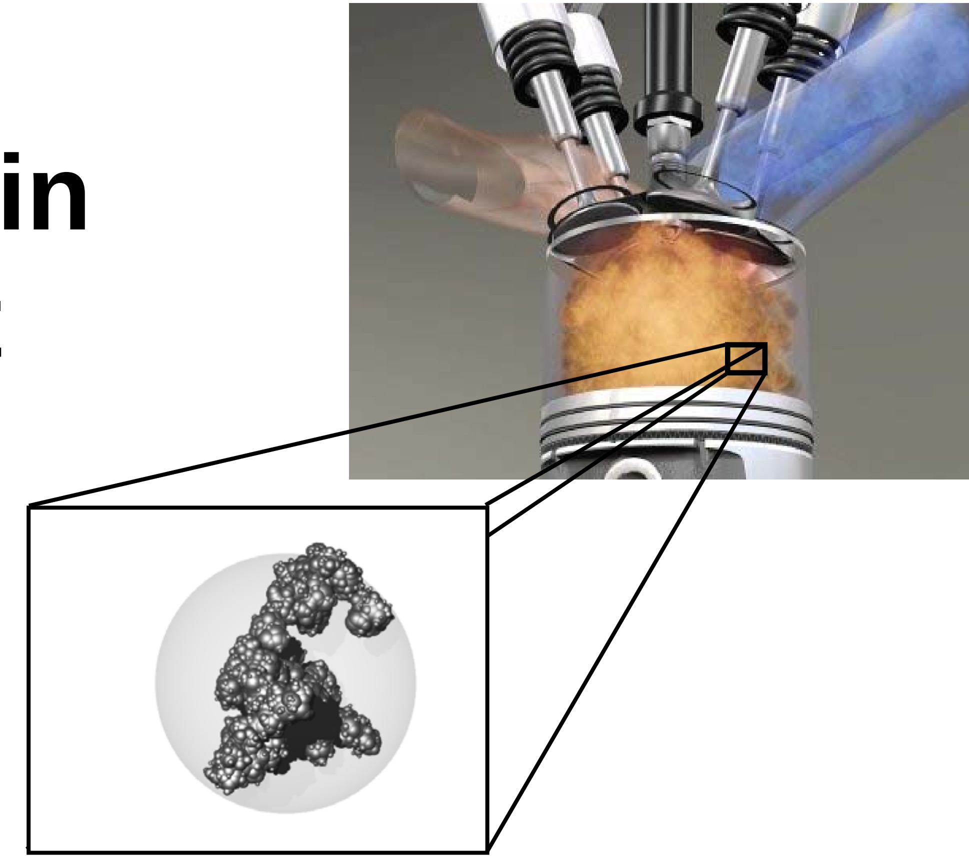
New Developments in Modelling Soot Formation in Engines



Dr Markus Kraft

Sebastian Mosbach, Jon Etheridge, Abhijeet Raj, Richard West, Matt Celnik, Rob Patterson, Tim Totton, Markus Sander, Raphael Shirley, Neal Morgan, Amit Bhave, Andrew Smallbone

16 March 2009

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Part 1:

- Quantum chemistry
- Kinetic Monte Carlo
- Basin hopping
- Population balance

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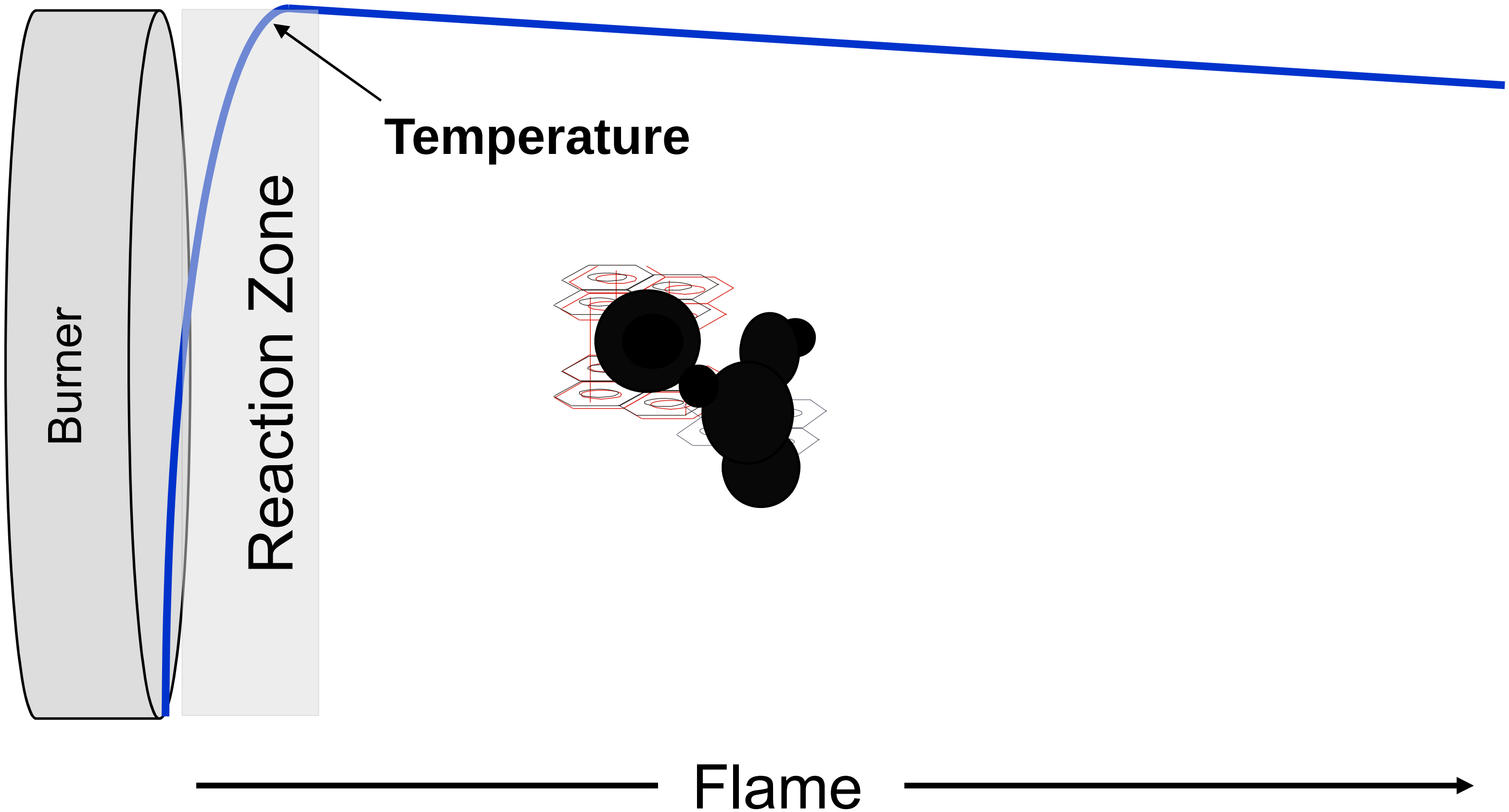
Soot Formation



