Modelling of aerosol synthesis of silica nanoparticles in laminar and turbulent flames

UKCTRF Annual Meeting 2022

Presenter: **Malamas Tsagkaridis** (mt6018@ic.ac.uk)

Supervisors: Dr Stelios Rigopoulos and Prof George Papadakis

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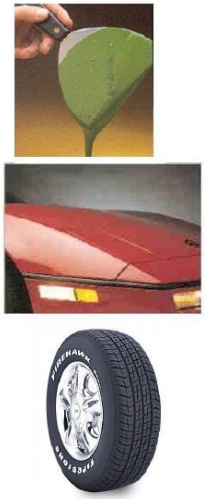
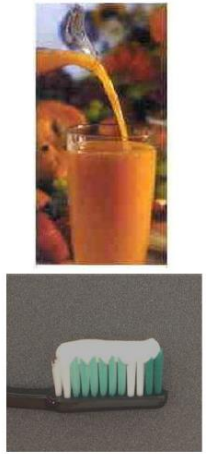
Application and background

- The flame is the reactor
- carbon black, TiO2, SiO2
- Size between 1 - 100 nm
- Wide range of applications
- Manufacturing of materials with enhanced properties
  - Nanocomposites
  - Gas sensors / Catalysts
  - Biomaterials / Photonics





Picture borrowed from Dr. Frank Ernst's lecture notes

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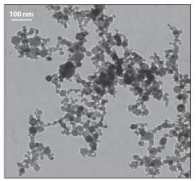
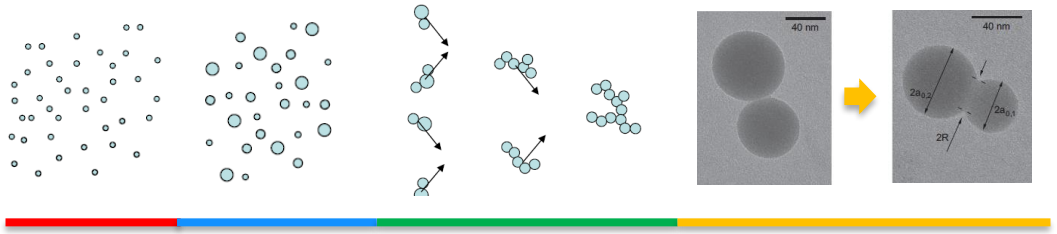
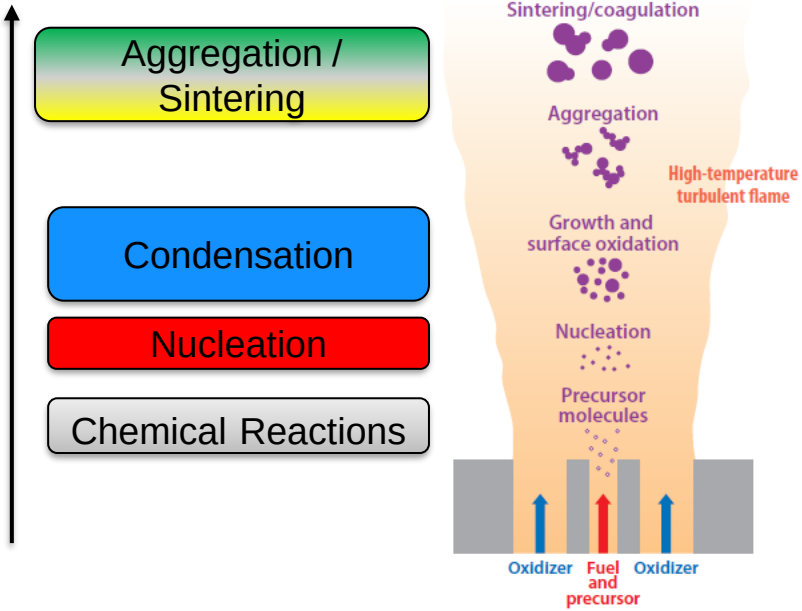
Flame synthesis of nanoparticles

- All these processes take place at different scales!
- **Prediction of particle morphology is a challenge**







Schematic borrowed from (Raman & Fox, 2016)

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Objectives of the study

- Propose a novel **extended one-PBE model** for aggregation and sintering
- Couple the PBE model with CFD
- Use the same model to simulate flame synthesis of silica nanoparticles in both **laminar** and **turbulent** flows
  - Simulate "***S2***" and "**S10**" flames of Camenzind et al. (2008)
- Compare with available experimental ***in-situ*** *SAXS* data
- Identify main sources of **uncertainties**

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

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Extended one-PBE model

Unknowns

- $n(v)$ = number density of aggregates of volume v
- N_p = number concentration of primary particles

