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EXPERIMENTAL AND NUMERICAL STUDY OF THE EVOLUTION OF SOOT PRIMARY PARTICLES IN A DIFFUSION FLAME

Maria Botero, Nick Eaves, Jochen Dreyer, Yuan Sheng, Jethro Akroyd, Wenming Yang, Markus Kraft

2 August 2018

CAM.CREATE C4T Cambridge Centre for Carbon Reduction in Chemical Technology

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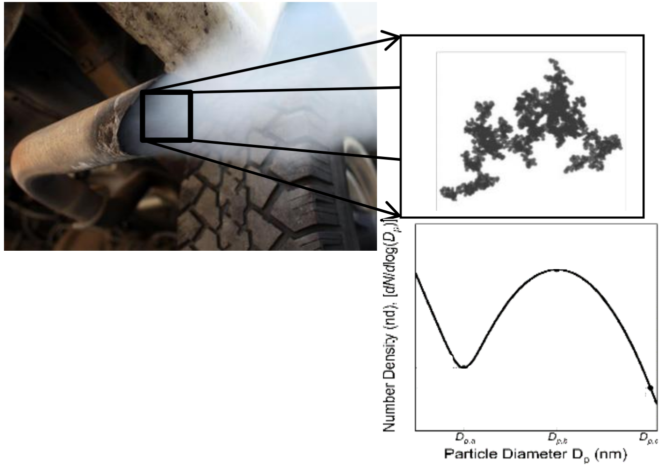
Motivation

Understand processes involved in <u>primary particle</u> formation and growth



Limitations:

- Complexity of multiple processes – simultaneous.
- Studies report <u>only average PP size:</u> (monodisperse distribution)
- Lack of experimental data
- Limitations of soot models (particle description)

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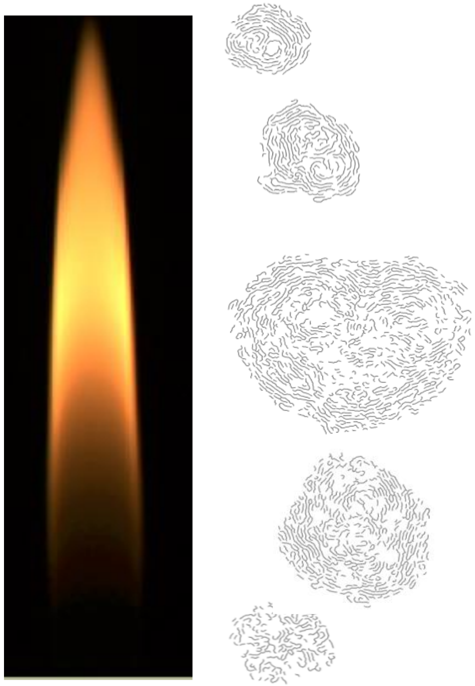
Objectives



1 – Investigate the evolution of soot primary particle size, nanostructure and morphology in a diffusion flame

2 – Through detailed modelling, investigate the sensitivity of the primary particle size distribution to different particle processes

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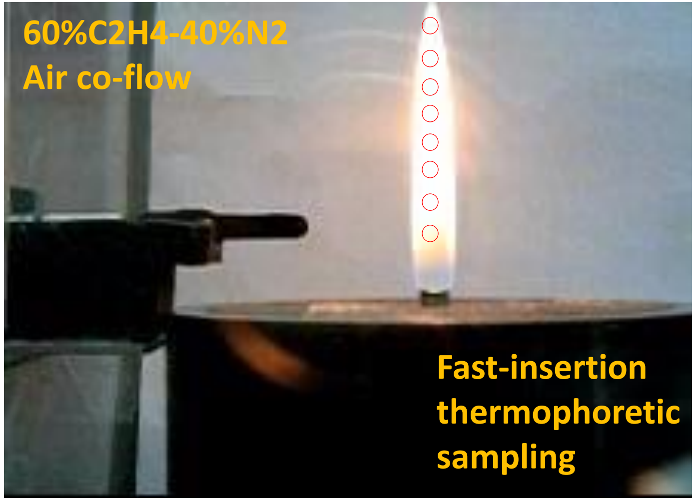
Experimental Methods

Flame system

Yale Burner[1] (ISF Co-Flame 3c)



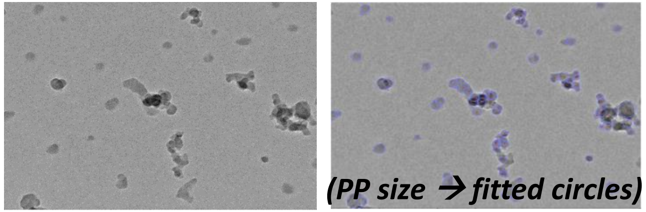
[1] http://guilford.eng.yale.edu/yalecoflowflames/steady_burner.html

- Temperature measurement: R-type thermocouple 75μm wire

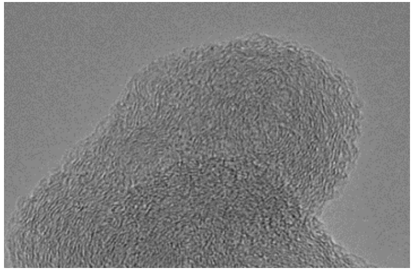
Soot characterization: morphology and nanostructure

HRTEM: Jeol 2100F (200 kV)

Primary particle



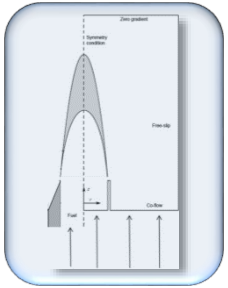
Nanostructure



Numerical Method

Nick Eaves

CoFlame Code[1]



Gas-phase species Temperature profile

- DLR chemical mechanism[2]
(up to A5: benzopyrene)
- Soot model solved via sectional method[1]

[1] N.A. Eaves *et. al.*, **(2016),** *Comp. Phys. Comm.*, *207*, 464-477.
[2] S.B. Dworkin *et. al.*, **(2011)**, *Combust. Flame*, 158 (9), 1682-1695

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Numerical Methods

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Nick Eaves

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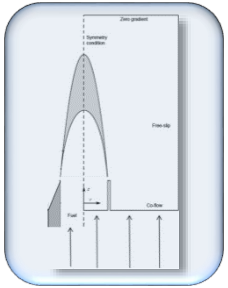
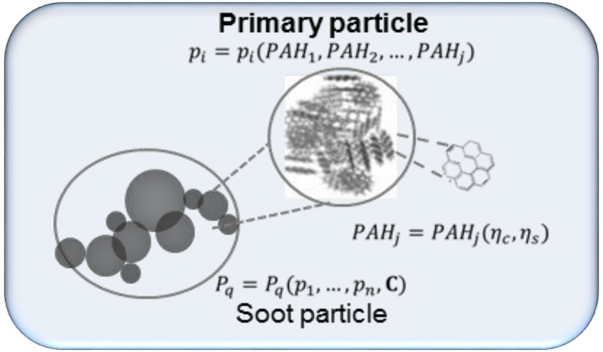


