



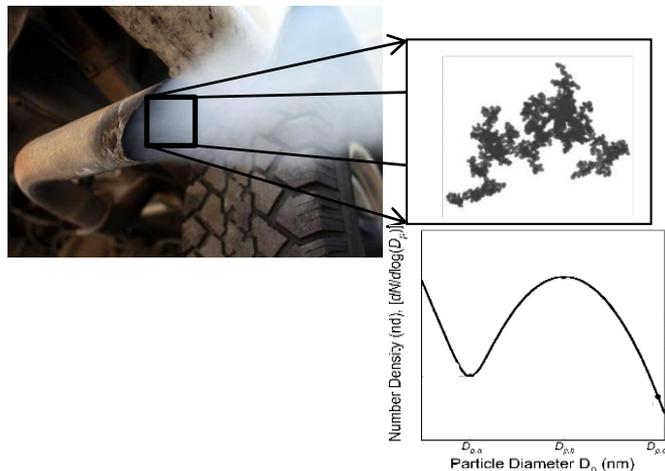
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# EXPERIMENTAL AND NUMERICAL STUDY OF THE EVOLUTION OF SOOT PRIMARY PARTICLES IN A DIFFUSION FLAME

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

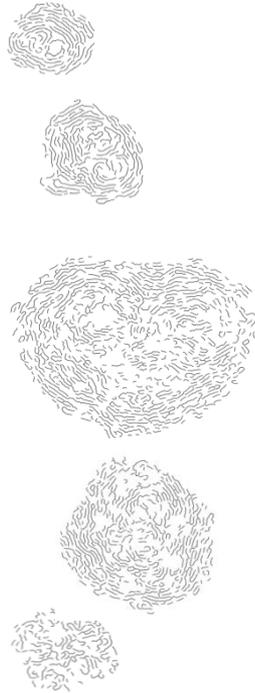
**2 August 2018**

## Understand processes involved in primary particle formation and growth



### Limitations:

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

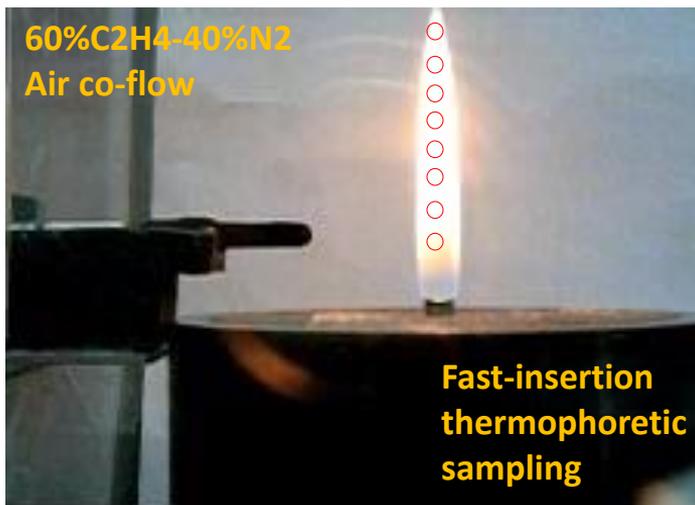


**1 – Investigate the evolution of soot primary particle size, nanostructure and morphology in a diffusion flame**

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

## Flame system

### Yale Burner<sup>1</sup> (ISF Co-Flame 3c)



<sup>1</sup> [http://guilford.eng.yale.edu/yalecoflowflames/steady\\_burner.html](http://guilford.eng.yale.edu/yalecoflowflames/steady_burner.html)

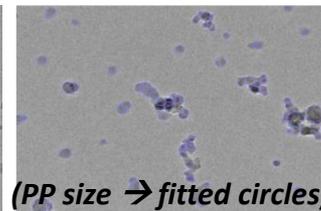
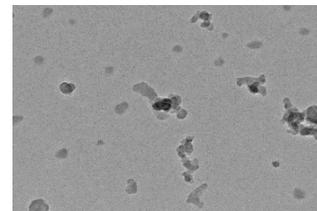
- Temperature measurement: R-type thermocouple 75 $\mu$ m wire

## Soot characterization: morphology and nanostructure

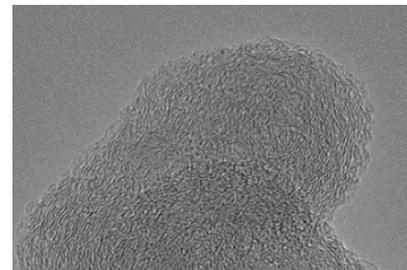


HRTEM: Jeol 2100F (200 kV)

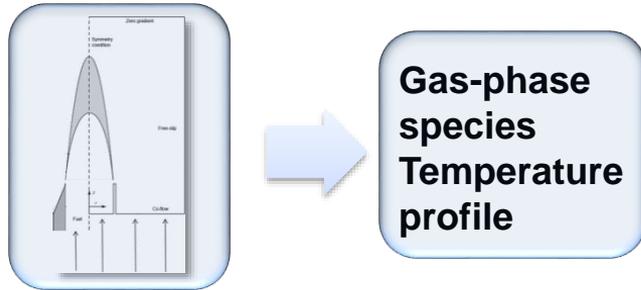
### Primary particle



### Nanostructure



## CoFlame Code<sup>1</sup>



- DLR chemical mechanism<sup>2</sup>  
(up to A5: benzopyrene)
- Soot model solved via sectional method<sup>1</sup>

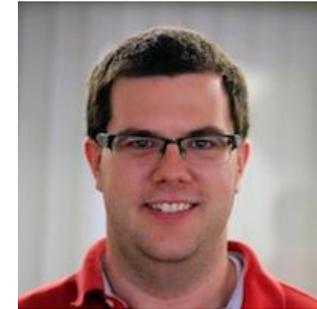
<sup>1</sup> N.A. Eaves *et al.*, (2016), *Comp. Phys. Comm.*, 207, 464-477.

<sup>2</sup> S.B. Dworkin *et al.*, (2011), *Combust. Flame*, 158 (9), 1682-1695

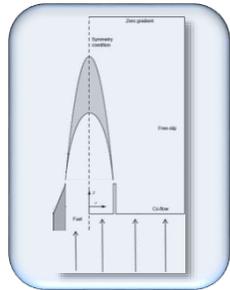
Nick Eaves



Nick Eaves



## CoFlame Code<sup>1</sup>



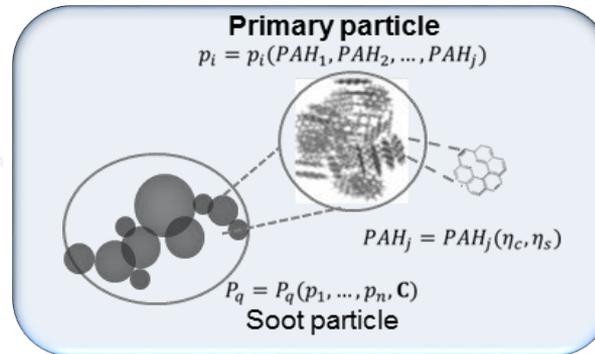
Gas-phase  
species  
Temperature  
profile

- DLR chemical mechanism<sup>2</sup>  
(up to A5: benzopyrene)
- Soot model solved via sectional method<sup>1</sup>

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## Detailed Particle Model PAH-PP<sup>3</sup>



- PAH growth: KMC-ARS<sup>4</sup>
- Particle dynamics solved by Smoluchowski eqn:  
+ inception + surface growth + oxidation + condensation +  
particle rounding + sintering

<sup>3</sup> Sander *et al.*, (2011), *Proc. Combust. Inst.*, 33(1), 675-683.