Processes

- **Nucleation**
- **Condensation**
- **Aggregation**
- **Sintering**

$v_p = \frac{V}{N_p}$ Primary Particle Volume

$n_p = \frac{N_p}{N}$ Number of Primary Particles per aggregate

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

$$\frac{\partial n}{\partial t} + u_j \frac{\partial n}{\partial x_j} = \frac{\partial}{\partial x_j}\left(D_p \frac{\partial n}{\partial x_j}\right) + B\delta(v - v_{nuc}) + C(Y, v)$$
$$+ \frac{1}{2}\int_0^v \beta(w, v-w)\, n(w) n(v-w)\, dw - \int_0^\infty \beta(v, w) n(v) n(w)\, dw$$

$$\frac{\partial N_p}{\partial t} + \frac{\partial (u_j N_p)}{\partial x_j} - \frac{\partial}{\partial x_j}\left(D_p \frac{\partial N_p}{\partial x_j}\right) = J - \frac{3}{\tau_s}\left(\frac{V}{v_p} - \frac{M_{23}}{v_p^{2/3}}\right)$$

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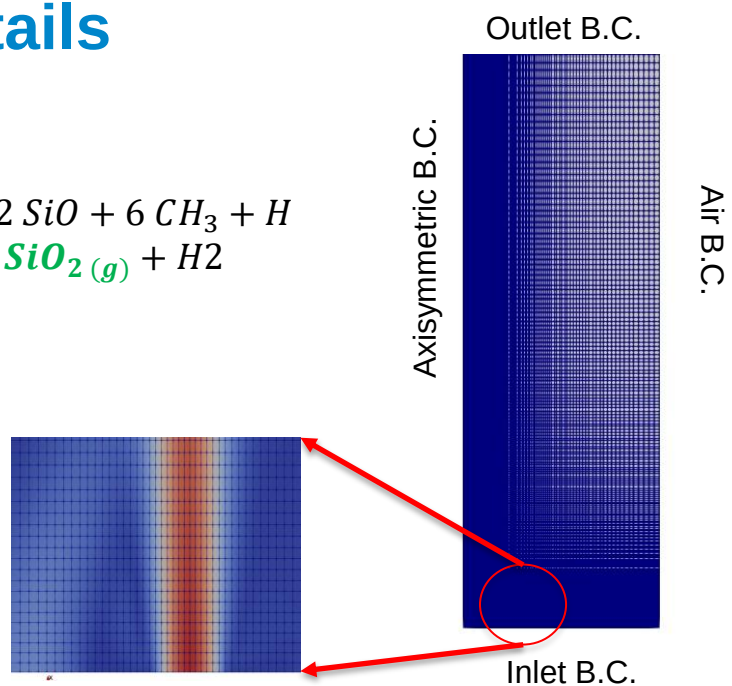
Model summary and numerical details

- Our in-house CFD code ***BOFFIN***
- GRI 1.2 + 2-step mechanism*
- Aerosol kinetics
  - *Formation of dimers (Shekar et al., 2012)*
  - *Condensation (free molecular)*
  - *Coagulation (Pratsinis, 1988)*
  - *Sintering (Tsantilis et al, 2001)*
- Radiation from gas species and particles
- Turbulent flow: PBE-PDF stochastic fields
- Laminar flow: 2-D domain (# Cells = 43000)

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



*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

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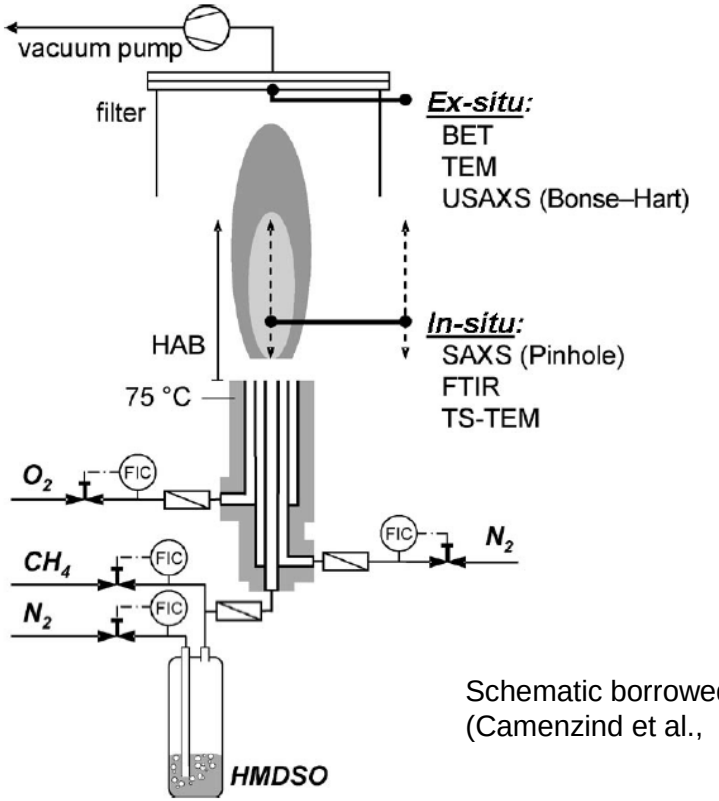
Reactor