Gas-phase species Temperature profile

Detailed Particle Model PAH-PP[3]



Primary Particle size distribution

- DLR chemical mechanism[2]
(up to A5: benzopyrene)
- Soot model solved via sectional method[1]

- PAH growth: KMC-ARS[4]
- Particle dynamics solved by Smoluchowski eqn:

+ inception + surface growth + oxidation + condensation + particle rounding + sintering

1 N.A. Eaves *et. al.*, **(2016),** *Comp. Phys. Comm.*, *207*, 464-477.
2 S.B. Dworkin *et. al.*, **(2011)**, *Combust. Flame*, 158 (9), 1682-1695

3 Sander *et. al.*, **(2011),** *Proc. Combust. Inst.*, *33(1)*, **675-683**.
4 Raj *et. al.*, **(2009)**, *Combust. Flame*, 156 (4), 896-913

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Numerical Methods

Parameters used in the model

Parameter	Range	Value
1) Minimum number of 6-member aromatic rings in a PAH for inception	-	5
2) Minimum number of 6-member aromatic rings in a PAH for condensation	-	5
3) Minimum number of 6-member aromatic rings in a PAH in a particle ($n_{\mathrm{PAHs}} \geq n_{\mathrm{crit}}$) below which it is removed	-	4
4) Soot density, ρ	$1\ \mathrm{g\ cm^{-3}} \leq \rho \leq 2\ \mathrm{g\ cm^{-3}}$	$1.88\ \mathrm{g\ cm^{-3}}$
5) Smoothing factor, σ	$0 \leq \sigma \leq 2$	1.69
6) Growth factor, g	$0 \leq g \leq 1$	0.15
7) Critical number of PAHs in a primary particle before the growth factor is applied, n_{crit}	≥ 2	4
8) Sintering model:		
- A_{s}	-	$1.1 \times 10^{-14}\ \mathrm{s\ m^{-1}}$
- E_{s}	$1.8 \times 10^{4}\ \mathrm{K} \leq E_{\mathrm{s}} \leq 1.8 \times 10^{5}\ \mathrm{K}$	$9.61 \times 10^{4}\ \mathrm{K}$
- $d_{\mathrm{p,crit}}$	$1\ \mathrm{nm} \leq d_{\mathrm{p,crit}} \leq 5\ \mathrm{nm}$	1.58 nm

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Numerical Methods

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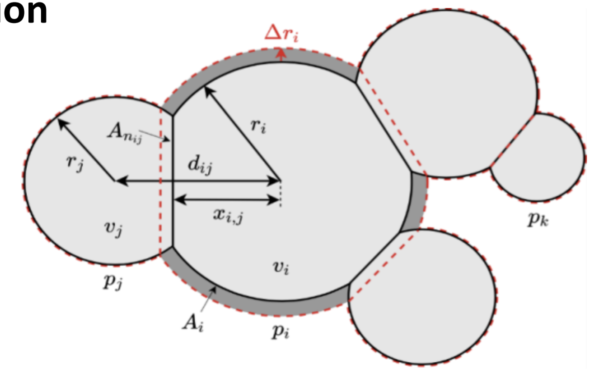
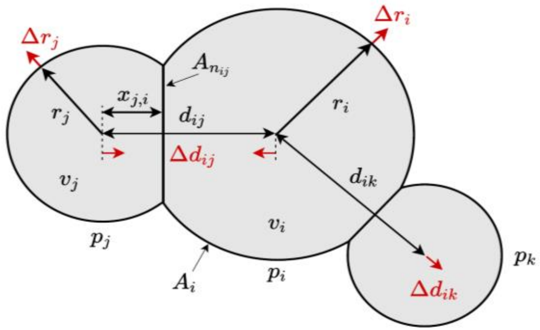
Particle rounding:

<u>Smoothing factor, s:</u>
Rate of change in joint surface area by **mass addition**

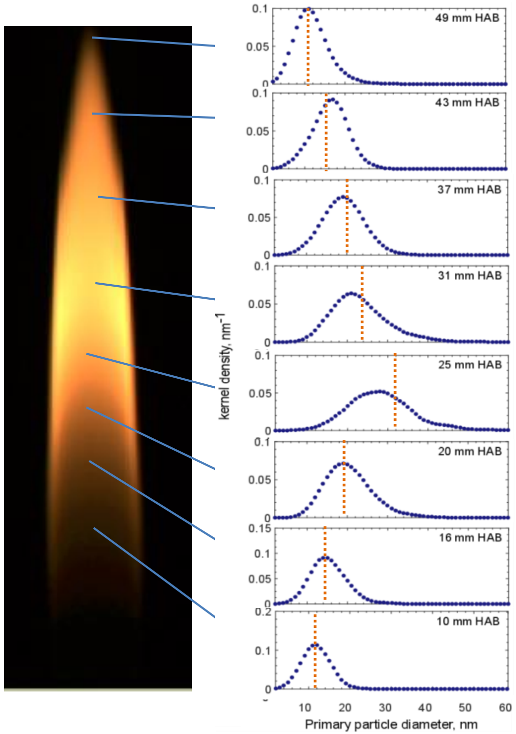


Sintering model: Arrhenius type

- <u>Pre-exponential factor</u> and activation energy
- <u>$D_{p,crit}$:</u> instantaneous sintering



Primary particle size distribution



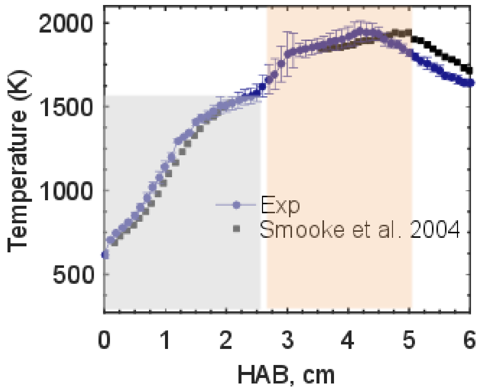
Particle shrinkage (31- 49 mm HAB):

- PPSD shifts back to smaller sizes and narrows
- Initially **graphitisation** (compaction)
- At the tip, combined graphitisation and **oxidation**

Particle growth (10 – 25 mm HAB):

- PPSD shifts progressively to larger sizes and becomes wider
- Combination of growth processes