Carbon Addition Reactions

Condensation of PAHs

Particle Inception

Coagulation

Aggregation

Oxidation by O_2 and OH,

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Soot model hierarchy

Quantum Chemistry (DFT)

↓

Kinetic Monte-Carlo (KMC)

↓

Site-Counting Model (ARSC)

↓

Population Balance

Full representation of molecules
Determine kinetic parameters

Single planar PAH simulations
Generate structure correlations

Functional site description
Particle model for population balances
Structure described by correlations (fast)

Particle ensemble modelling
Particles described by ARSC Model
Inception, growth and coagulation

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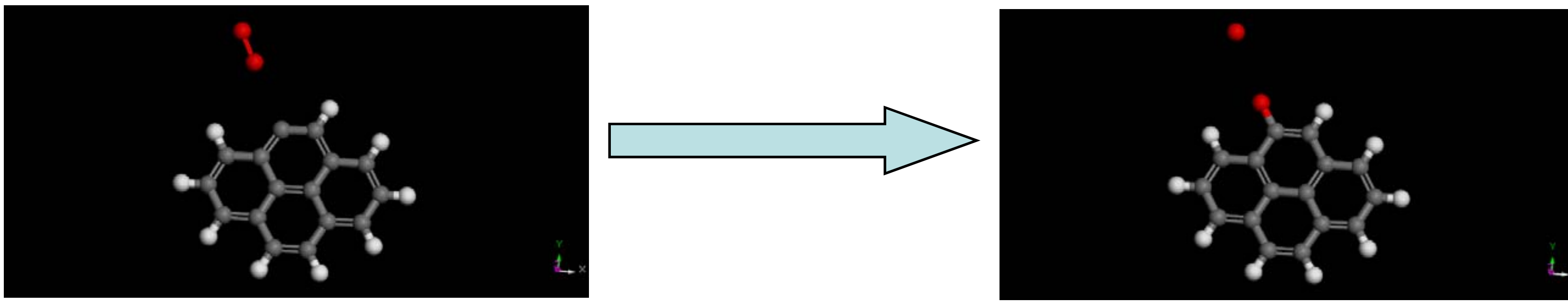
Oxidation processes in PAHs

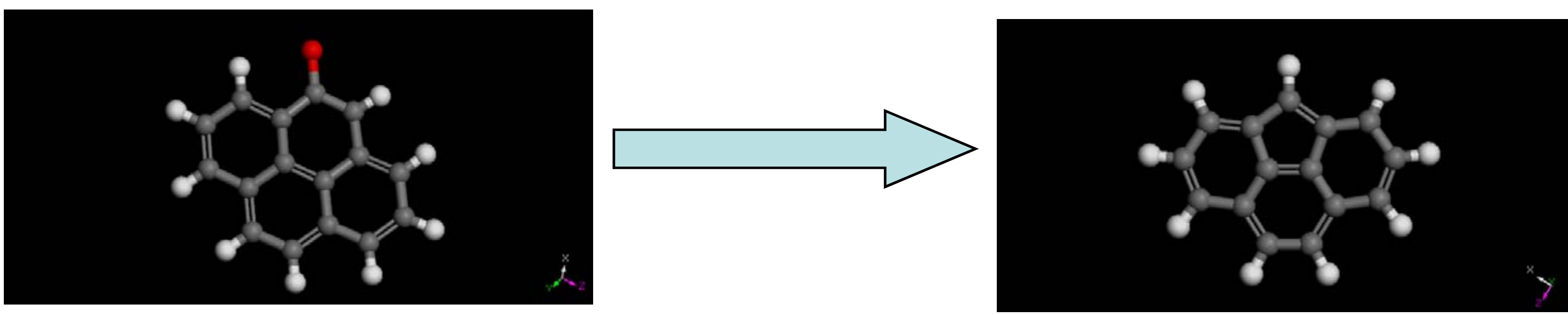
Investigated reactions:

PAH: Polyaromatic hydrocarbons

Oxidation process:



Decomposition process:



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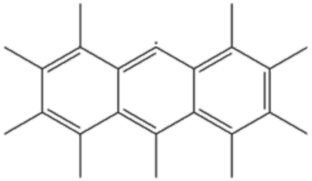
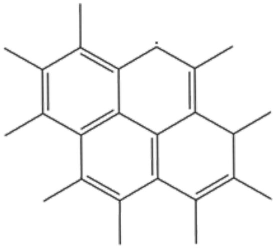
Oxidation rates of different site types

Zigzag next to zigzag (zz)



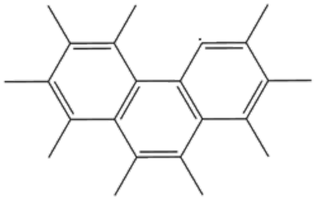
E_{act}=156 kJ/mole

Zigzag next to free edge (zf)

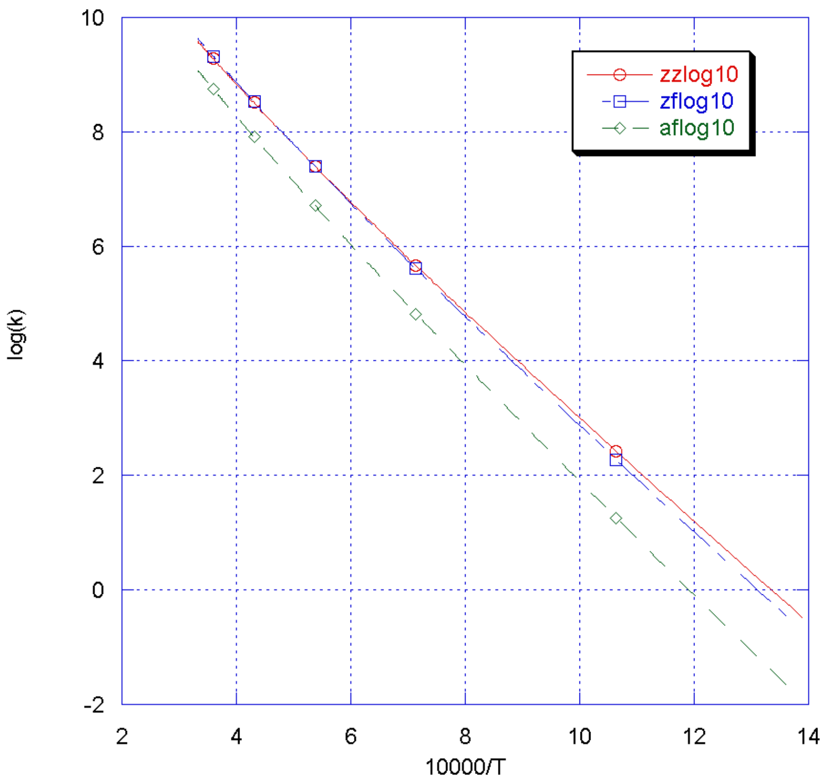


E_{act}=161 kJ/mole

Armchair next to free edge (af)



