical Reaction | Nucleation | Growth/Surface Reaction

- **Condensation** of monomers on particles!
- Particles grow in size.
- Number concentration is not affected
- Unlike soot, surface reaction is usually ignored in studies of synthesis of metal oxides





Schematic borrowed from (Raman & Fox, 2016)

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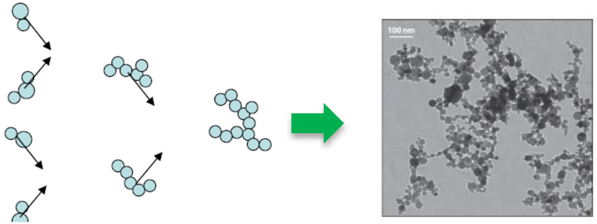
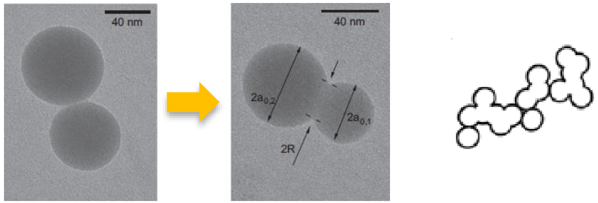
Flame synthesis of nanoparticles

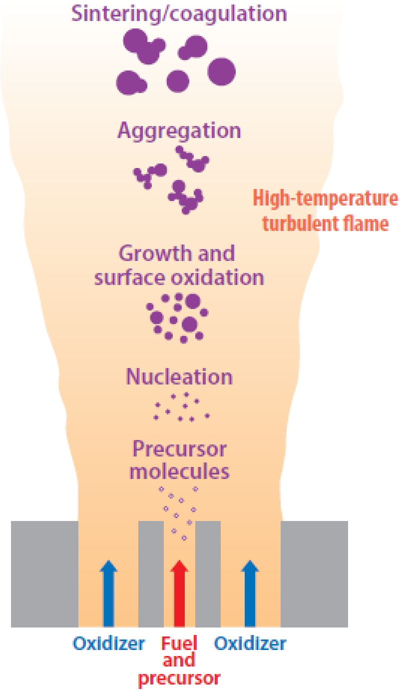
Chemical Reaction	Nucleation	Growth/Surface Reaction	Aggregation / Sintering

- **Aggregation** = collision of particles
- Number concentration is reduced



- **Sintering (Coalescence)** = particles partially coalesce
- sinter bonds and **neck formation**
- Surface area is reduced





Schematic borrowed from (Raman & Fox, 2016)

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Sources of uncertainty

- Precursor decomposition chemical kinetics
- Aerosol Dynamics
- Turbulence and subgrid-scale modelling / Complex interacting phenomena
- Uncertainties in measurements (difficult to detect nucleus-size particles)

Objective of the study

- We aim to simulate flame synthesis of silica nanoparticles in turbulent flow
- Detailed comparison with experimental data
- Identification of the main sources of uncertainties (model limitations)

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Monodisperse Model

Unknowns

- **N** = Number concentration
- **A** = Surface concentration
- **V** = Particle volume fraction

Processes

- **Nucleation**
- **Aggregation / Coagulation**
- **Sintering**

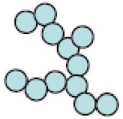
Variables

- J = particle formation rate
- a_{nuc}, v_{nuc}= surface area and volume of a nucleus
- τ_s = sintering characteristic time
- a_s = surface area of a fully fused (spherical) particle