Temperature Profile



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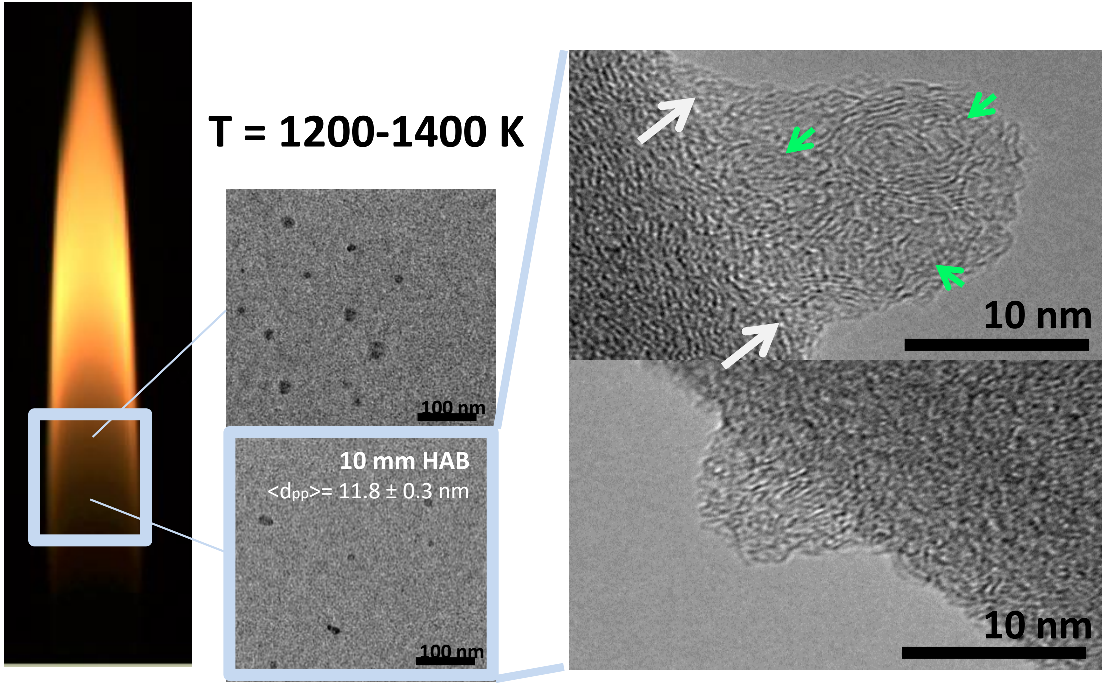
Results: Experimental

Low HAB: initial growth

T = 1200-1400 K

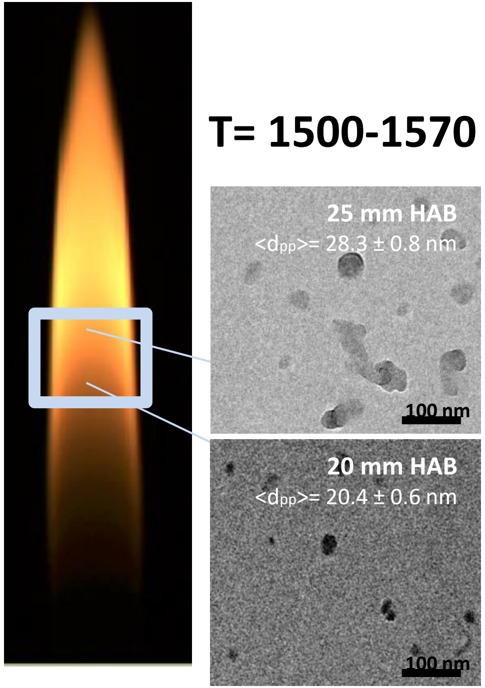


Smallest particles sampled:

- 4-5 nm (detection limit TEM)
- Formed from coalescence of smaller soot primary particles (green arrows)
- Show a small splashing on the grid (white arrows)
- **Have a shot-range nano-structural graphitic order**

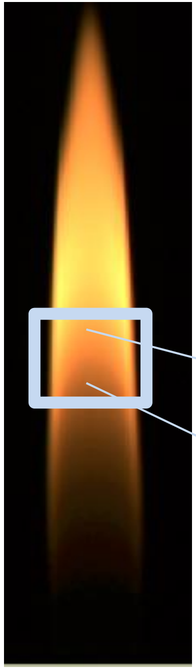
Medium-Low HAB: growth and aggregation

T= 1500-1570 K



- Small aggregates
- Irregular shapes undefined boundaries
- Wax-like structure, spreads over the grid

Medium-Low HAB: growth and aggregation



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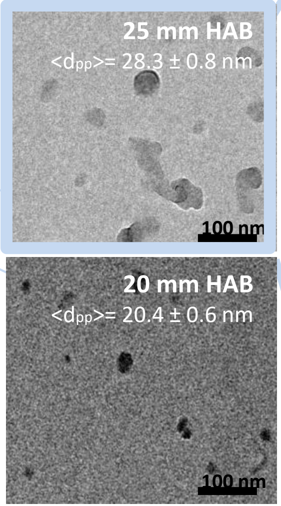
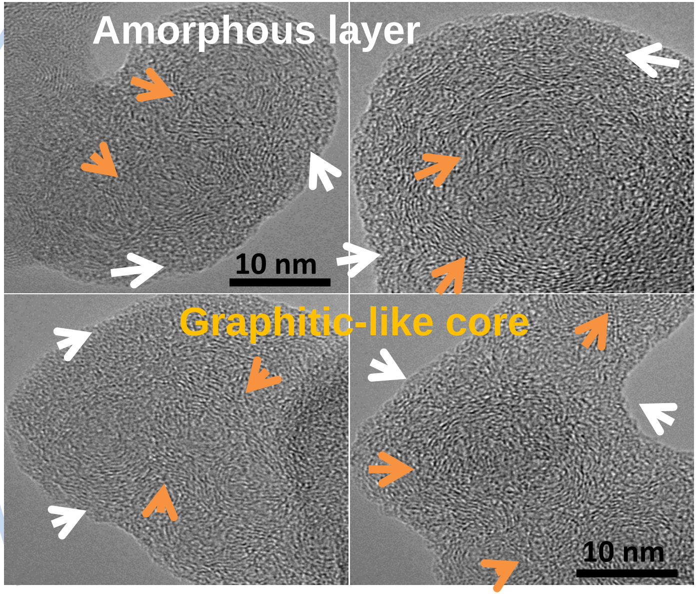




Amorphous material

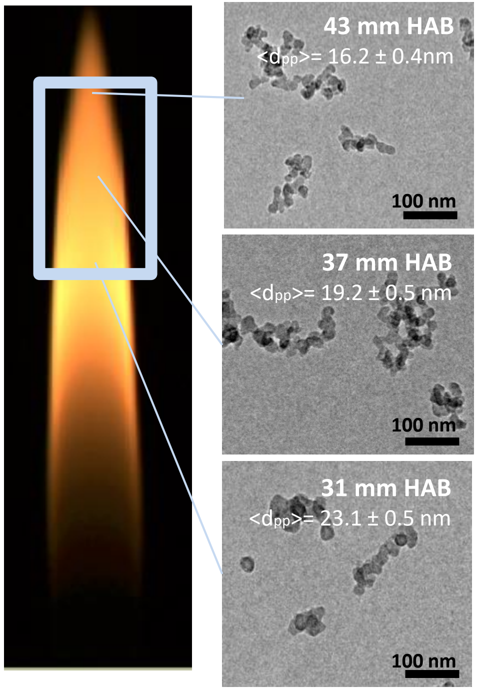
- Condenses around the soot primary particles
- Sticks particles together → promotes aggregation