<sup>4</sup> Raj *et al.*, (2009), *Combust. Flame*, 156 (4), 896-913

Primary Particle  
size distribution

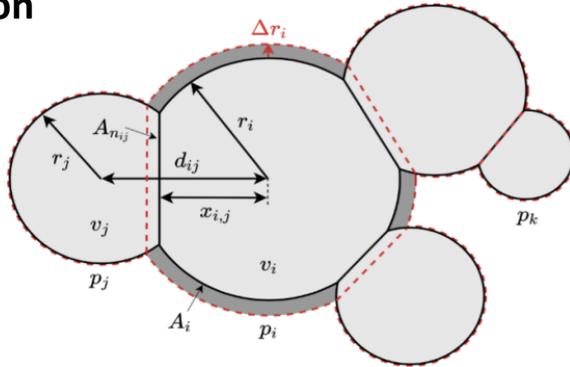
## Parameters used in the model

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 ( $n_{\text{PAHs}} \geq n_{\text{crit}}$ ) below which it is removed	-	4
4) Soot density, $\rho$	$1 \text{ g cm}^{-3} \leq \rho \leq 2 \text{ g cm}^{-3}$	$1.88 \text{ g cm}^{-3}$
5) Smoothing factor, $\sigma$	$0 \leq \sigma \leq 2$	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, $n_{\text{crit}}$	$\geq 2$	4
8) Sintering model:		
- $A_s$	-	$1.1 \times 10^{-14} \text{ s m}^{-1}$
- $E_s$	$1.8 \times 10^4 \text{ K} \leq E_s \leq 1.8 \times 10^5 \text{ K}$	$9.61 \times 10^4 \text{ K}$
- $d_{\text{p,crit}}$	$1 \text{ nm} \leq d_{\text{p,crit}} \leq 5 \text{ nm}$	1.58 nm

## Particle rounding:

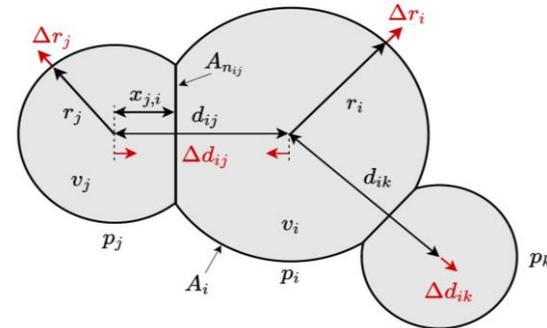
Smoothing factor,  $s$ :

Rate of change in joint surface area by  
**mass addition**

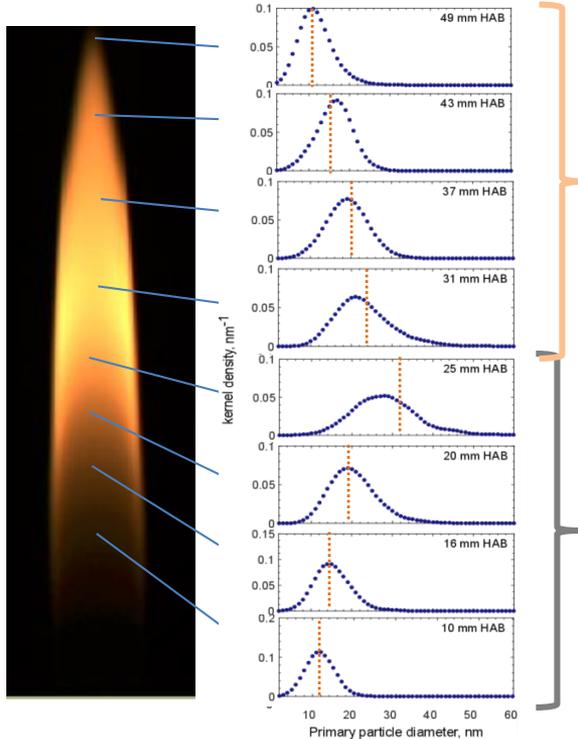


## Sintering model: Arrhenius type

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



## Primary particle size distribution



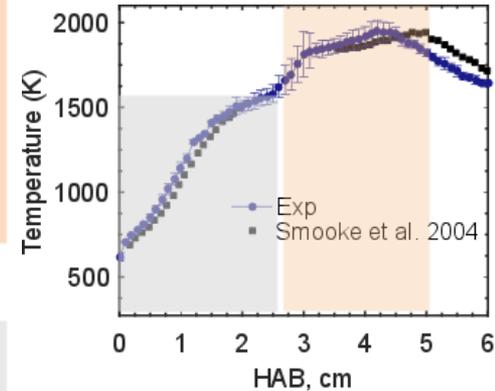
### Particle shrinkage (31- 49 mm HAB):