- HMDSO + CH4
- By changing the O2 flow rate we change the flow regime!
- Laminar case (Re ≈ 1430)
- Turbulent case (Re = 4461)
- Same set of models for gas-phase chemistry and aerosol dynamics
- We aim to shed light on the nature of discrepancies between predictions and experimental results



Schematic borrowed from (Camenzind et al., 2008)

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Laminar Flame

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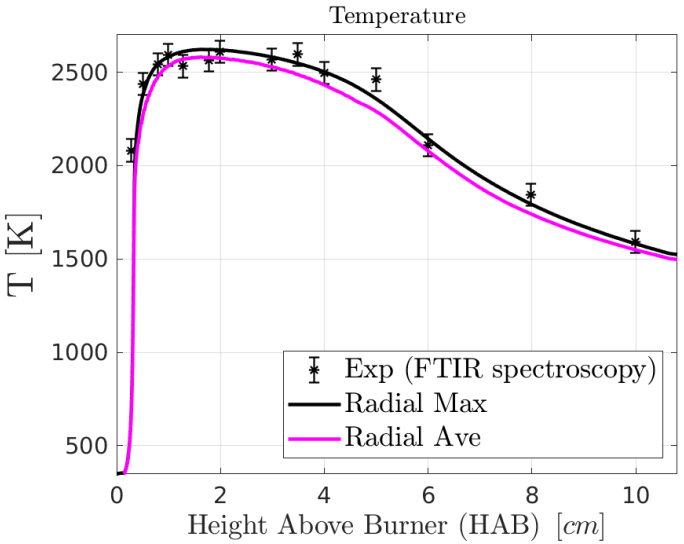
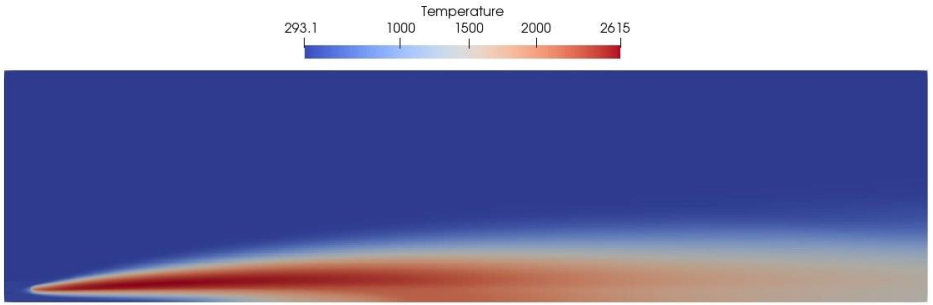
Comparison of temperature with FTIR data



- Centreline data ≠ Exp data
- FTIR* => line-of-sight technique
- Radial Averaging ($C_{CO2} > 0.8\, C_{CO2,max}$)
- Error bars (±60K)



*FTIR = Fourier Transform Infrared Spectroscopy

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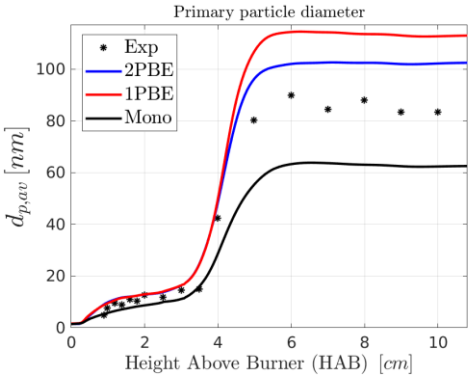
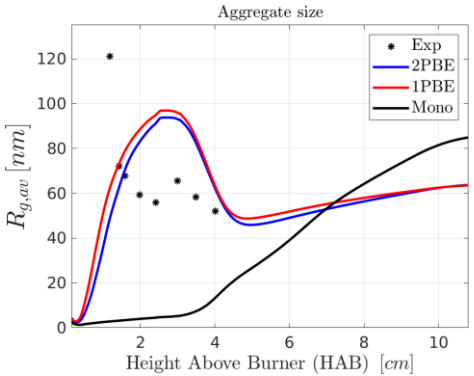
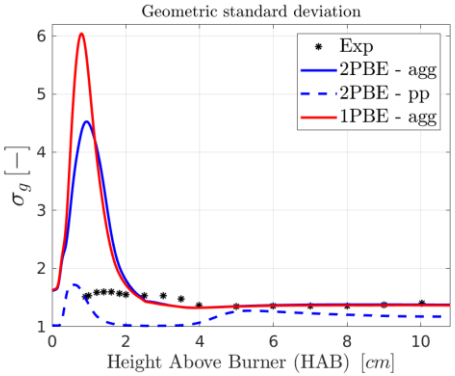
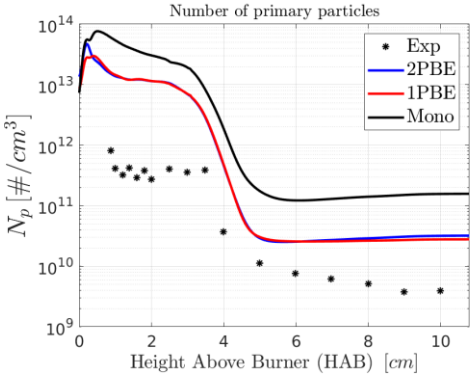
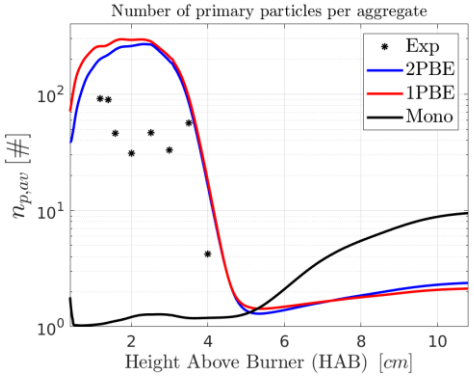
Comparison with experimental *in-situ* SAXS data