E_{act}=173 kJ/mole



Units: k in $cm^3/(mole*s)$, T in K

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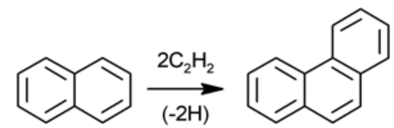
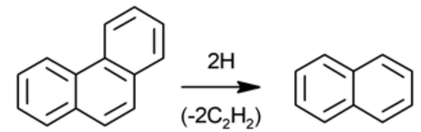
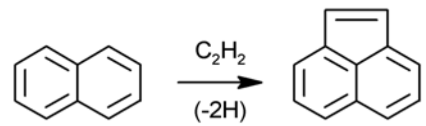
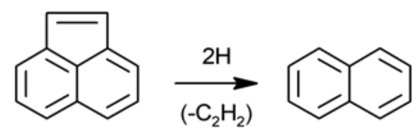
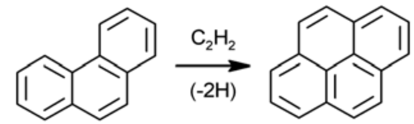
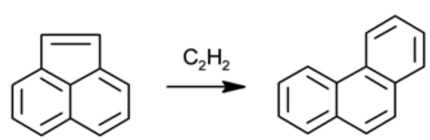
PAH reactions (selection)

S1	Free-edge growth	
S2	Free-edge desorption	
S3	5-member ring addition	
S4	5-member ring desorption	
S5	Armchair growth	
S6	5- to 6-member ring	

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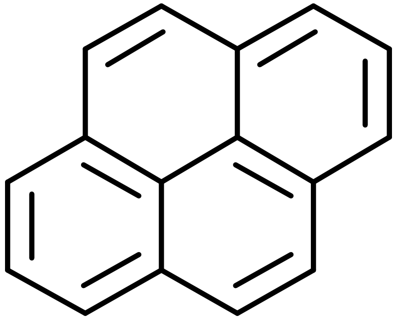
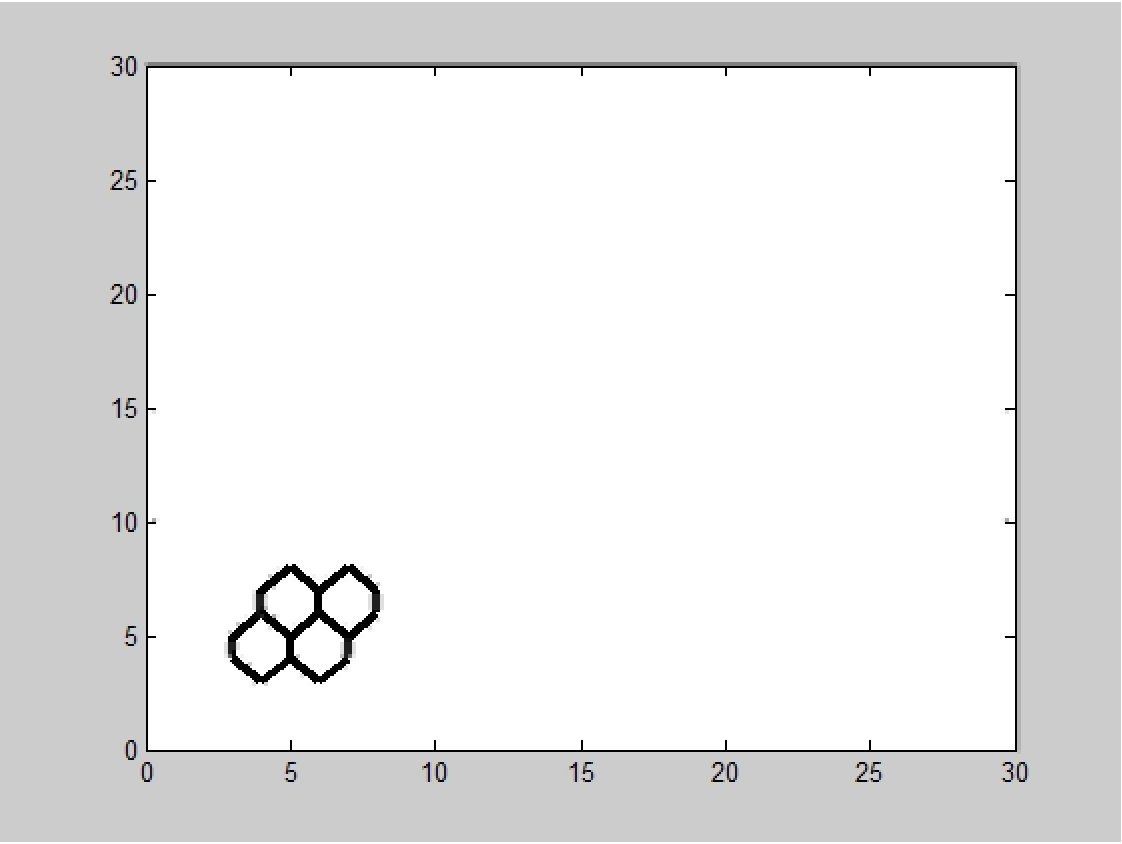
PAH growth simulation