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

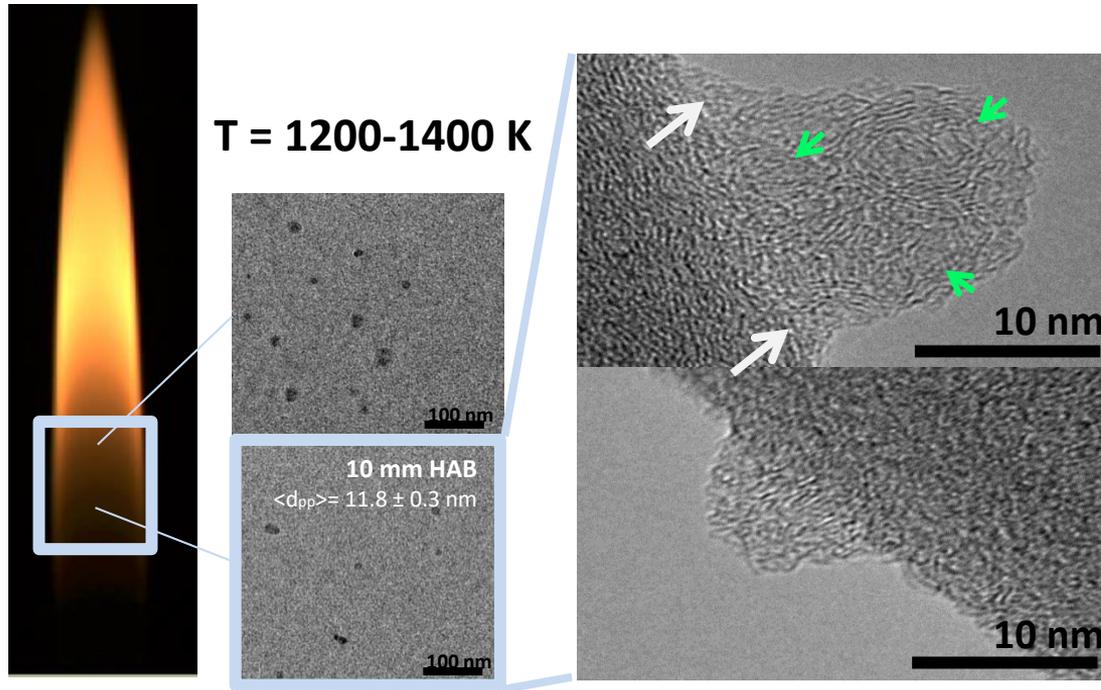
### Particle growth (10 – 25 mm HAB):

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

### Temperature Profile



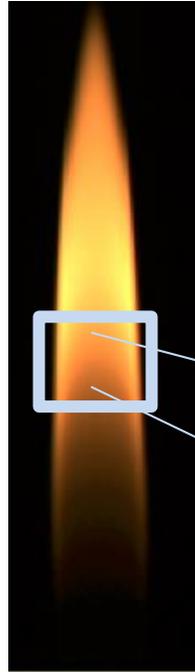
## Low HAB: initial growth



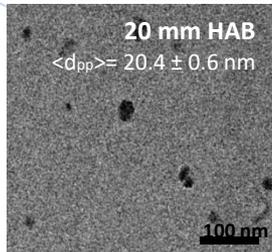
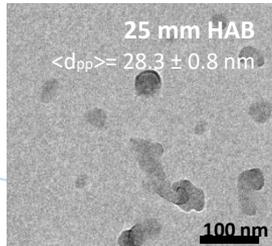
### Smallest particles sampled:

- 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

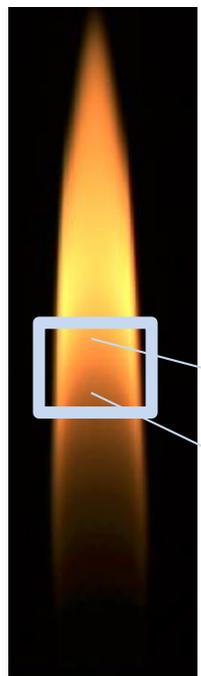


T= 1500-1570 K

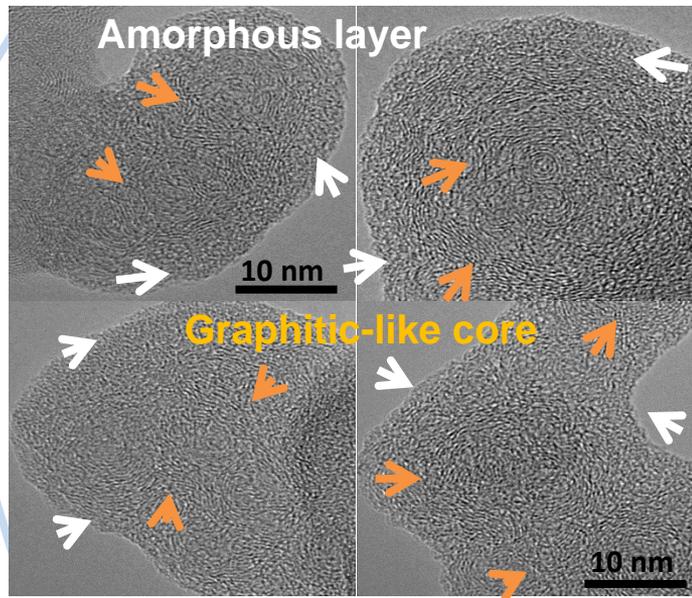
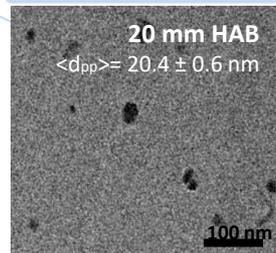
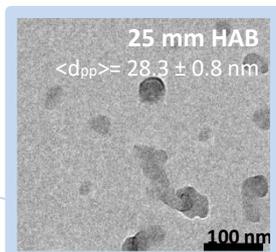


- Small aggregates
- Irregular shapes undefined boundaries
- Wax-like structure, spreads over the grid

## Medium-Low HAB: growth and aggregation



T= 1500-1570 K



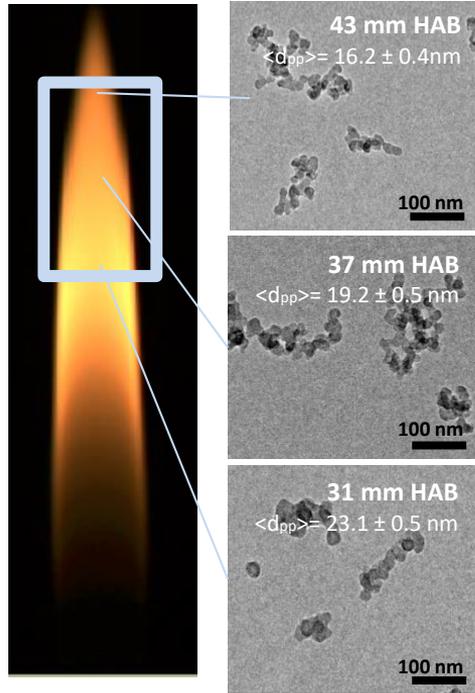
### Amorphous material

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

### Graphitic-like core

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

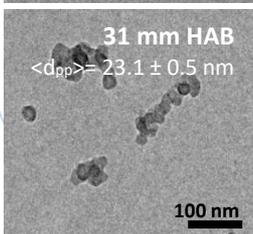
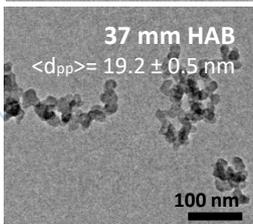
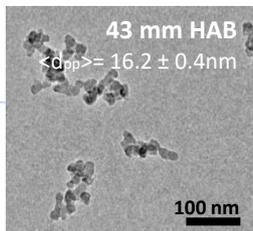
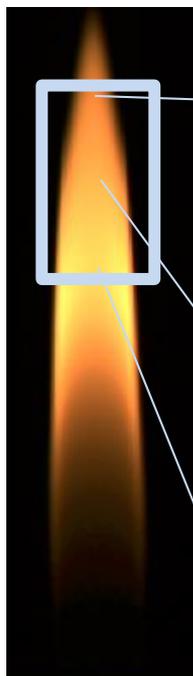
## Medium-High HAB: graphitisation