$$\begin{cases} \dfrac{\partial(\rho \boldsymbol{N})}{\partial t} + \dfrac{\partial(\rho u_j \boldsymbol{N})}{\partial x_j} - \dfrac{\partial}{\partial x_j}\left(\dfrac{\mu}{Sc}\dfrac{\partial \boldsymbol{N}}{\partial x_j}\right) = \boldsymbol{\rho\, J} - \boldsymbol{\rho \frac{1}{2}\, \beta\, N^2} \\ \dfrac{\partial(\rho \boldsymbol{A})}{\partial t} + \dfrac{\partial(\rho u_j \boldsymbol{A})}{\partial x_j} - \dfrac{\partial}{\partial x_j}\left(\dfrac{\mu}{Sc}\dfrac{\partial \boldsymbol{A}}{\partial x_j}\right) = \boldsymbol{\rho\, J\, a_{nuc}} - \boldsymbol{\rho \frac{(A - N\, a_s)}{\tau_s}} \\ \dfrac{\partial(\rho \boldsymbol{V})}{\partial t} + \dfrac{\partial(\rho u_j \boldsymbol{V})}{\partial x_j} - \dfrac{\partial}{\partial x_j}\left(\dfrac{\mu}{Sc}\dfrac{\partial \boldsymbol{V}}{\partial x_j}\right) = \boldsymbol{\rho\, J\, v_{nuc}} \end{cases}$$

$$\boldsymbol{dp = \frac{6\, V}{A}}$$

Primary Particle Diameter



$$\boldsymbol{n_p = \frac{6\, V}{N \pi dp^3}}$$

Number of Primary Particles per aggregate

$$\boldsymbol{d_g = d_p\, n_p^{\frac{1}{Df}}}$$

Collision diameter

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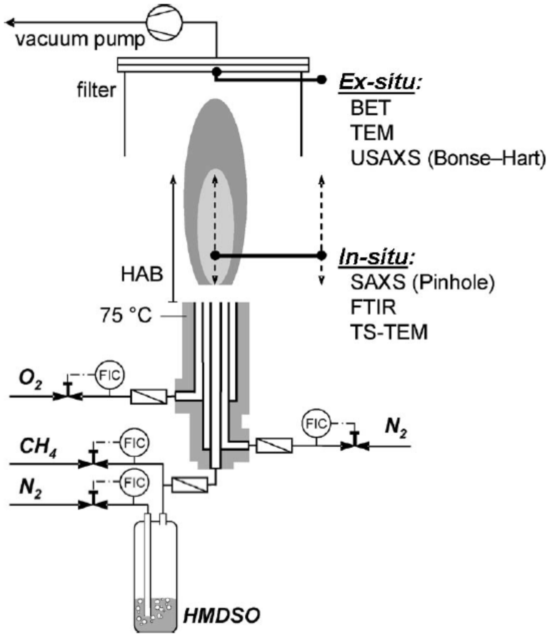
Experimental set up



- (Camenzind et al., 2008)
- ***CH4 / O2*** diffusion flame
- HMDSO => precursor (high enthalpy content)
- Silica production rate (4.8 g/h)

- Djet = **1.8 mm**!! (D1 = 3.5, D2= 4.8 mm)
- Wall Thickness = 0.3 mm
- Vjet = 5.24 m/s (V1 = 1.6 , V2 = 34 m/s)
- Re ≈ 4500
- No other simulation for this experiment

Camenzind, Adrian, et al. "Nanostructure evolution: from aggregated to spherical SiO2 particles made in diffusion flames." (2008): 911-918

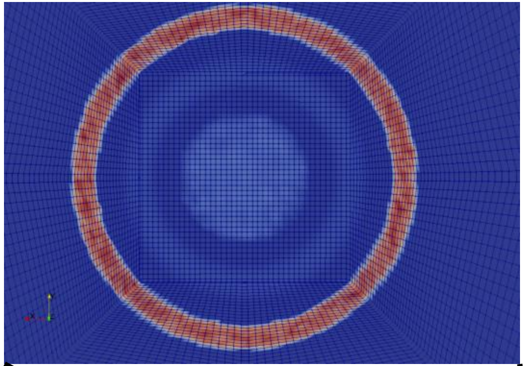
Numerical Method

- The in-house, block-structured, boundary conforming coordinate LES code BOFFIN-LES was employed.
- The pdf - stochastic field method was employed to describe turbulence-chemistry interaction and was extended for the particle monodisperse model
- GRI 1.2 + 2-step mechanism (34 gas species and 177 reactions)

$$HMDSO + OH \rightarrow 2\,SiO + 6\,CH_3 + H$$
$$SiO + H_2O \rightarrow \boldsymbol{SiO_{2\,(g)}} + H2$$