Seed molecule:
Pyrene



Growth of a PAH molecule

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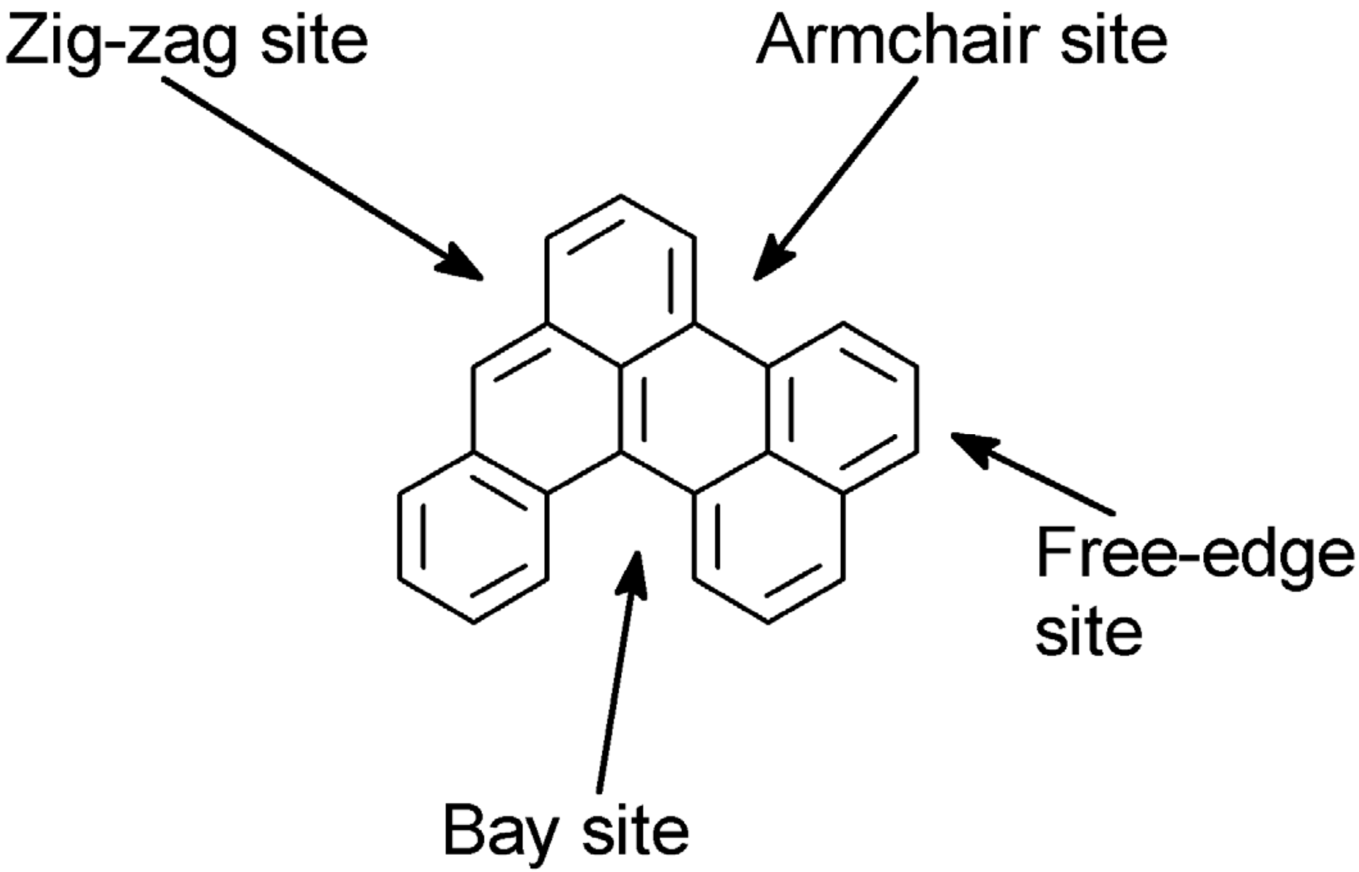
Adding structural information



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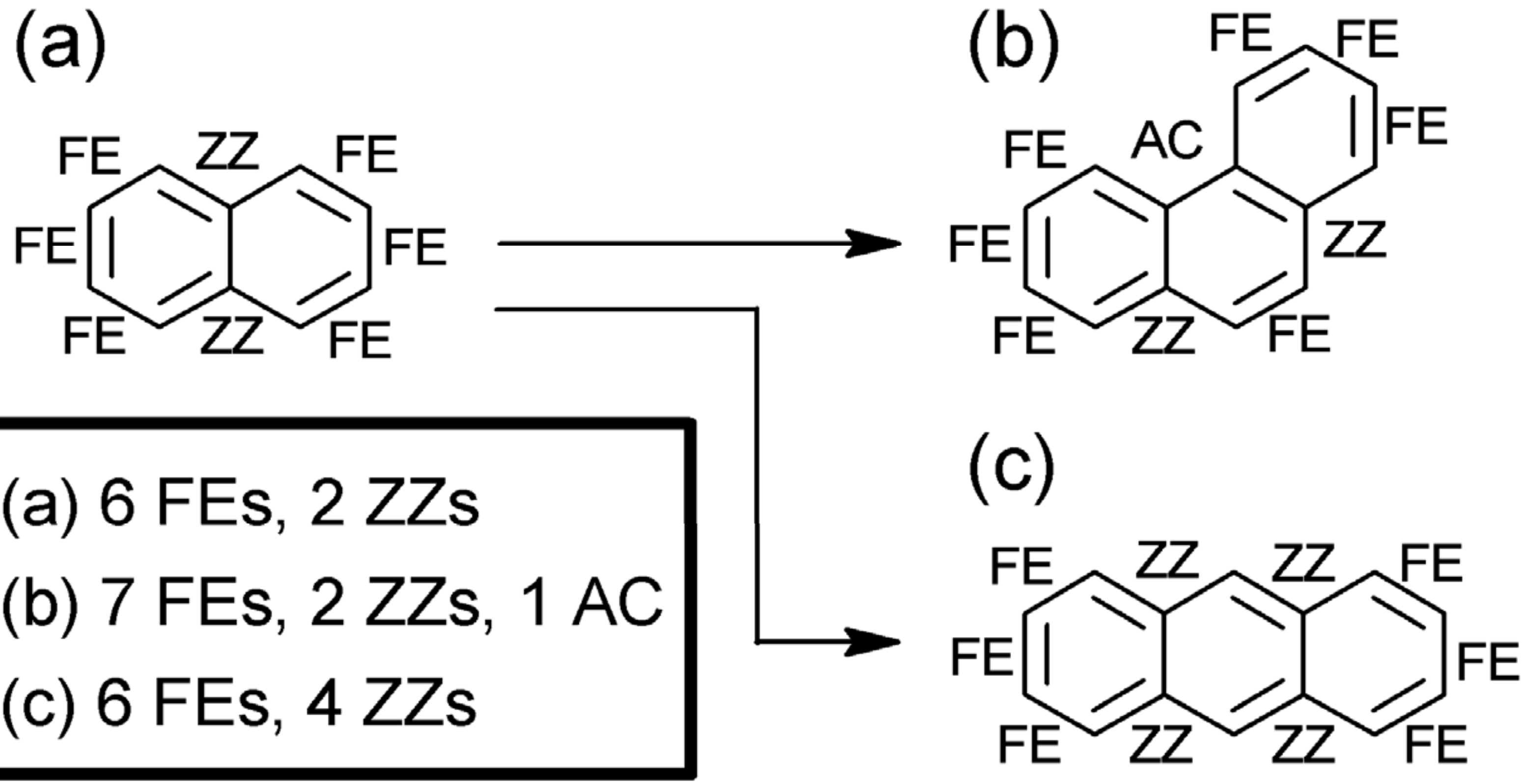
S1: Free edge growth