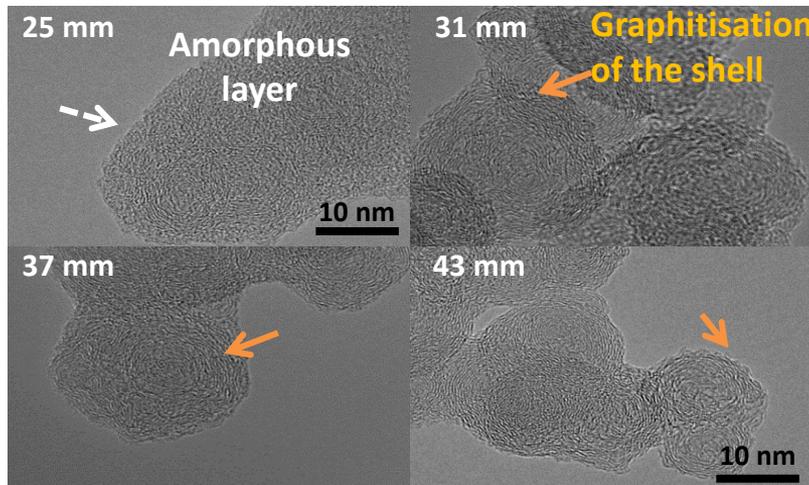
T= 1720-1810 K

- High contrast
- Well defined spherical shape
- Aggregation

## Medium-High HAB: graphitisation



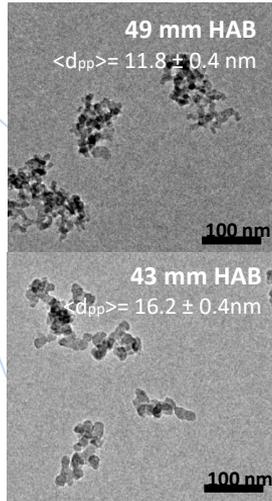
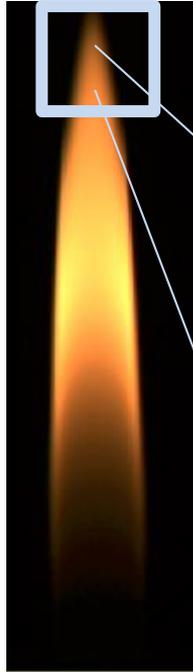
T= 1720-1810 K



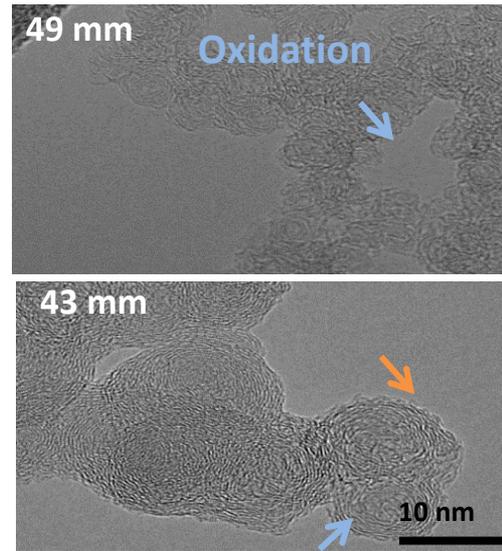
### Graphitisation

- 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



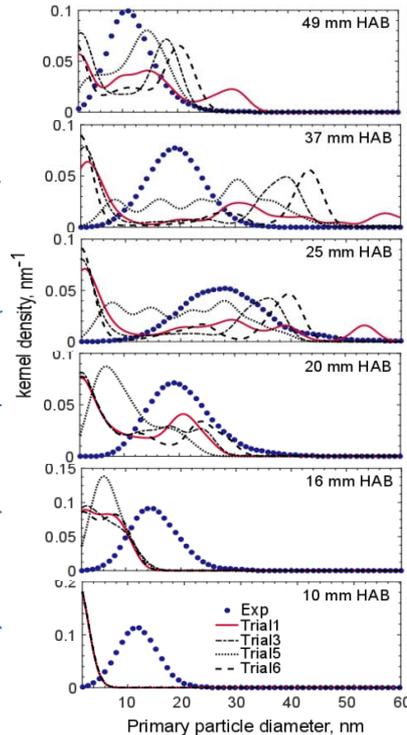
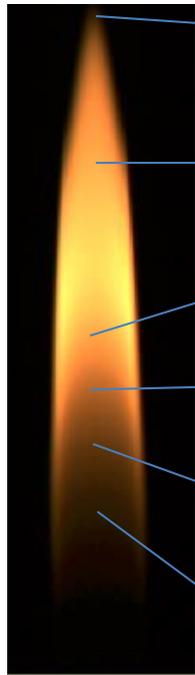
## Oxidation

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

## Test cases for sensitivity analysis

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

## Primary particle size distribution



### Trial 1: Base case

1) Delayed initial growth

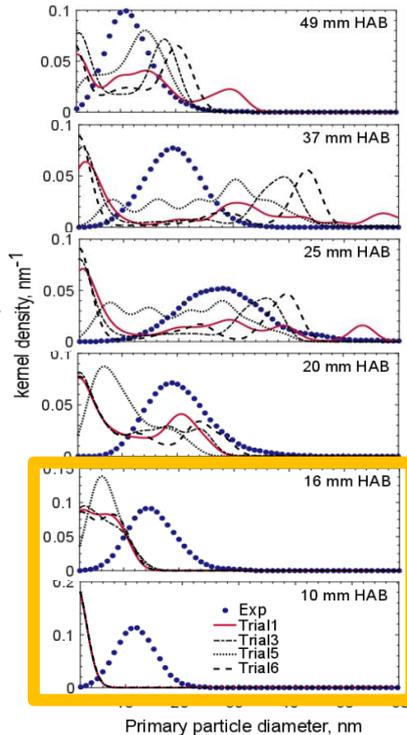
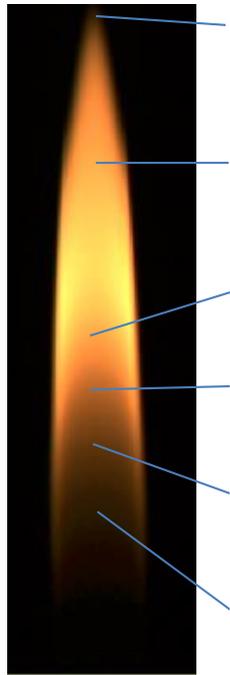
2)  $D_{crit}$  (Trial 5): fast coalescence of nascent particles