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CPU times

- Coagulation kernel is tabulated for computational speed up
- The extended 1PBE model is **only two times slower** that the Monodisperse model

Laminar Flow	**Mono**	**2PBE**	**1PBE – tabulated**
CPU time (s) / timestep	0.187	1.145	**0.32**
No. of equations	3	114	**61**

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Turbulent Flame

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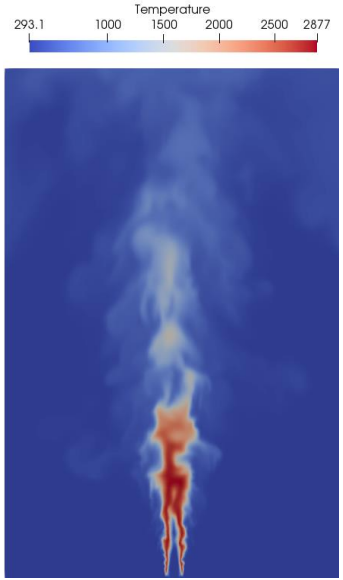
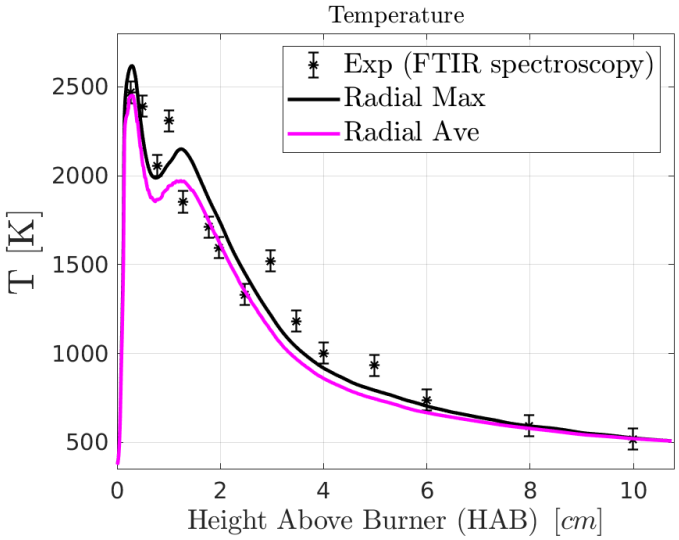
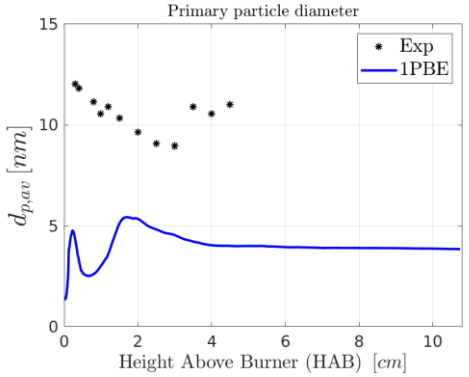
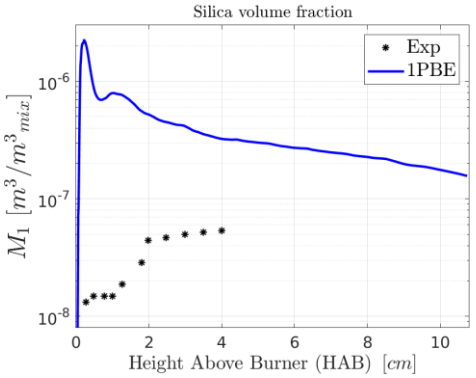
Turbulent flame









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Conclusions

- An **extended one-PBE** model for aggregation and sintering was developed and validated
- Flame synthesis of silica nanoparticles in both **laminar** and **turbulent** flames was simulated.
- Results were compared with available ***in-situ*** *SAXS* data.
- Coupling of CFD with the extended one-PBE is **computationally feasible**
- Results summary:
  - Excellent agreement was found for temperature profiles.
  - The model is capable to reproduce trends
  - Good agreement was found between the one-PBE and two-PBE models.