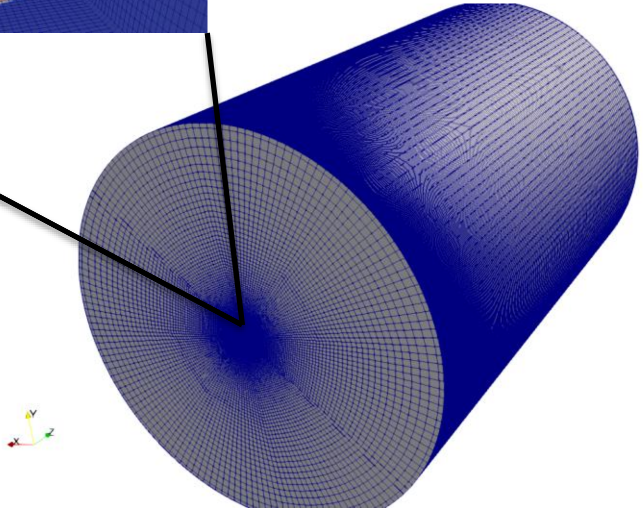
- Laminar closure for now!

Feroughi OM, Deng L, Kluge S, Dreier T, Wiggers H, Wlokas I, Schulz C. Experimental and numerical study of a HMDSO-seeded premixed laminar low-pressure flame for SiO2 nanoparticle synthesis. Proceedings of the Combustion Institute. 2017 Jan 1;36(1):1045-53



Simulation details

- Cylindrical domain (40D x 60D)
- 5M cells $(dx_{min} = 0.075\, mm)$
- 7-8 cells to capture the velocity profile
- Grid stretching in the streamwise and radial direction
- $dt = 10^{-6}\, sec$ (CFL = 0.2)
- Boundary conditions: Inlet / Symmetry / Convective outflow
- Test cases:
  - ***"InstNuc"*** = Instantaneous nucleation
  - ***"NucCond"*** = CNT + condensation



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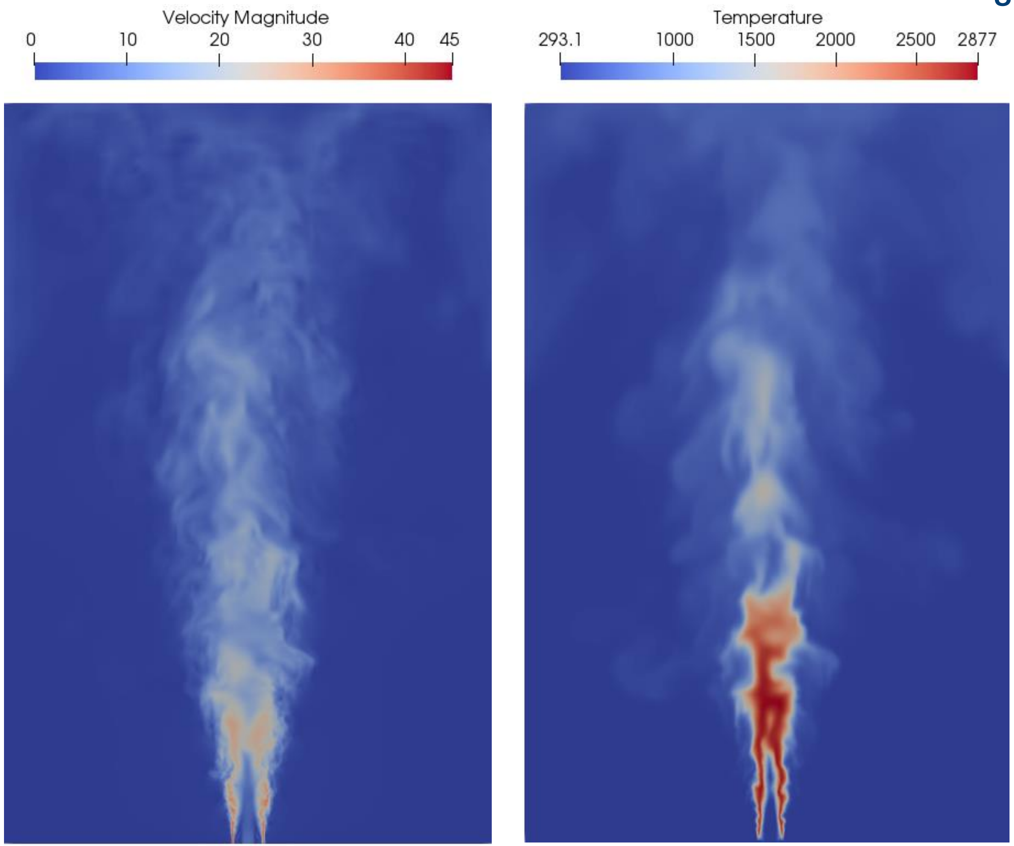
Instantaneous Fields