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

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

- Reduces multimodality

## Primary particle size distribution



Trial 1: Base case

1) Delayed initial growth

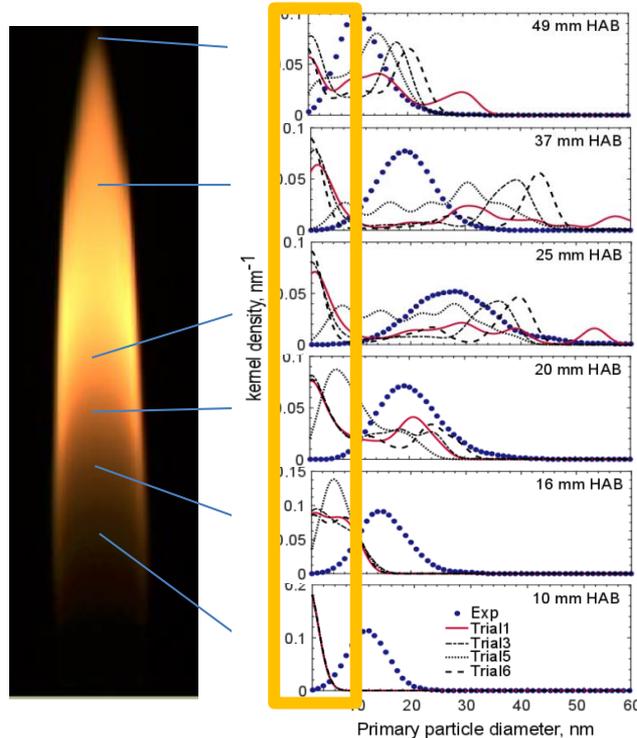
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## Primary particle size distribution



### Trial 1: Base case

1) Delayed initial growth

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

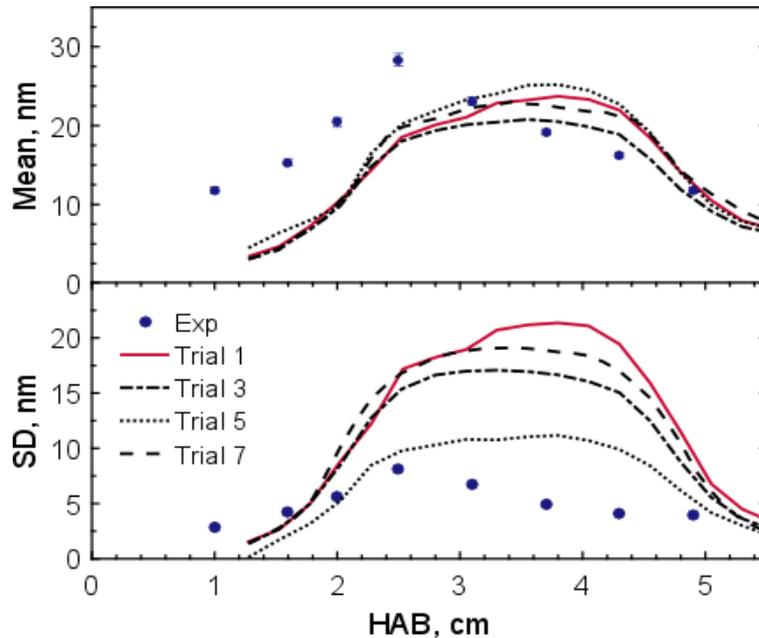
- Eliminates mode of sub 2 nm particles and very large particles

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

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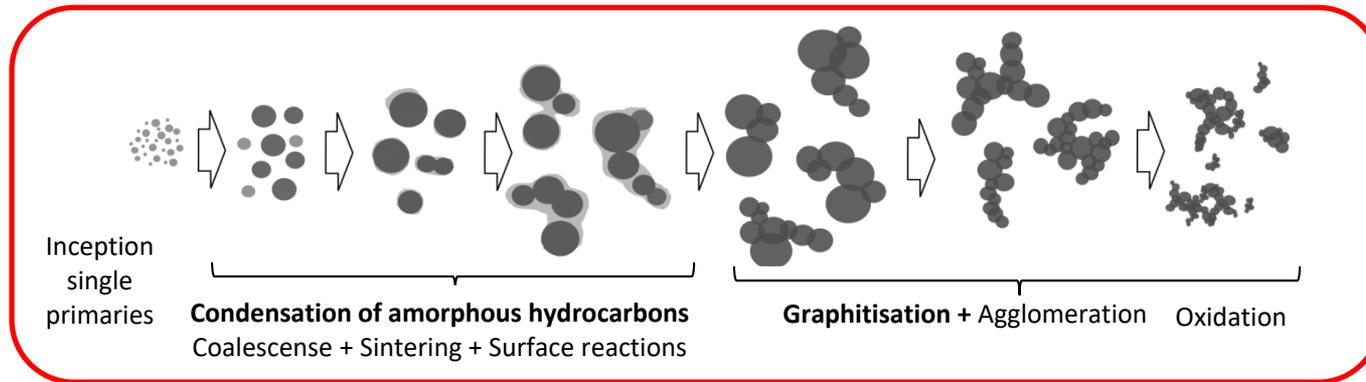
## Average primary particle size



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

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

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



- 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.**



**Thanks!**

# Future and Ongoing Work



Casper Lindberg  
2P048





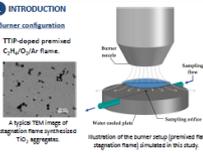

## Detailed population balance modelling of titanium dioxide nanoparticles in a premixed stagnation flame

The premixed stagnation flame synthesis of titanium dioxide nanoparticles (TiO<sub>2</sub>) is modelled using a two-step simulation capable of resolving the complex morphology of aggregate particles. The methodology facilitates simulation of quantities that are directly comparable to experimental observations and enables modelling of processes that require a detailed description of particle morphology.

### 1. INTRODUCTION

**Burner configuration**

- TiO<sub>2</sub>-doped premixed C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>/Ar flame.



A typical TEM image of aggregation flame synthesized TiO<sub>2</sub> aggregates.

- A detailed particle model is needed to simulate the complex aggregate morphology of flame synthesized TiO<sub>2</sub>.

### 2. DETAILED PARTICLE MODEL

**Type-space**

- An aggregate is composed of primary particles represented as overlapping spheres.
- Primary coordinates are tracked.
- The level of sintering between primaries is resolved by their centre to centre separation.

**Particle processes**

**Inception**

$$Ti(OH)_4 + Ti(OH)_4 \rightarrow P_2(n) + H_2O$$

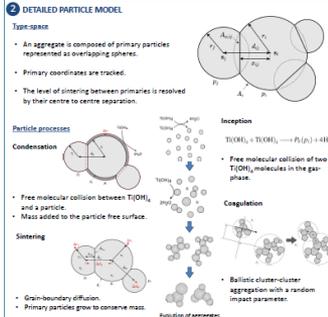
- Free molecular collision of two Ti(OH)<sub>4</sub> molecules in the gas-phase.