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Acknowledgment

- This work used the **ARCHER2** UK National Supercomputing Service (https://www.archer2.ac.uk).
- We are grateful to the UK Materials and Molecular Modelling Hub for computational resources, which is partially funded by EPSRC (EP/P020194/1 and EP/T022213/1).
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UK CTRF UK CONSORTIUM ON TURBULENT REACTING FLOWS 2014 - 2023

EPSRC Engineering and Physical Sciences Research Council

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Thank You!

Malamas Tsagkaridis
✉ *mt6018@ic.ac.uk*

Contributions

- ✓ Development and validation of an **extended one-PBE model** for aggregation and sintering
- ✓ Modelling of flame synthesis of silica nanoparticles in both **laminar** and **turbulent** flames
- ✓ Comparison with detailed in-situ SAXS data **for the first time**

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Appendix

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Contents

1. Introduction
2. Methodology
3. Results
4. Conclusions

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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 / **particle morphology**

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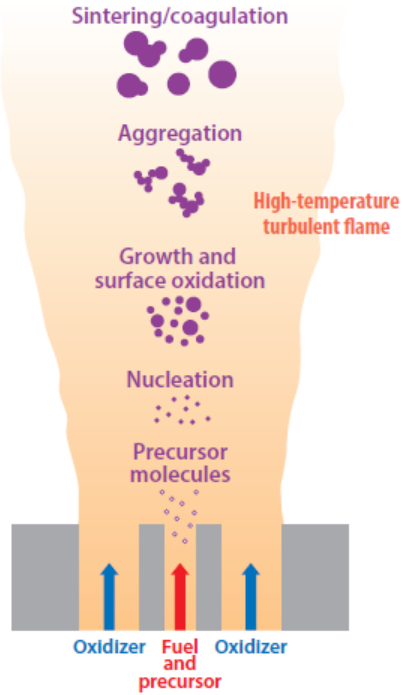
Flame synthesis of nanoparticles

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)

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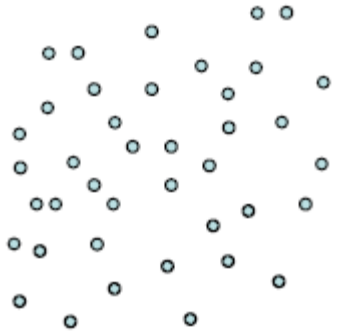
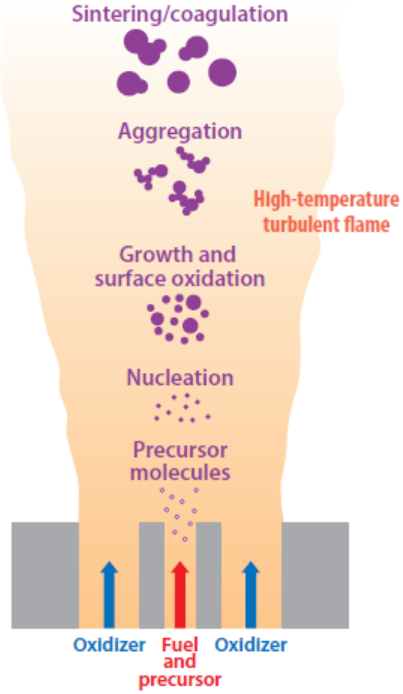
Flame synthesis of nanoparticles

Chemical Reaction | Nucleation

- **Nucleation** = Formation of initial clusters
- Three scenarios:
  1. *Classical Nucleation Theory (CNT)*
  2. *Instantaneous Nucleation Assumption*
  3. *Formation of dimers*





Schematic borrowed from (Raman & Fox, 2016)

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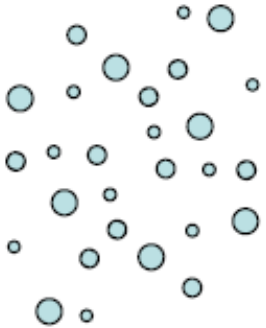
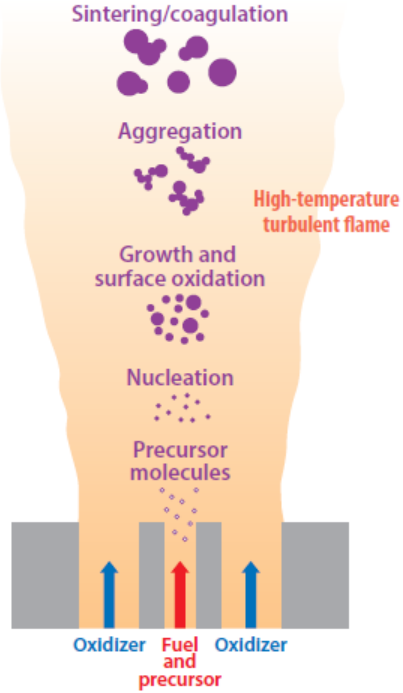
Flame synthesis of nanoparticles