(a) 6 FEs, 2 ZZs

(b) 7 FEs, 2 ZZs, 1 AC

(c) 6 FEs, 4 ZZs

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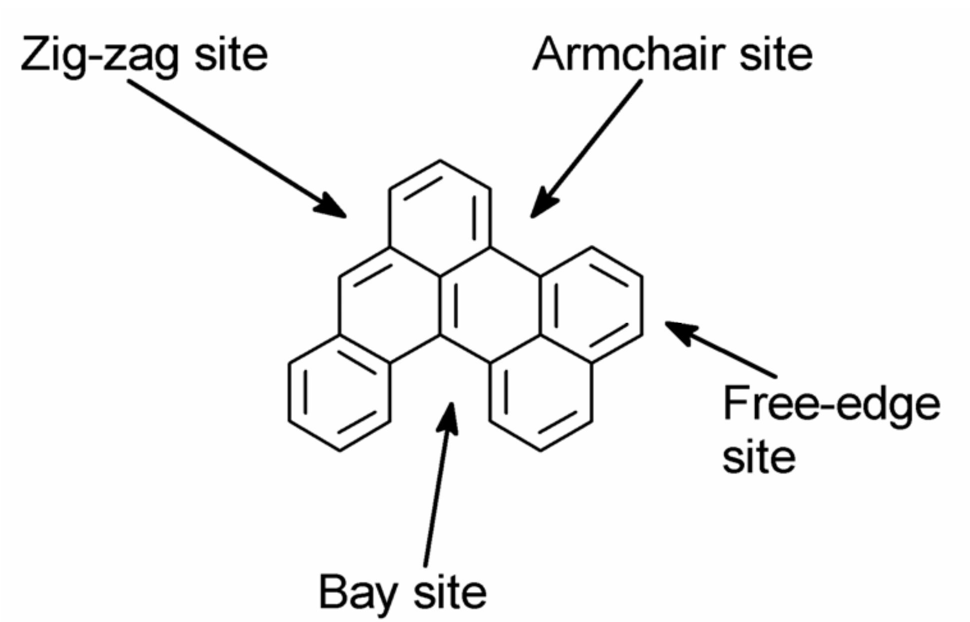
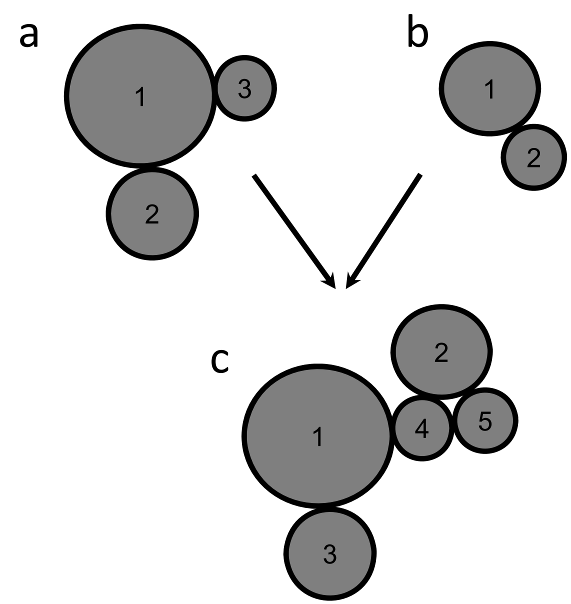
Particle state space

Describe soot particles by *9+N* dimensional state space (ARS-SC-PP model):

$$E = \left(C, H, N_{FE}, N_{ZZ}, N_{AC}, N_{BY}, N_{R5}, S_{a}, N_{PAH}, PP_{(1\text{-}N)}\right)$$

PP = primary particle list





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Molecular soot structure

- Nanoparticles (3 nm – 2 μm)
- 'Primary particles' occur due to dimerisation of PAH molecules
- What is the critical PAH size to form a dimer in flame conditions?
- How mobile are PAH molecules within a particle?
- How does morphology change and how does this affect the rates of sintering between primary particles?

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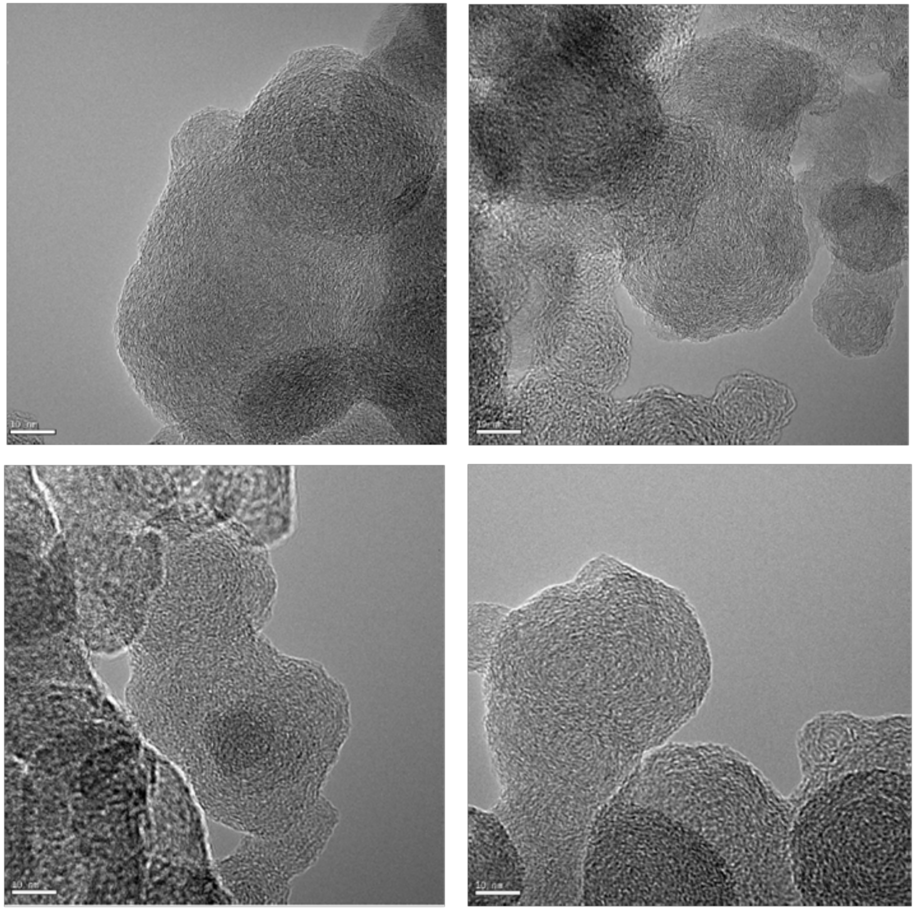
TEM images of soot