**Coagulation**

- Free molecular collision between Ti(OH)<sub>4</sub> and a particle.
- Mass added to the particle free surface.

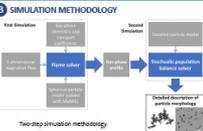
**Sintering**

- Ballistic cluster-cluster aggregation with a random impact parameter.
- Grain-boundary diffusion.
- Primary particles grow to coalesce mass.



### 3. SIMULATION METHODOLOGY

Two-step simulation methodology:

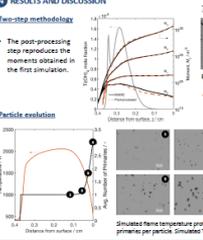


### 4. RESULTS AND DISCUSSION

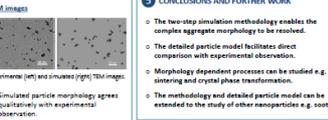
**Two-step methodology**

- The two-step simulation methodology enables the complex aggregate morphology to be resolved.
- The detailed particle model facilitates direct comparison with experimental observation.
- Morphology dependent processes can be studied e.g. sintering and crystal phase transformation.
- The methodology and detailed particle model can be extended to the study of other nanoparticles e.g. soot.

**Particle evolution**



**TEM images**



- Simulated particle morphology agrees qualitatively with experimental observation.
- The model predicts aggregate formation as the temperature decreases near the stagnation surface.
- The rate of sintering drops relative to the coagulation rate.

### 5. CONCLUSIONS AND FURTHER WORK

- The two-step simulation methodology enables the complex aggregate morphology to be resolved.
- The detailed particle model facilitates direct comparison with experimental observation.
- Morphology dependent processes can be studied e.g. sintering and crystal phase transformation.
- The methodology and detailed particle model can be extended to the study of other nanoparticles e.g. soot.

### 6. KEY REFERENCES

1. S. Jiang, J. He, J. Li, J. Li, and M. Kraft, A novel reaction for the thermal decomposition of titanium hydroxide, *Proc. Combust. Inst.*, 36(1):2011-2015, 2015.

2. J. Aguilera, C. D. Scales, H. J. Scales, and C. P. Frisvold, Aggregate morphology evolution by sintering, fracture and dissolution of primary particles, *Chemical Sci.*, 6(1):1-11, 2015.

3. A. S. Gnanapavan, S. A. S. Gnanapavan, and S. A. S. Gnanapavan, Sintering of titanium hydroxide particles, *Chemical Sci.*, 6(1):1-11, 2015.

4. M. Manu, S. A. S. Gnanapavan, C. P. Frisvold, and M. Kraft, Modelling TiO<sub>2</sub> formation in a stagnation flame, *Proc. Combust. Inst.*, 36(1):2011-2015, 2015.

5. H. Wang, X. Li, A. S. Gnanapavan, C. P. Frisvold, and M. Kraft, High-temperature combustion synthesis of TiO<sub>2</sub> nanoparticles, *Chemical Sci.*, 6(1):1-11, 2015.



Dingyou Hou  
2P039







## Modelling Soot Formation in a Benchmark Ethylene Stagnation Flame with a New Detailed Population Balance Model

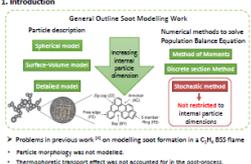
**Yanlei Hou<sup>1,2</sup>, Casper Lindberg<sup>1,3</sup>, Manoj Manuputty<sup>1,3</sup>, Xiaoping You<sup>1,4</sup> and Markus Kraft<sup>1,4,5</sup>**

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<sup>3</sup> Department of Chemical Engineering and Biotechnology, University of Cambridge, 7PPH3, Cambridge, CB3 0RA, United Kingdom  
<sup>4</sup> School of Chemical and Biomass Engineering, Hanyang Technological University, 47 Hanyang-dong, Seongbuk-gu, Seoul 135, South Korea  
<sup>5</sup> Cambridge Center for Advanced Research and Education in Singapore (CARES), 110115, Singapore

Numerical simulation of soot formation in a premixed C<sub>2</sub>H<sub>4</sub>/B55 flame was performed with a new detailed population balance model using a two-step method. The new model is capable of tracking aggregate morphology during simulation. Thermophoretic transport effect due to the large temperature gradient near the stagnation plate is accounted for in the post-processing. A thorough parametric sensitivity study is carried out to investigate the influence of key model parameters on the computed PSDs and soot morphology. The capability of the new model to predict PSDs in B55 flame is studied by comparing simulated PSDs with the measured ones in the literature. We provide insight into individual soot formation processes and suggest future work which are imperative to make further progress on soot modelling.

### 1. Introduction

**General Outline Soot Modelling Work**



- Particle description: spherical model, surface-volume model, detailed model.
- Numerical methods to solve Population Balance Equation: Method of Moments, Discrete section Method, stochastic methods.
- Post-processing: Thermophoretic Correction<sup>1</sup>, Population Balance Solver, Particle size distribution, Aggregate morphology.

**Problems in previous work<sup>2,3</sup> on modelling soot formation in a C<sub>2</sub>H<sub>4</sub>/B55 flame**

- Particle morphology was not modelled.
- Thermophoretic transport effect was not accounted for in the post-process.

### 2. Modelling Methodology

**Flow model** (1D, 2D, 3D)

**Gas-phase model** (Detailed, Simplified)

**Particle model** (Spherical, Detailed)

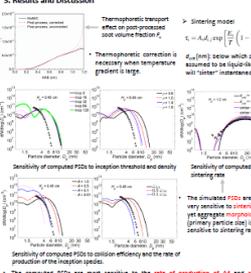
**Post-processing** (Thermophoretic Correction<sup>1</sup>, Population Balance Solver, Particle size distribution, Aggregate morphology)

**Detailed Particle Process** (Inception, Coagulation, Surface growth, Condensation, Coalescence, Sintering)

**Detailed Type Space** (Detailed Particle Model)

### 3. Results and Discussion

**Thermophoretic transport effect on post-processed soot morphology**



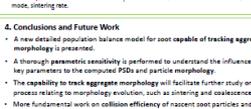
**Stiering model**

$$k = A \cdot \exp\left(-B \cdot \left(\frac{d_p}{d_0}\right)^n\right)$$

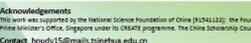
$d_0$  (nm) below which soot is assumed to be liquidlike and will sinter instantaneously.