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 flame synthesis of metal oxides





Schematic borrowed from (Raman & Fox, 2016)

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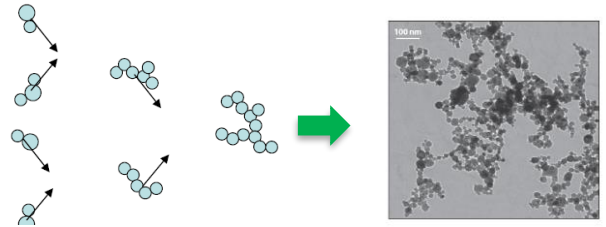
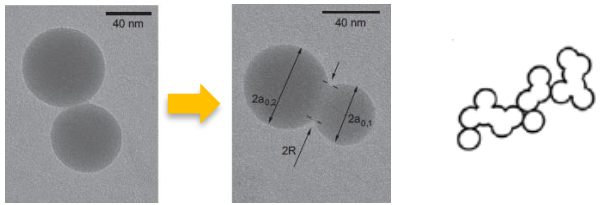
Flame synthesis of nanoparticles

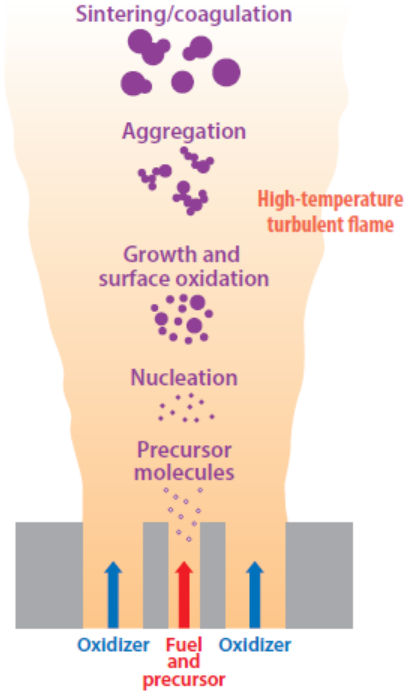
Chemical Reaction	Nucleation	Growth/Surface Reaction	Aggregation / Sintering

- **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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Precursor kinetics

- Gas phase chemical reactions
- Vapor product (precursor)
- Precursor decomposition to monomer species
- Monomer diameter $d_o = 0.44\ nm$
- Two step global mechanism (Chemkin format):

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

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

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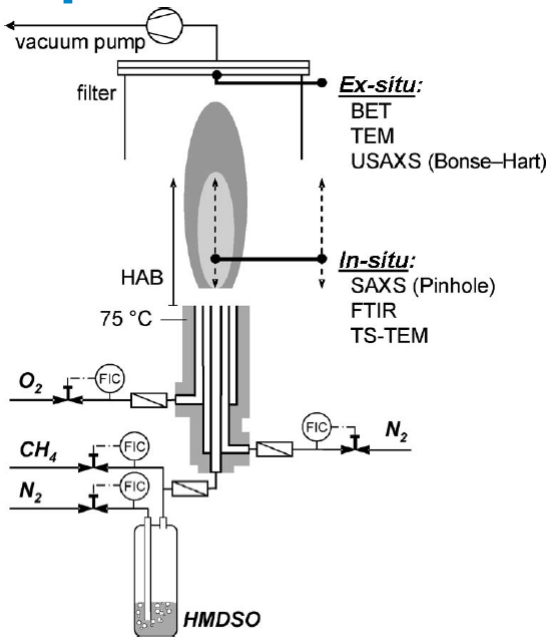
Experimental set up



- (Camenzind et al., 2008)
- **SAXS** data (detectable sizes **1nm** -100nm)
- ***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 = 0.3 mm
- Vjet = 6.81 m/s (V1 = 2.08, V2 = 8.69 m/s)
- Re ≈ 1430 for laminar case
- Re ≈ 4460 for turbulent case
- No other simulations for this experiment!

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

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Literature Review (1/2) - Study of Silica formation via CFD

- Ji, Y., Sohn, H. Y., Jang, H. D., Wan, B., & Ring, T. A. (**2007**). Computational fluid dynamic modeling of a flame reaction process for silica nanopowder synthesis from tetraethylorthosilicate. *Journal of the American Ceramic Society*, *90*(12), 3838-3845.
- Widiyastuti, W., Purwanto, A., Wang, W. N., Iskandar, F., Setyawan, H., & Okuyama, K. (**2009**). Nanoparticle formation through solid-fed flame synthesis: Experiment and modeling. *AIChE journal*, *55*(4), 885-895.
- Gröhn, Arto J., et al. "Design of turbulent flame aerosol reactors by mixing-limited fluid dynamics." *Industrial & engineering chemistry research* 50.6 (**2011**): 3159-3168.
- Buddhiraju, V. S., & Runkana, V. (**2012**). Simulation of nanoparticle synthesis in an aerosol flame reactor using a coupled flame dynamics–monodisperse population balance model. *Journal of aerosol science*, *43*(1), 1-13.
- Shekar, Shraddha, et al. "Modelling the flame synthesis of silica nanoparticles from tetraethoxysilane." *Chemical Engineering Science* 70 (**2012**): 54-66. (No CFD here)
- Vo, S., et al. "Multiple mapping conditioning for silica nanoparticle nucleation in turbulent flows." *Proceedings of the Combustion Institute* 36.1 (**2017**): 1089-1097.
- Rittler, A., et al. "Large eddy simulations of nanoparticle synthesis from flame spray pyrolysis." *Proceedings of the Combustion Institute* 36.1 (**2017**): 1077-1087.