- Some evidence for different soot structures based on different fuels
- Top: ‘graphitic’
- Bottom: ‘amorphous’



Pictures from: Uitz, Cracknell, Jansma and Makkee, “Impact of diesel fuel composition on soot oxidation Characteristics”, SAE 2009-01-0286

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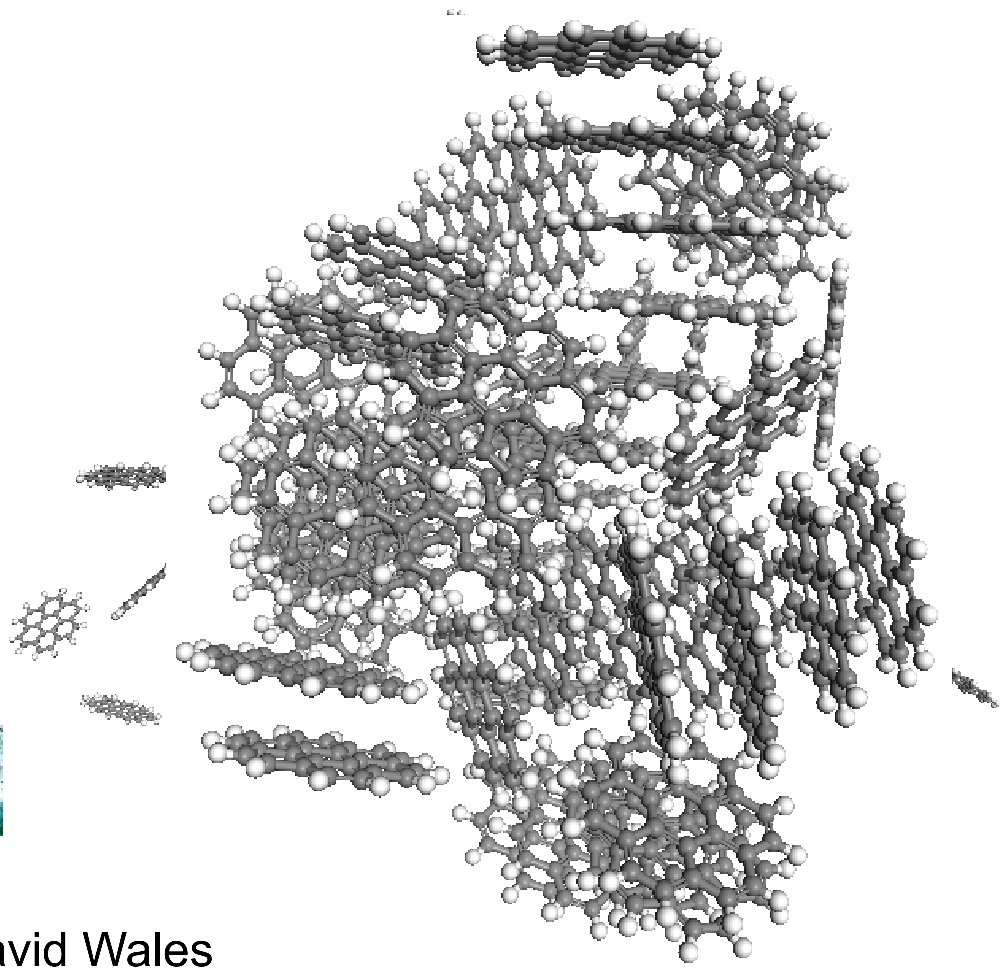
Investigating structure

- How do PAH molecule form clusters?
- Driven by intermolecul potentials
- How do these clusters grow?



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Dwaipayan Chakrabarti, Mark Miller, David Wales

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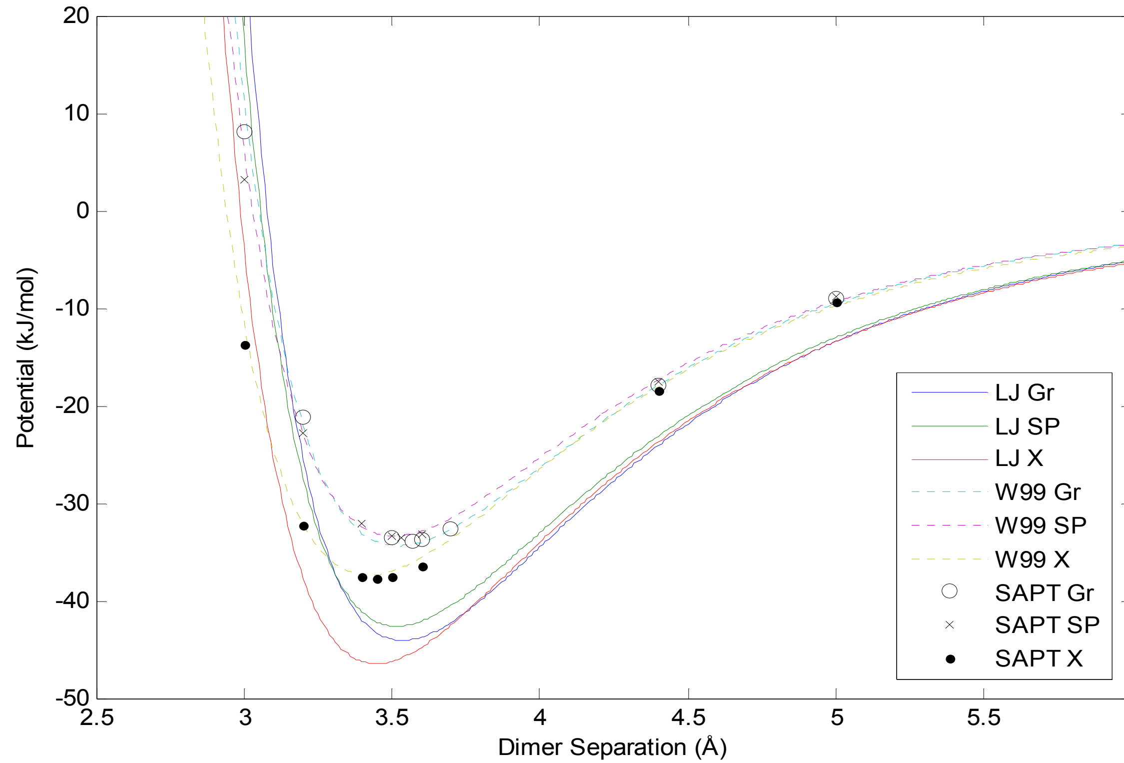
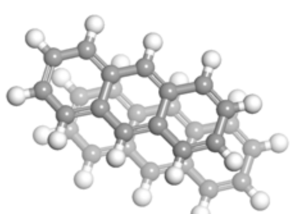
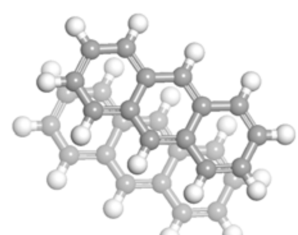
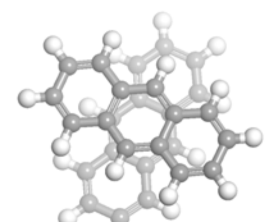
Comparison of potentials