**Thermophoretic correction is necessary when temperature gradient is large.**

**Stability of computed PSD to inception threshold and soot density**



**Stability of computed PSD to sintering rate**



**Computed PSDs were not very sensitive to sintering rate, yet aggregate morphology (primary particle size) is very sensitive to sintering rate.**

**Stability of computed PSD to ignition efficiency and the rate of production of inception nuclei**



**The computed PSDs are most sensitive to the rate of production of AA and collision efficiency, while not sensitive to inception threshold, coagulation threshold, inception mode, sintering rate.**

**Simulated PSDs vs Measured PSDs<sup>4,5</sup>**



**Computed PSDs (blue line) compared to experimental measurements (blue and black symbols) simulated to experimental measurements (blue and black symbols) simulated to experimental measurements (blue and black symbols).**

**Good agreement between simulation and experiment results can be achieved for  $d_p < 400$  nm.**

**Collision efficiency is suggested to be increasing with particle size.**

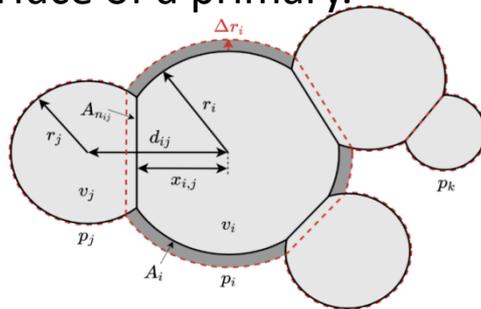
**Acknowledgements** This work was supported by the National Science Foundation of China (NSFC) [21422012], the Foundation of State Key Laboratory of Coal Conversion (FKJ2014-1-1), the National Research Foundation, Prime Minister's Office, Singapore under its CREATE programme, The China Scholarship Council (Jingyuan Zhang).

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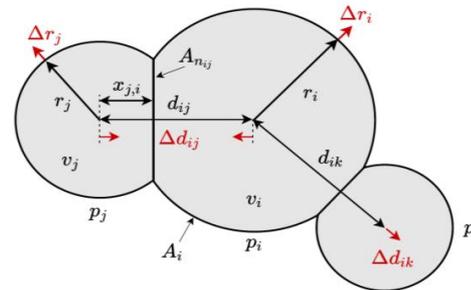
## Particle process models

**Coagulation:** Ballistic cluster-cluster aggregation with a random impact parameter.<sup>1</sup>

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



**Sintering:** viscous flow.<sup>2</sup>



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.

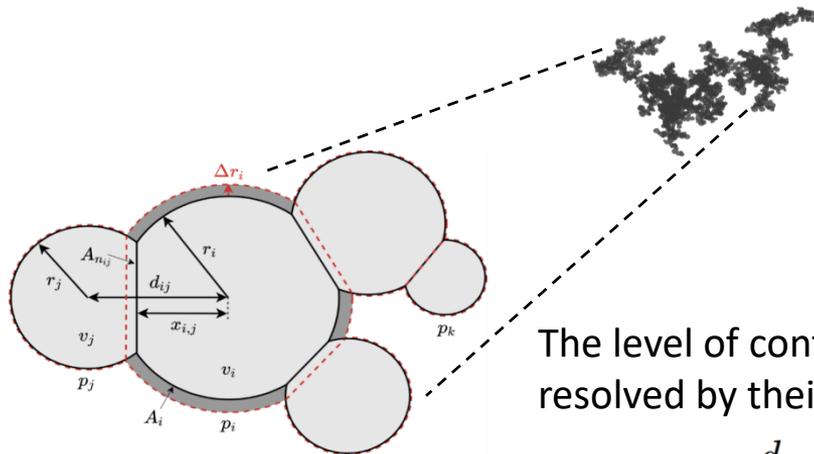


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## Particle type space

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

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



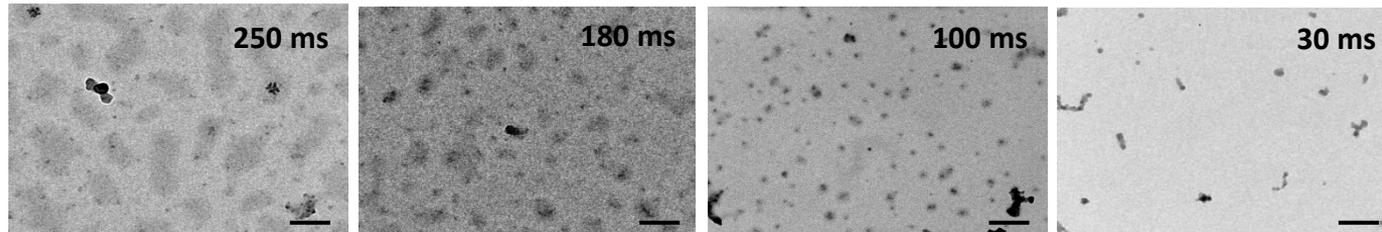
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## Liquid blobs - Sampling artifacts

Liquid-like material surrounding the particles depend on:

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

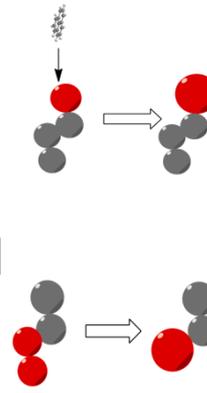


Sufficiently short insertion periods can avoid condensable material on the grids

## 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
3) Minimum number of 6-member aromatic rings in a PAH in a particle ( $n_{\text{PAHs}} \geq n_{\text{crit}}$ ) below which it is removed	-	4
4) Soot density, $\rho$	$1 \text{ g cm}^{-3} \leq \rho \leq 2 \text{ g cm}^{-3}$	$1.88 \text{ g cm}^{-3}$
5) Smoothing factor, $\sigma$	$0 \leq \sigma \leq 2$	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, $n_{\text{crit}}$	$\geq 2$	4
8) Sintering model:		
- $A_s$	-	$1.1 \times 10^{-14} \text{ s m}^{-1}$
- $E_s$	$1.8 \times 10^4 \text{ K} \leq E_s \leq 1.8 \times 10^5 \text{ K}$	$9.61 \times 10^4 \text{ K}$
- $d_{\text{p,crit}}$	$1 \text{ nm} \leq d_{\text{p,crit}} \leq 5 \text{ nm}$	1.58 nm

## Particle rounding processes:



Smoothing factor,  $s$ :