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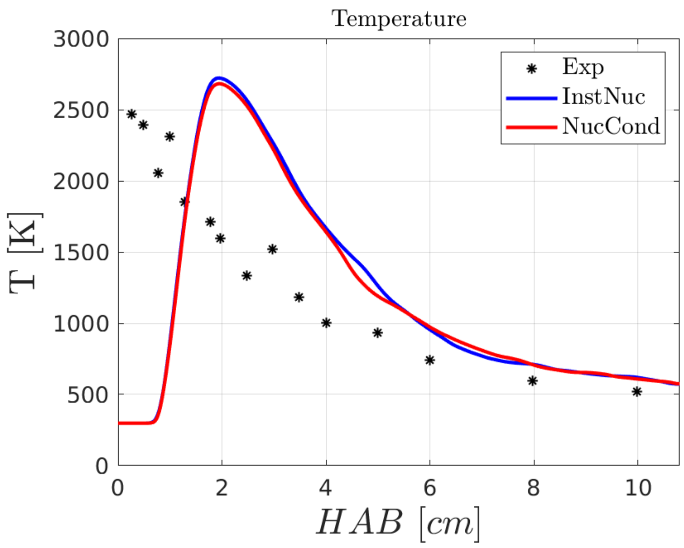
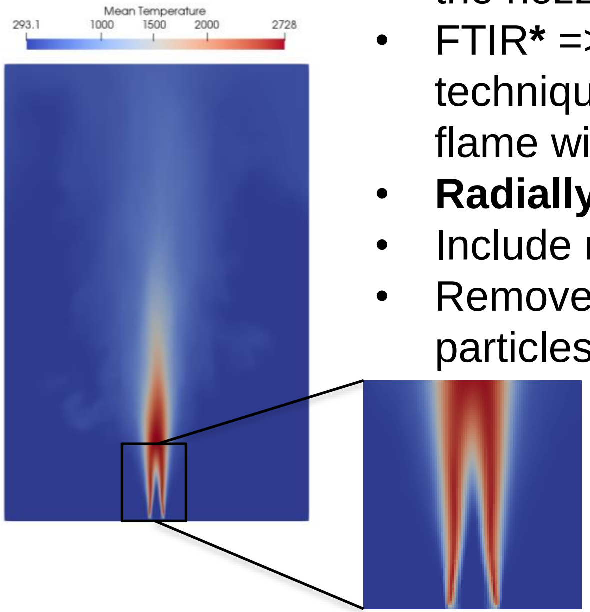
Temperature





- Discrepancies close to the nozzle are expected
- FTIR* => **line-of-sight** technique over the total flame width
- **Radially average**
- Include radiation model
- Remove enthalpy of particles