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Literature Review (2/2) - Study of Silica formation via CFD

- Feroughi, O. M., Deng, L., Kluge, S., Dreier, T., Wiggers, H., Wlokas, I., & Schulz, C. (**2017**). Experimental and numerical study of a HMDSO-seeded premixed laminar low-pressure flame for SiO2 nanoparticle synthesis. *Proceedings of the Combustion Institute*, *36*(1), 1045-1053.
- Neuber, G., Garcia, C. E., Kronenburg, A., Williams, B. A., Beyrau, F., Stein, O. T., & Cleary, M. J. (**2019**). Joint experimental and numerical study of silica particulate synthesis in a turbulent reacting jet. *Proceedings of the Combustion Institute*, *37*(1), 1213-1220.
- Dasgupta, D., Pal, P., Torelli, R., Som, S., Paulson, N., Libera, J., & Stan, M. (**2022**). Computational fluid dynamics modeling and analysis of silica nanoparticle synthesis in a flame spray pyrolysis reactor. *Combustion and Flame*, *236*, 111789.

- CFD studies for TiO2 or other ceramics will not be presented here.
- Most of the studies compared exp and sim data only for primary particle sizes!
- Only Neuber et al., (2019) did laminar flow but focused on chemical precursor kinetics.
- **Nobody has compared sim with detailed SAXS in-situ data along the centreline!**

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Aerosol kinetics – Nucleation models

- **Classical Nucleation Theory**
  - (Girshick and Chiu, 1989)
- **Instantaneous Nucleation**
  - $J = \frac{dC_{SiO2}}{dt} \cdot N_A$
  - Monomer: $d_o = 0.44\,nm$
- **Nucleation of dimers**
  - Similar to the approach in (Shekar et al., 2012)

$$J = \frac{1}{2} K^{fm} N_A^2 C_{SiO_2}^2$$

$$K^{fm} = E_f \, 4 \sqrt{\frac{\pi \, k_B T}{m_{SiO_2}}} \, d_o^2$$

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Aerosol kinetics – Sintering

- Sintering Models summarised in (Goudeli et al. 2015)
  - **(Tsantilis et al, 2001)** $\tau_s = 6.5 \cdot 10^{-13}\, d_p\, e^{\frac{8.3 \cdot 10^4}{T}\left(1 - \frac{d_{p,min}}{d_p}\right)}$
  - **(Ehrman et al., 1998)** $\tau_s = 6.3 \cdot 10^{-8}\, d_p\, e^{\frac{6.1 \cdot 10^4}{T}\left(1 - \frac{d_{p,min}}{d_p}\right)}$
  - **(Kirchhof et al., 2012)** $\tau_s = \frac{\left(1-\frac{1}{e}\right) r_s^2}{2^{\frac{2}{3}}\left(3.5 \cdot 10^{-4} \frac{m^2}{s}\right)} e^{\frac{4.4 \cdot 10^4}{T}\left(1 - \frac{d_{p,min}}{d_p}\right)}$
- $d_{p,min}$ = ?

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Aerosol kinetics

- **Coagulation** (Pratsinis, 1988) $\beta^t(v,w) = \frac{\beta^{fm}(v,w) \cdot \beta^c(v,w)}{\beta^{fm}(v,w)+\beta^c(v,w)}$
- **Condensation** (free molecular) $\omega_{cond} = C_{SiO_2} N_A \int \beta^{fm}(v_o,w) n(w) dw$
- **No Evaporation** /Growth /Oxidation
- **Particle Radiation** Model $Qrad = -\frac{4\sigma}{\rho} \boldsymbol{C_s} f_v (T^5 - T_{amb}^5)$
  - $\boldsymbol{C_s}$ depends on the complex refractive index of particles