Graphitic-like core

- Surrounded by amorphous layer
- **young particles ≠ amorphous layer**

Results: Experimental

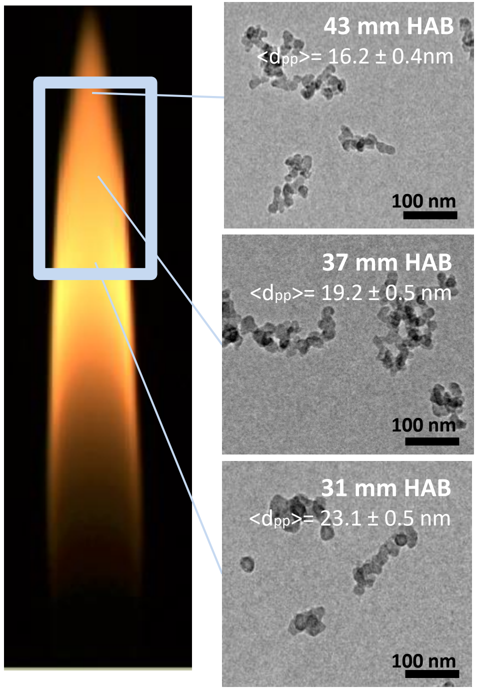
Medium-High HAB: graphitisation



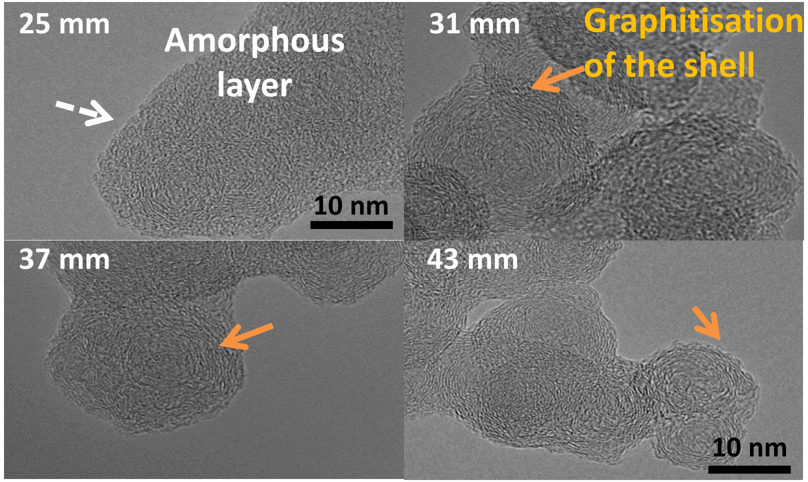
T= 1720-1810 K

- High contrast
- Well defined spherical shape
- Aggregation

Medium-High HAB: graphitisation



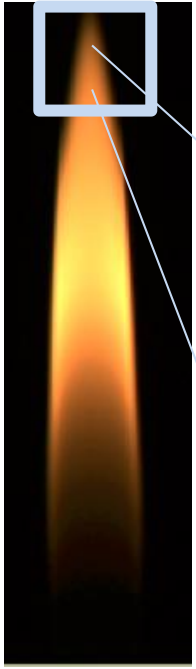
T= 1720-1810 K

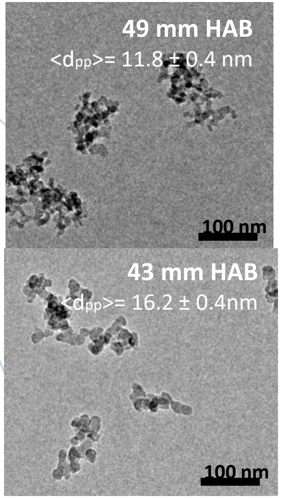


Graphitisation

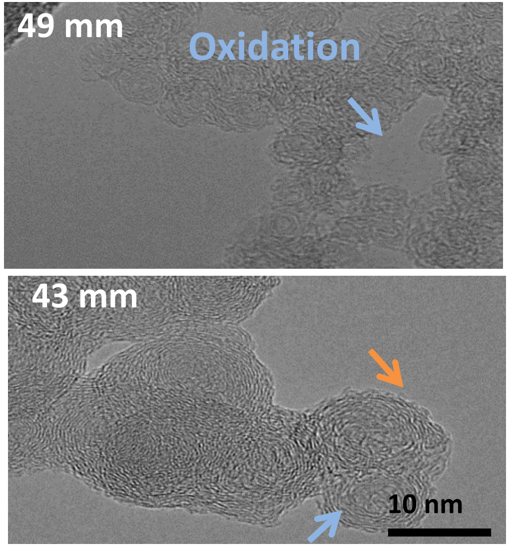
- Amorphous layer graphitises fast due to the high flame temperature
- A graphitic-like layer forms
- Particles become more compact

Flame tip: oxidation





T= 1750-1810 K



Oxidation

- At the tip of the flame
- Both aggregate and primary particle size decrease substantially

Results: Numerical

Test cases for sensitivity analysis

Trial	A_s (s m^{-1})	$d_{p,crit}$ (nm)	σ	
1	1.1×10^{-14}	1.58	1.69	[Base case]
2	1.1×10^{-13}	1.58	1.69	Sintering pre-factor
3	1.1×10^{-12}	1.58	1.69	
4	1.1×10^{-14}	3	1.69	Critical diameter for coalescence
5	1.1×10^{-14}	5	1.69	
6	1.1×10^{-14}	1.58	1.0	Smoothing factor
7	1.1×10^{-14}	1.58	0.5	