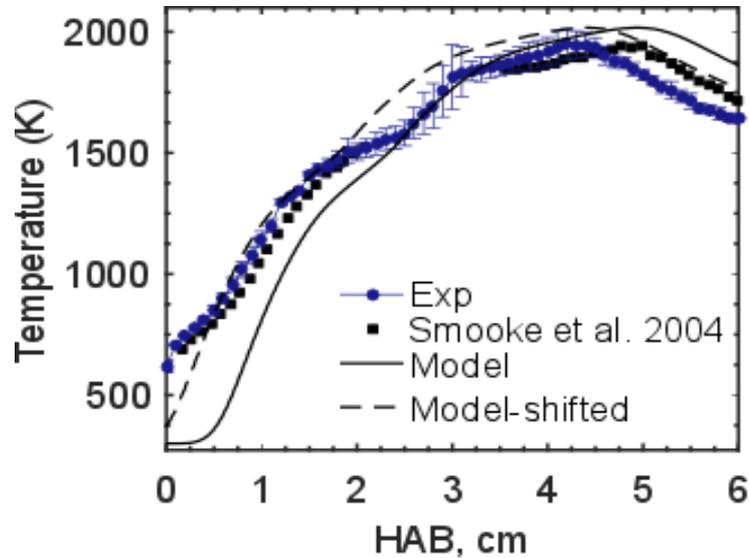
Rate of change in joint surface area by **mass addition**

Sintering model: Arrhenius type

- Pre-exponential factor and activation energy

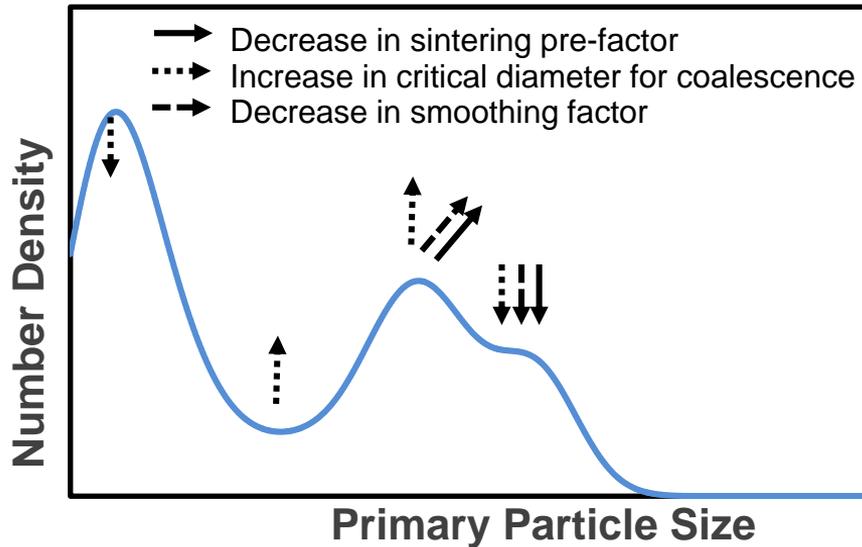
-  $D_{\text{p,crit}}$ : instantaneous sintering

## Temperature Profile



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

## Sensitivity analysis



### Sintering prefactor

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

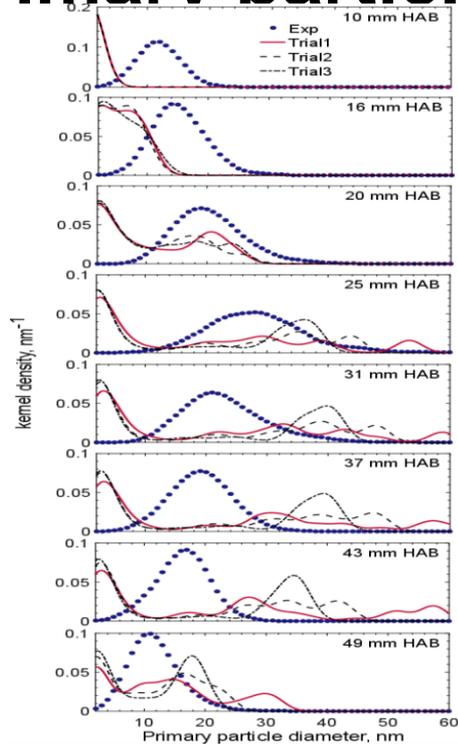
### Critical diameter for coalescence

- **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**

# Primary particle size distribution

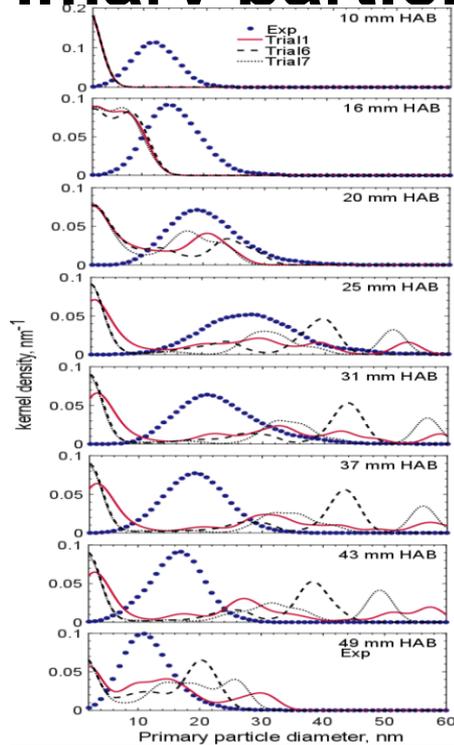


Sintering prefactor  $A_s$ : (decreasing)

- 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)	$\sigma$
1	$1.1 \times 10^{-14}$	1.58	1.69
2	$1.1 \times 10^{-13}$	1.58	1.69
3	$1.1 \times 10^{-12}$	1.58	1.69

# Primary particle size distribution



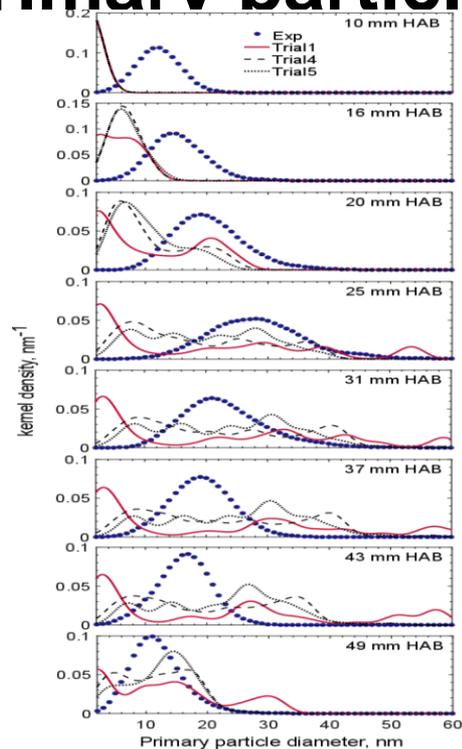
Smoothing factor,  $\sigma$ : (decrease)

- 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)	$\sigma$
1	$1.1 \times 10^{-14}$	1.58	1.69
6	$1.1 \times 10^{-14}$	1.58	1.0
7	$1.1 \times 10^{-14}$	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)	$\sigma$
1	$1.1 \times 10^{-14}$	1.58	1.69
4	$1.1 \times 10^{-14}$	3	1.69
5	$1.1 \times 10^{-14}$	5	1.69