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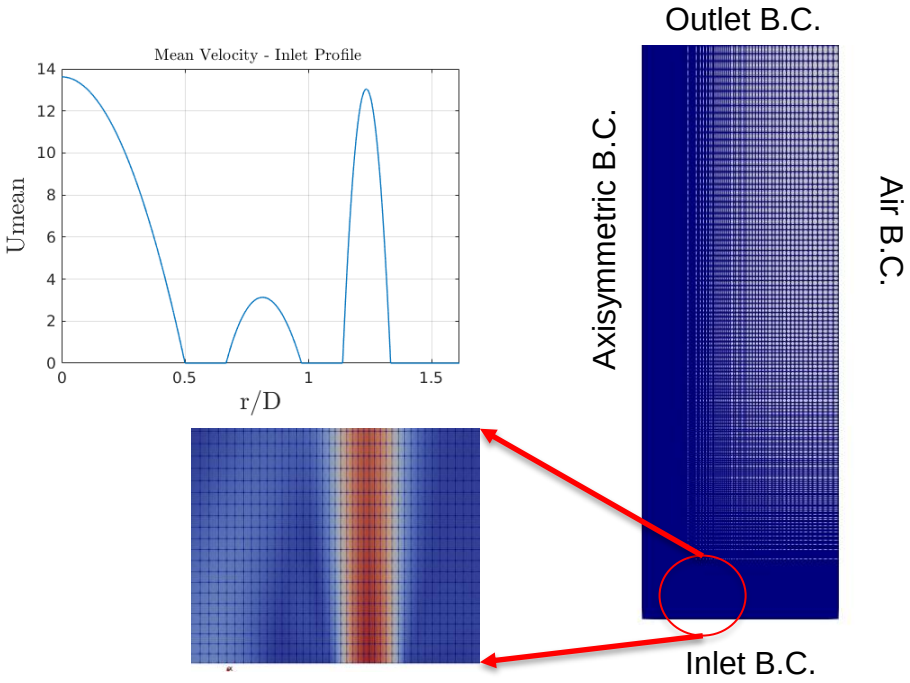
Simulation details

- 2-D domain (60D x 15D)
- # Cells 264x162 = 42768 ($dx_{min} = 0.026\ mm$)
- Grid refinement (10 cells to capture the velocity profile)
- Grid stretching in the streamwise and radial direction
- $dt = 10^{-7}\ sec$ (CFL = 0.2)
- Boundary conditions: Inlet / Axisymmetric / Outflow
- Entrainment velocity at inlet Vair = 0.4 m/s



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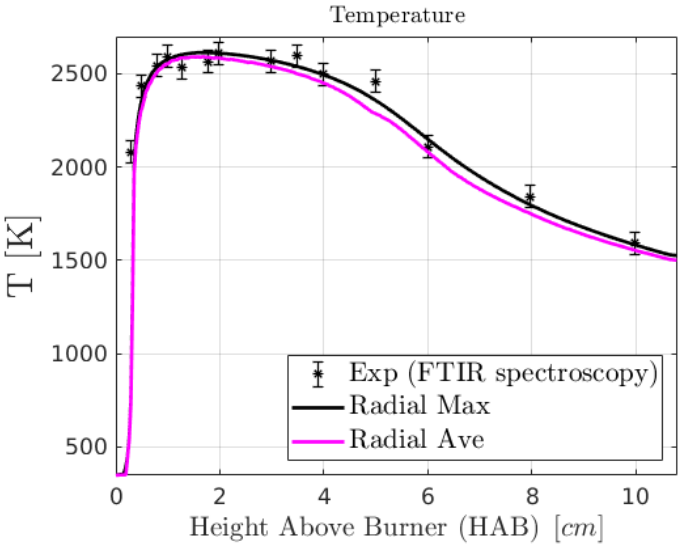
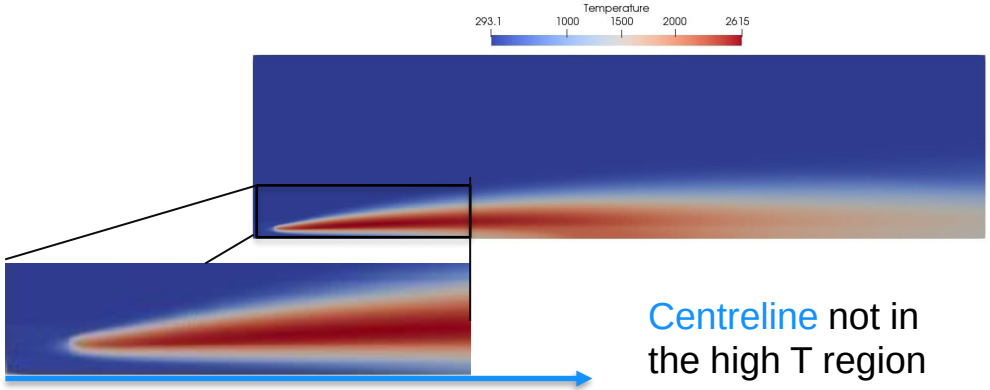
Comparison of temperature with FTIR data



- Centreline data ≠ Exp data
- FTIR* => **line-of-sight** technique
- Radial Averaging ($C_{CO2} > 0.8\, C_{CO2,max}$)
- Error bars (±60K)



Centreline not in the high T region

*FTIR = Fourier Transform Infrared Spectroscopy