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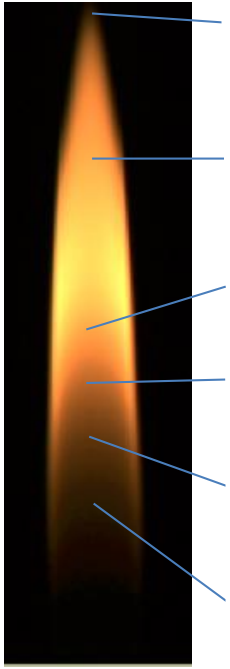
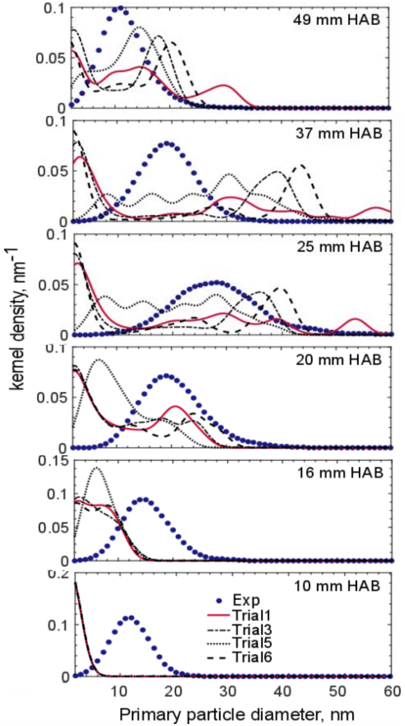
Results: Numerical

Primary particle size distribution





Trial 1: Base case

1) Delayed initial growth

2) D_{crit} (Trial 5): fast coalescence of nascent particles

- **Eliminates mode of sub 2 nm particles** and very large particles

3) Sintering pre-factor (Trial 3) and Smoothing factor (Trial 6)

- Reduces multimodality

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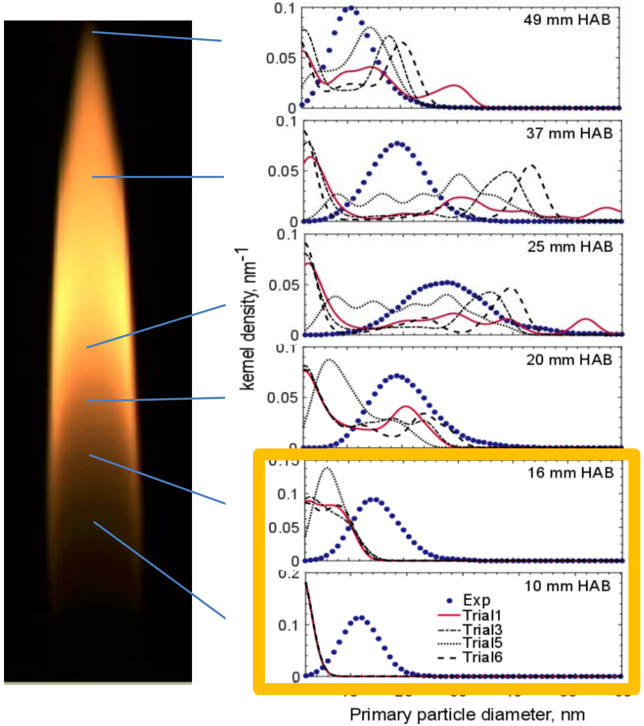
Primary particle size distribution



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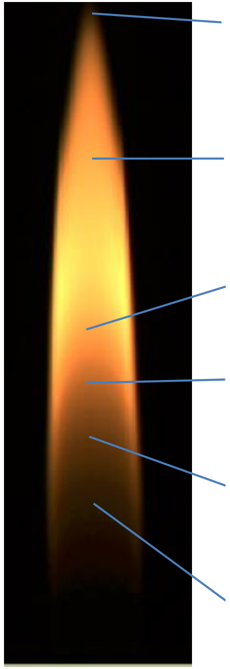
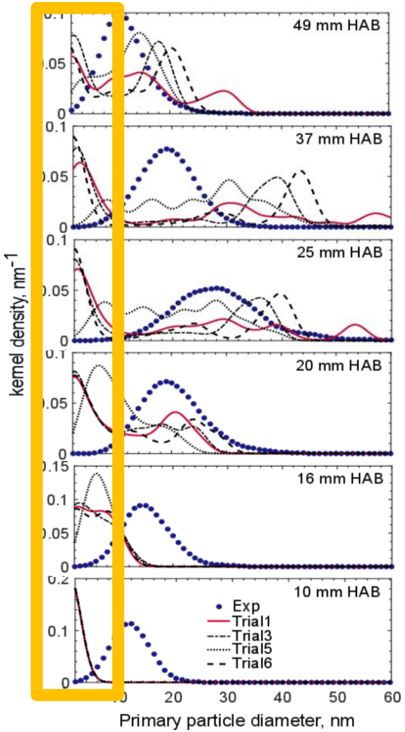
Results: Numerical

Primary particle size distribution





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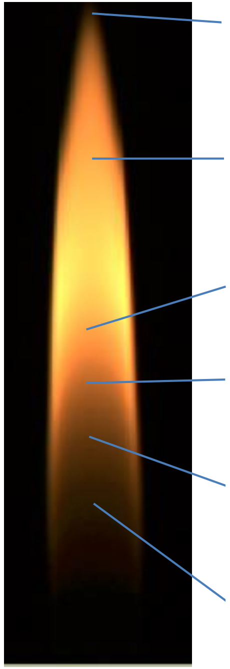
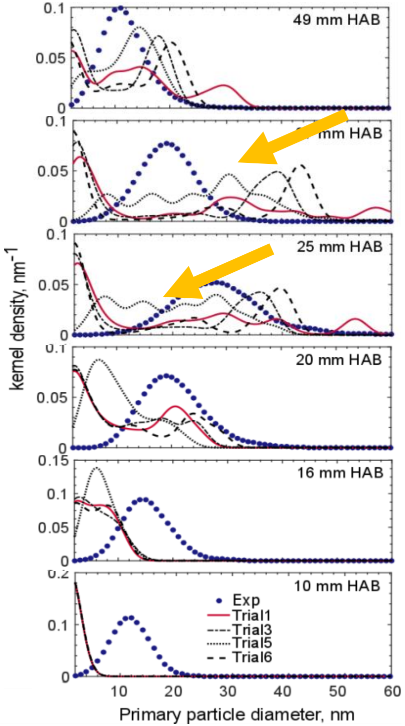
Primary particle size distribution





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- **Eliminates mode of sub 2 nm particles** and very large particles

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- Reduces multimodality

Model needs to account for the variable nano-structural mobility

Results: Numerical

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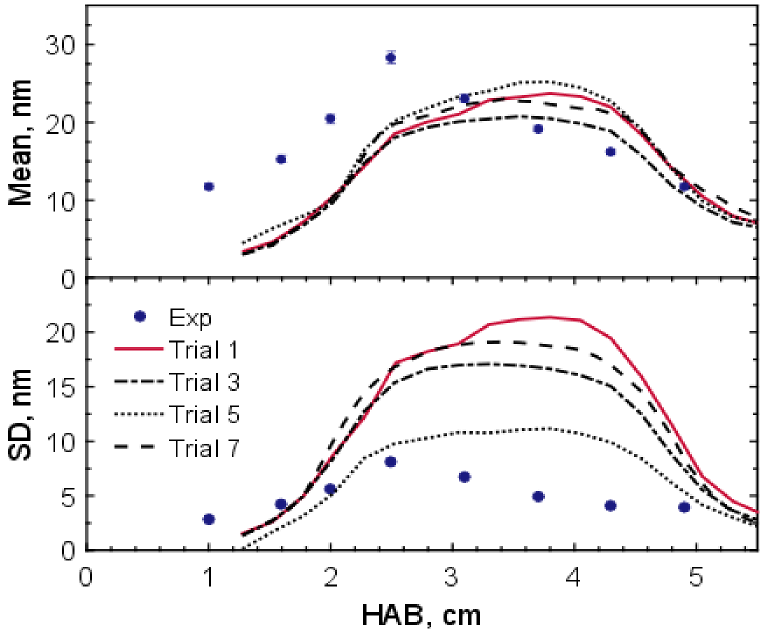
Average primary particle size



Average primary particles size **is not very sensitive** to investigated parameters

Reasonable prediction of average sizes **does not** ensure reasonable prediction of the distribution.