*FTIR = Fourier Transform Infrared Spectroscopy

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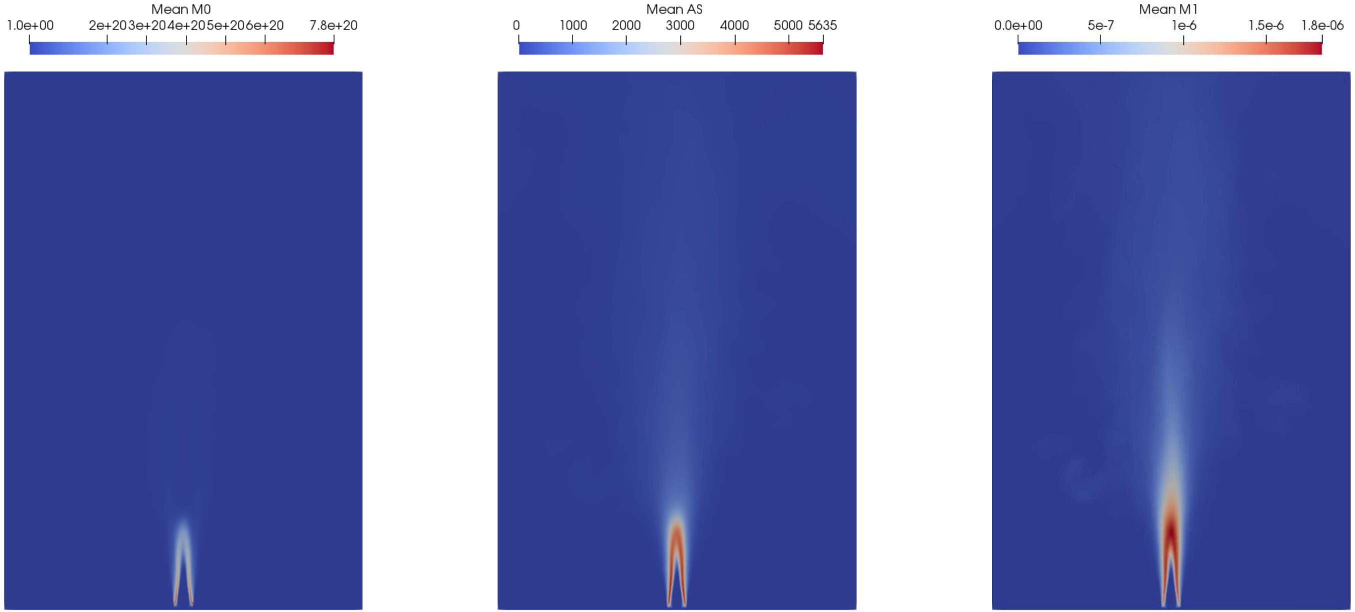
Moments