- Poor agreement between L-J potential and SAPT(DFT) results
- Good agreement with W99 potential




Graphite (Gr)


Slipped Parellel (SP)


Crossed (X)

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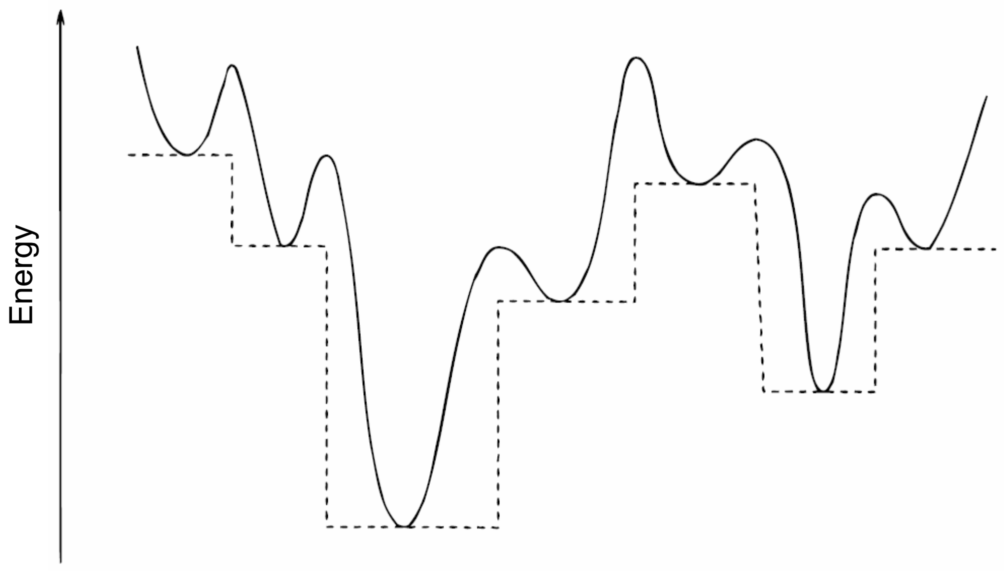
basin hopping

- Finds stable molecular clusters by searching for minima
- Based on potential energy 'landscape'
- Uses Monte-Carlo criterion when 'jumping' between minima



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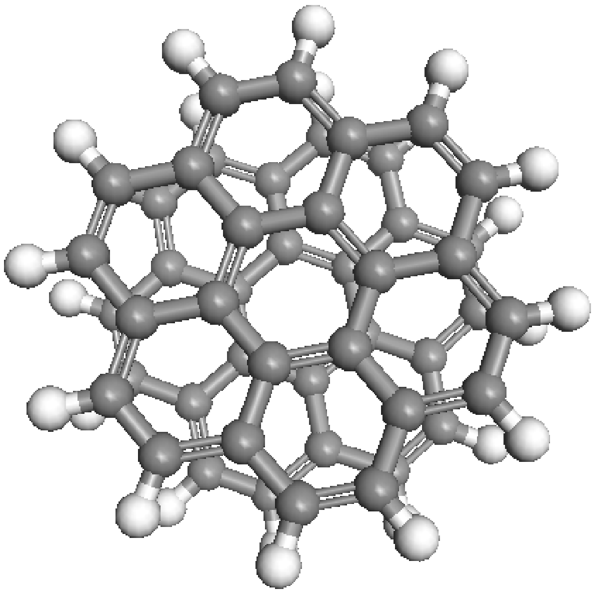
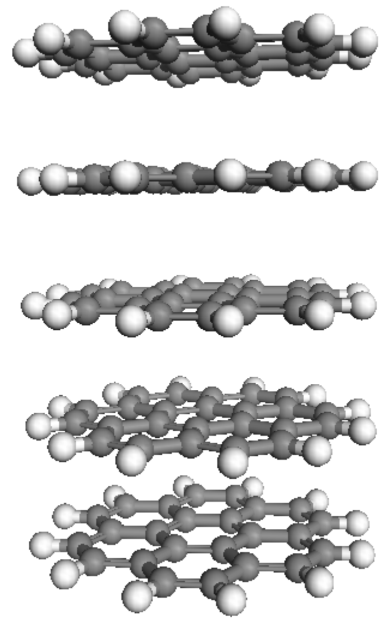
global minimum clusters