Conclusions

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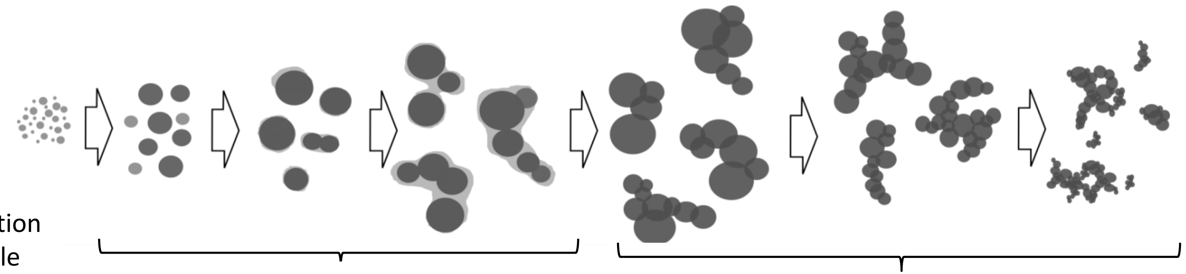
The evolution of the PPSD of soot in a co-flow diffusion flame was investigated experimentally and numerically:



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Conclusions

- Model development: variable sintering and rounding of particles throughout the flame.
- Average primary particle size is not sensitive to the parameters evaluated, **whereas PPSD is sensitive.**

Reasonable prediction of average PP sizes does not ensure reasonable prediction of the distribution.

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Thanks!

Future and Ongoing Work

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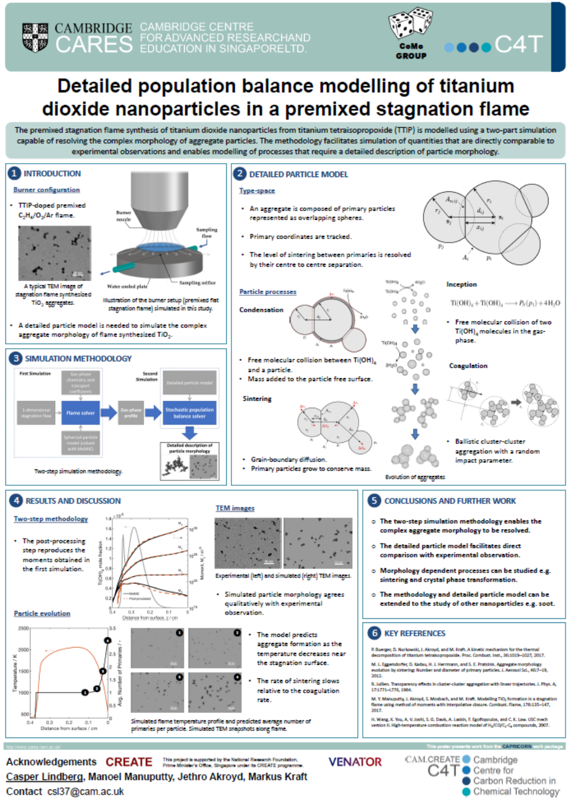
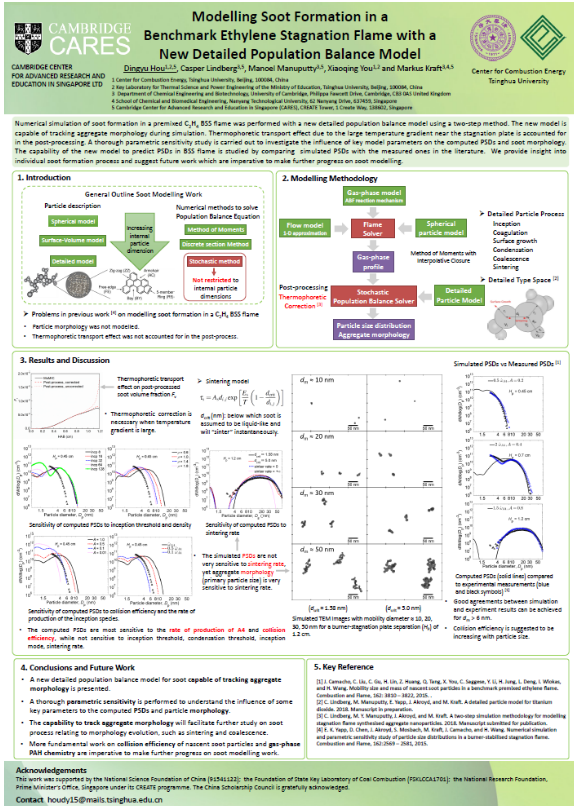
2P048



Dingyou Hou
2P039



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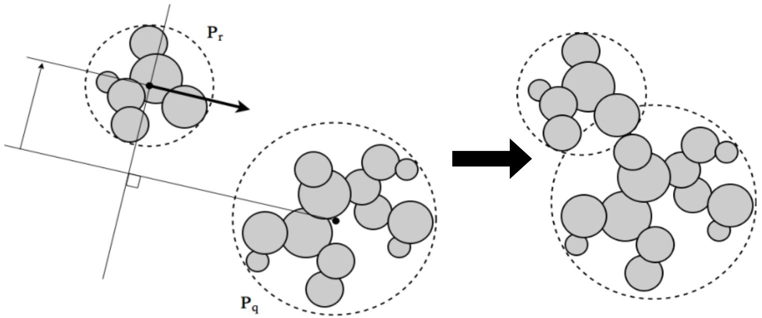
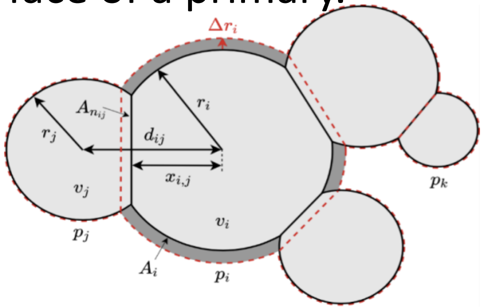
Future and Ongoing Work

Particle process models

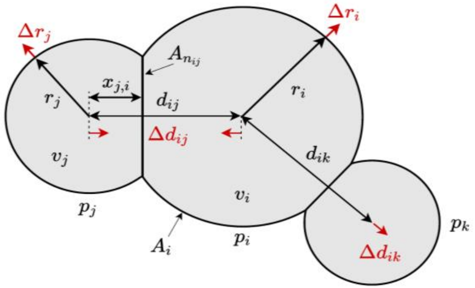
Coagulation: Ballistic cluster-cluster aggregation with a random impact parameter.[1]



Surface growth: Mass is added to the free surface of a primary.