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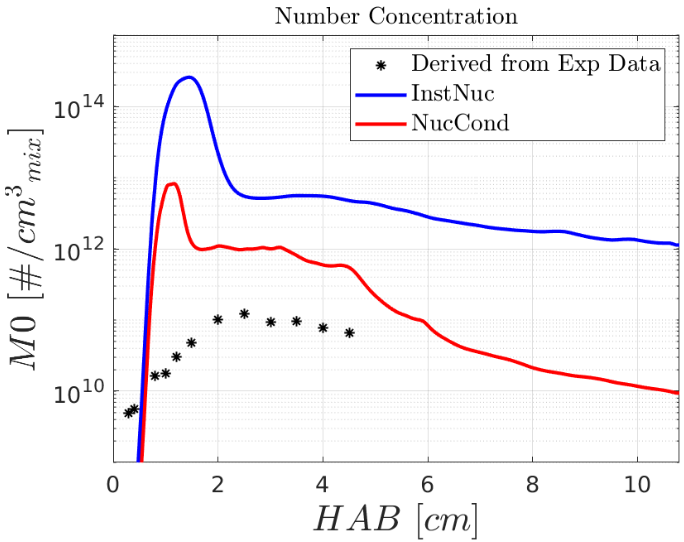
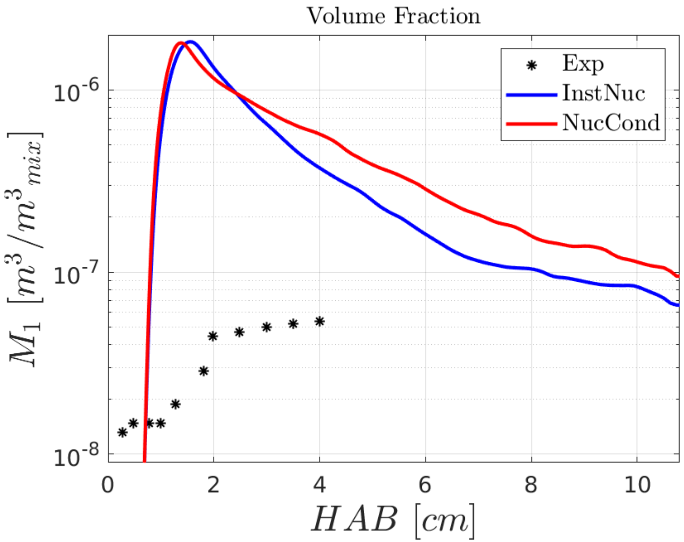
Moments





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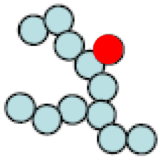
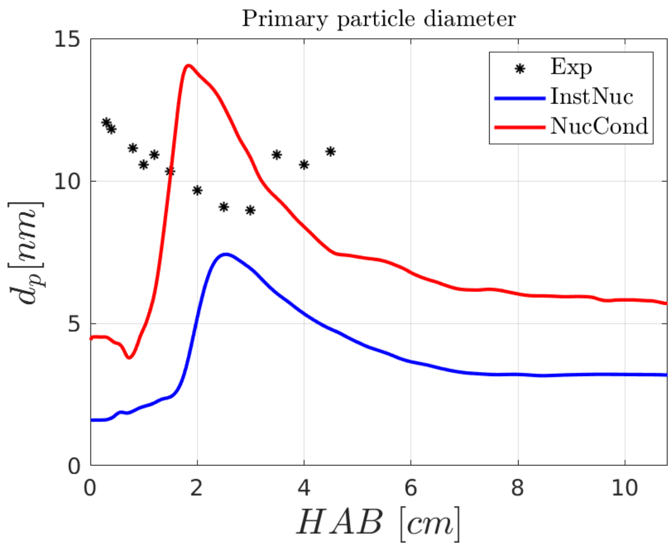
Primary Particle Diameter



$$dp = \frac{6\,V}{A}$$



- The model underpredicts the primary particle diameter
- Similar trend has been reported in other studies
- The *NucCond* kinetics give better results. => Particles grow by **condensation**!!

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Future work

- Simulate synthesis of silica nanoparticles in a **laminar flame**
- Test detailed reaction mechanism for the decomposition of the precursor
- Use discretized population balance models
- Use information from laminar case to simulate the turbulent case

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Conclusions

- Flame synthesis of silica nanoparticles in a diffusion flame was simulated.
- A monodisperse model was employed.
- Results were compared with detailed experimental data.
- The model overpredicted the particle volume fraction and the number concentration of particles.
- Presumably, because of uncertainties the precursor-decomposition kinetics or in the validity of the instantaneous-nucleation assumption

Acknowledgment

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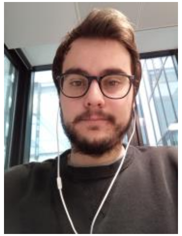
Thank You!



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Dr Stelios Rigopoulos

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Aerosol synthesis in turbulent flows

- In most of the cases, particle formation and growth occur in turbulent flows

- **Numerical simulations** → powerful tool to:
  - Describe such complex phenomena (gain physical insight)
  - Design efficient systems in industrial processes (aerosol chambers)