Sintering: viscous flow.[2]



1. Jullien R., **(1984)**, *J. Phys. A: Math. Gen*, *17*, L771-L776.
2. Eggersdorfer, M. L., Kadau, D., Herrmann, H. J. & Pratsinis, S. E., **(2011)**, *Langmuir*, *27*, 6358-6367.

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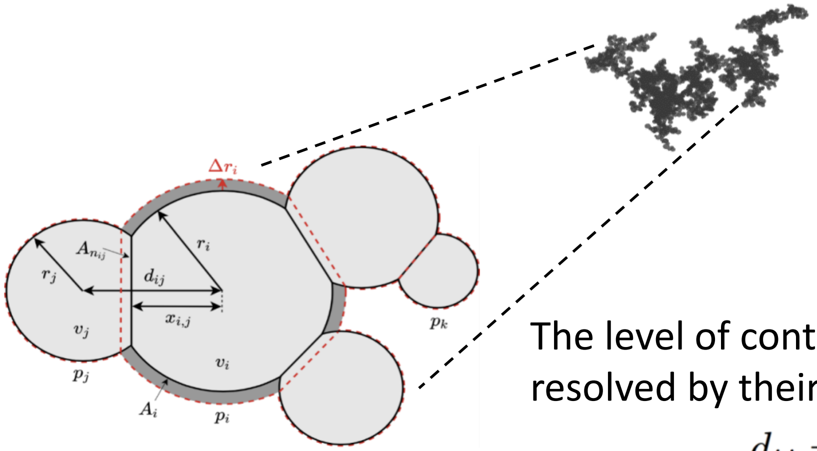
Future and Ongoing Work

Particle type space

An aggregate is composed of primary particles modelled as **overlapping spheres.**



The level of contact between primaries is resolved by their centre to centre separation

$$d_{ij} = |\mathbf{x}_i - \mathbf{x}_j|$$

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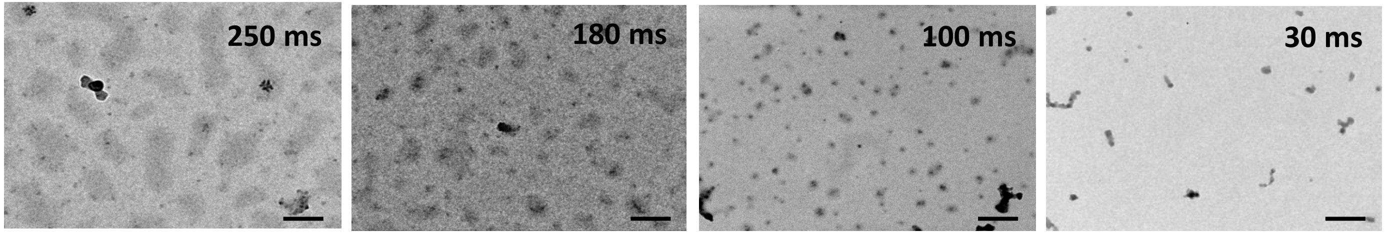
Results: Experimental

Liquid blobs - Sampling artifacts

Liquid-like material surrounding the particles depend on:

- Sampling time
- Concentration in the flame (at the sampling position)



Sufficiently short insertion periods can avoid condensable material on the grids

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Numerical Methods

Numerical parameters used in the model

Parameter	Range	Value
1) Minimum number of 6-member aromatic rings in a PAH for inception	-	5
2) Minimum number of 6-member aromatic rings in a PAH for condensation	-	5
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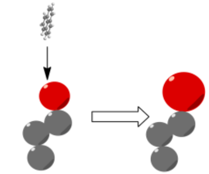
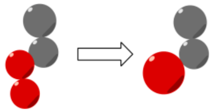
6) Growth factor, g	$0 \leq g \leq 1$	0.15
7) Critical number of PAHs in a primary particle before the growth factor is applied, n_{crit}	≥ 2	4
8) Sintering model:		
- A_{s}	-	$1.1 \times 10^{-14}\ \mathrm{s\ m^{-1}}$
- E_{s}	$1.8 \times 10^{4}\ \mathrm{K} \leq E_{\mathrm{s}} \leq 1.8 \times 10^{5}\ \mathrm{K}$	$9.61 \times 10^{4}\ \mathrm{K}$
- $d_{\mathrm{p,crit}}$	$1\ \mathrm{nm} \leq d_{\mathrm{p,crit}} \leq 5\ \mathrm{nm}$	1.58 nm

Particle rounding processes:



Smoothing factor, s:
Rate of change in joint surface area by **mass addition**



Sintering model: Arrhenius type
- Pre-exponential factor and activation energy
- $D_{p,crit}$: instantaneous sintering

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Results: Numerical

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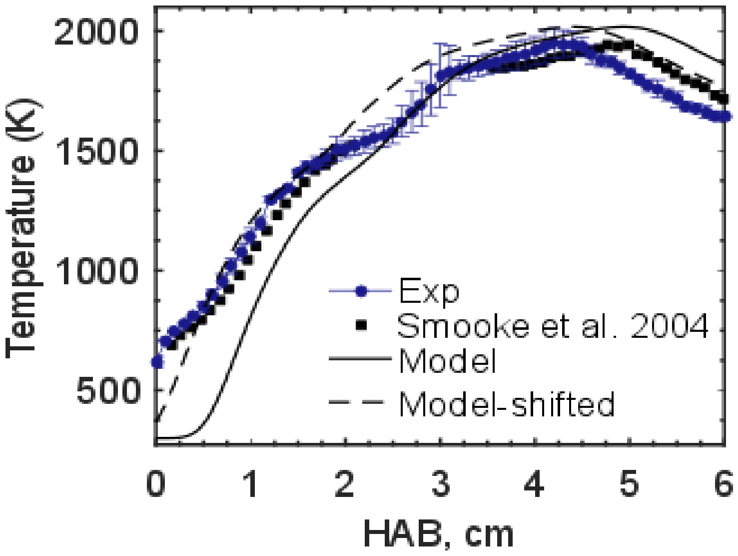
Temperature Profile



The simulated temperature profile was shifted by −5 mm in order to match the HAB at which the maximum temperature

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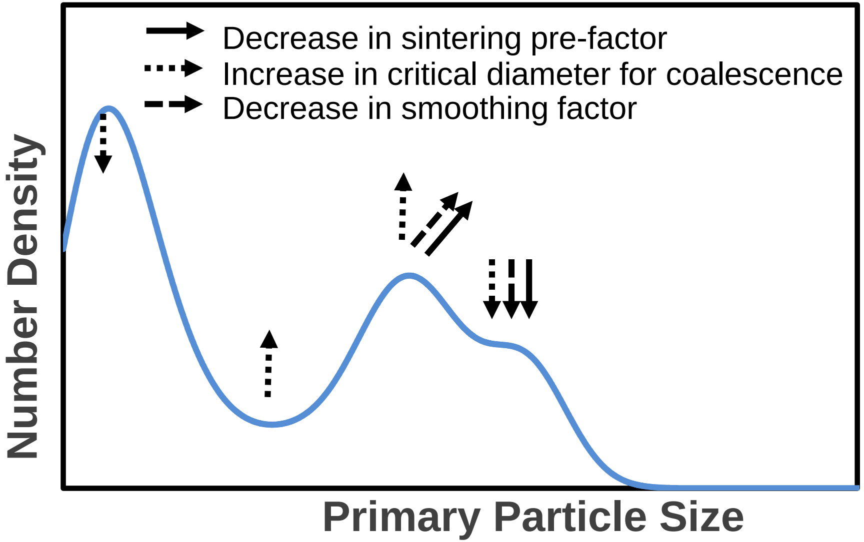
Results: Numerical

Sensitivity analysis



Sintering prefactor

- Reduces multimodality
- Sintering rate high at low HAB (from experiments)
- **Sintering rate should decrease with increasing HAB**

Critical diameter for coalescence

- **Eliminates mode of sub 2 nm** and very large particles.
- Represents the structural mobility of nascent particles.
- Does not influence multimodality

Smoothing factor

- Reduces multimodality
- **Decreases sintering level due to condensation and surface growth**

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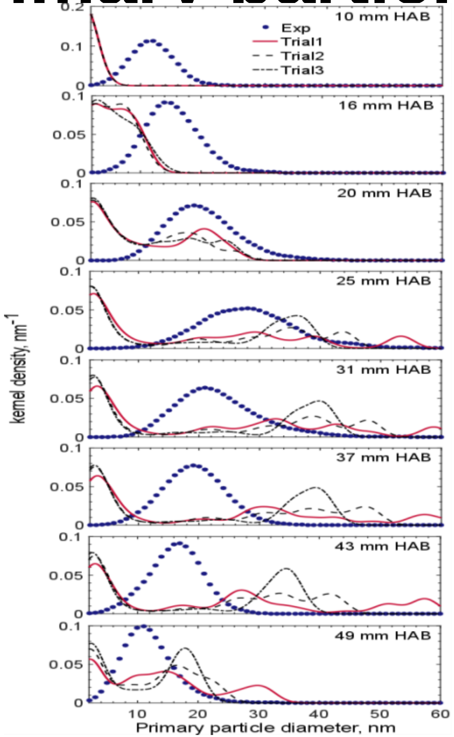
Primary particle size distribution

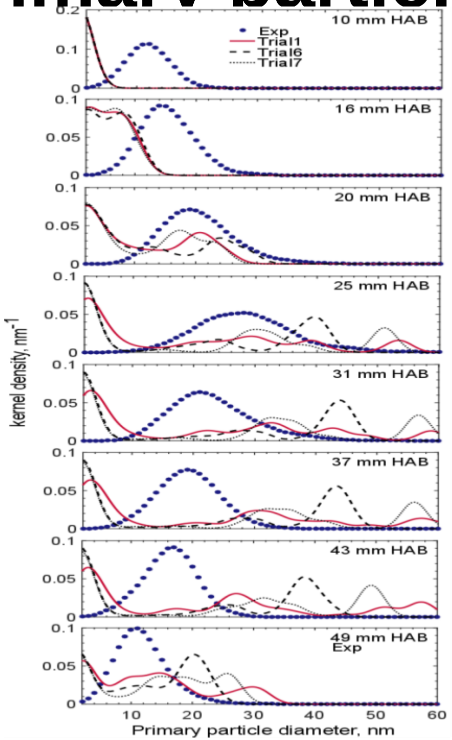


Sintering prefactor *As*: (decreasing)

- Reduces multimodality
- Sintering rate high at low HAB (from experiments)
- **Sintering rate should decrease with increasing HAB**

Trial	A_s (s m^{-1})	$d_{p,crit}$ (nm)	σ
1	1.1×10^{-14}	1.58	1.69
2	1.1×10^{-13}	1.58	1.69
3	1.1×10^{-12}	1.58	1.69

Primary particle size distribution

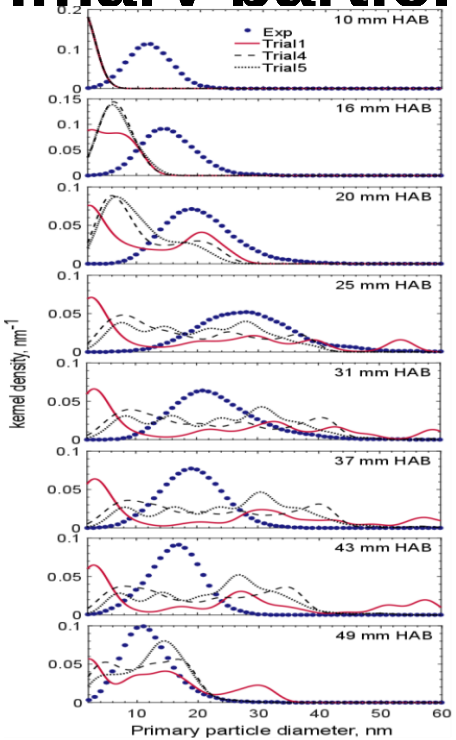


Smoothing factor, σ: (decrease)

- Reduces multimodality
- **Decreases sintering level due to condensation and surface growth**
- If too low (Trial7) shifts PPSD to very large d_p

Trial	A_s (s m^{-1})	$d_{p,crit}$ (nm)	σ
1	1.1×10^{-14}	1.58	1.69
6	1.1×10^{-14}	1.58	1.0
7	1.1×10^{-14}	1.58	0.5

Primary particle size distribution



Coalescence $d_{p,crit}$: (increasing)

- **Eliminates mode of sub 2 nm particles** and very large particles.
- Representation of the structural mobility of nascent particles.
- Does not influence multimodality

Trial	A_s (s m^{-1})	$d_{p,crit}$ (nm)	σ
1	1.1×10^{-14}	1.58	1.69
4	1.1×10^{-14}	3	1.69
5	1.1×10^{-14}	5	1.69