2 Coronene molecules



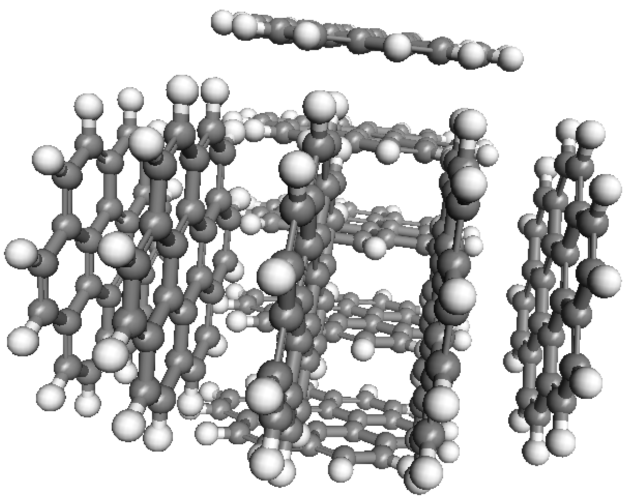
E = -94.90 kJ/mol

5 Coronenes molecules



E = -394.35 kJ/mol

10 Coronene molecules



E = -926.42 kJ/mol

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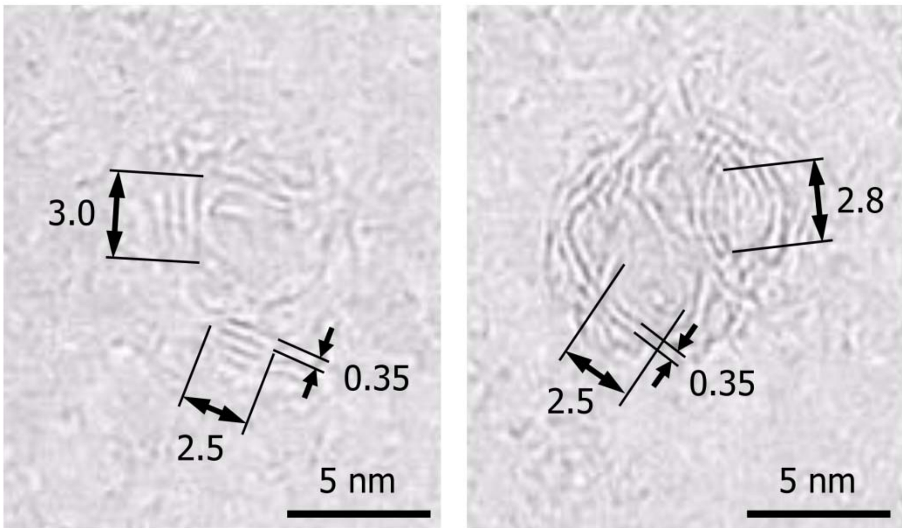
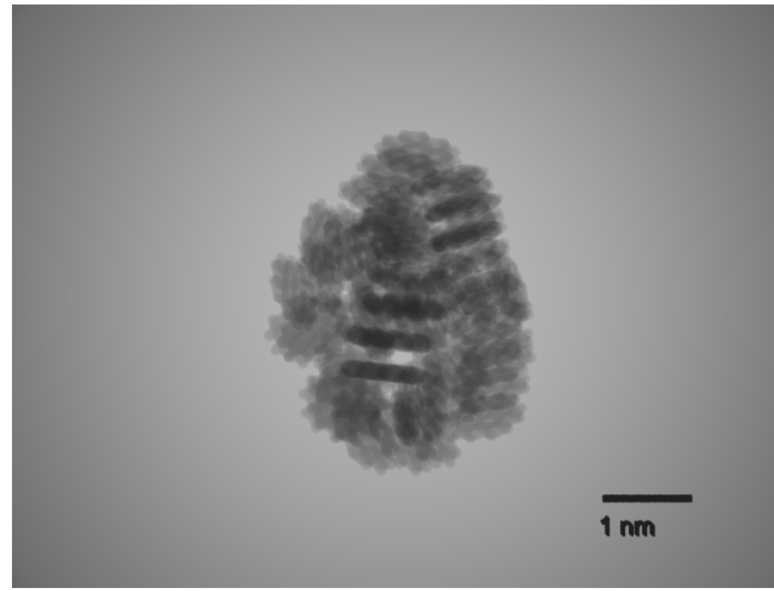
Experimental comparison



Experimental HR-TEM images of an aggregate sampled from a diesel engine. Indicated are length scales of structures within a primary particle (from Mosbach *et al.*, 2009, Combustion and Flame).



A TEM-style projection of a cluster of 50 coronene molecules

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Part 2:

- Soot model validation in SRM
- Converted SI – HCCI engine
- SRM – SI
- Soot in DISI

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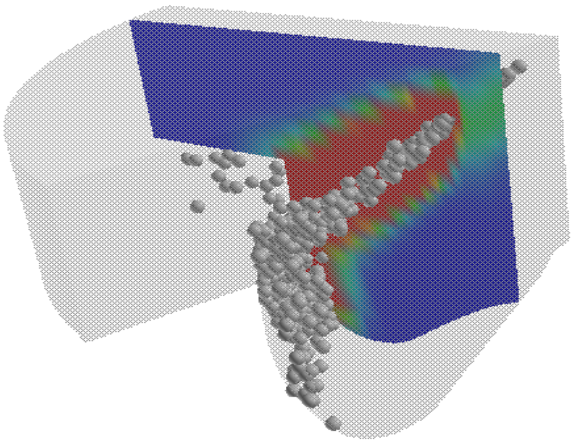
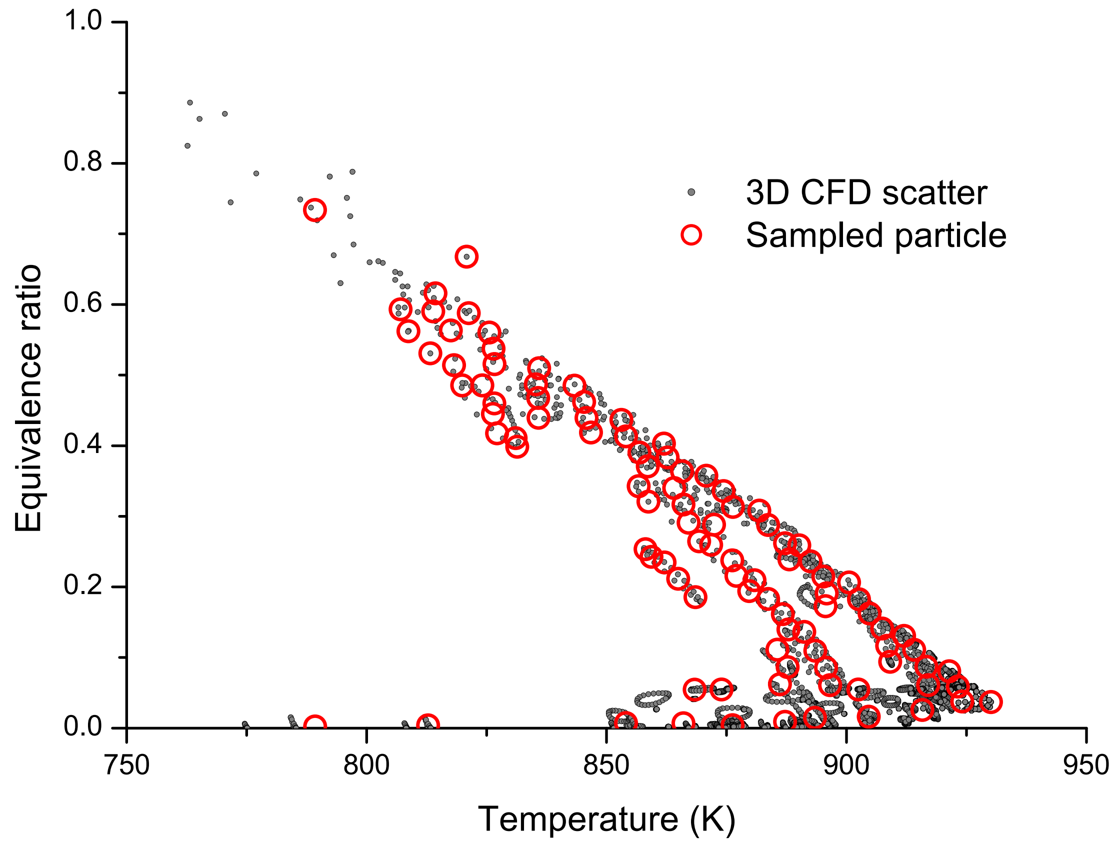
Engine model: SRM





Diesel engine

SOI= -50□ ATDC

Spray Cone angle=100□

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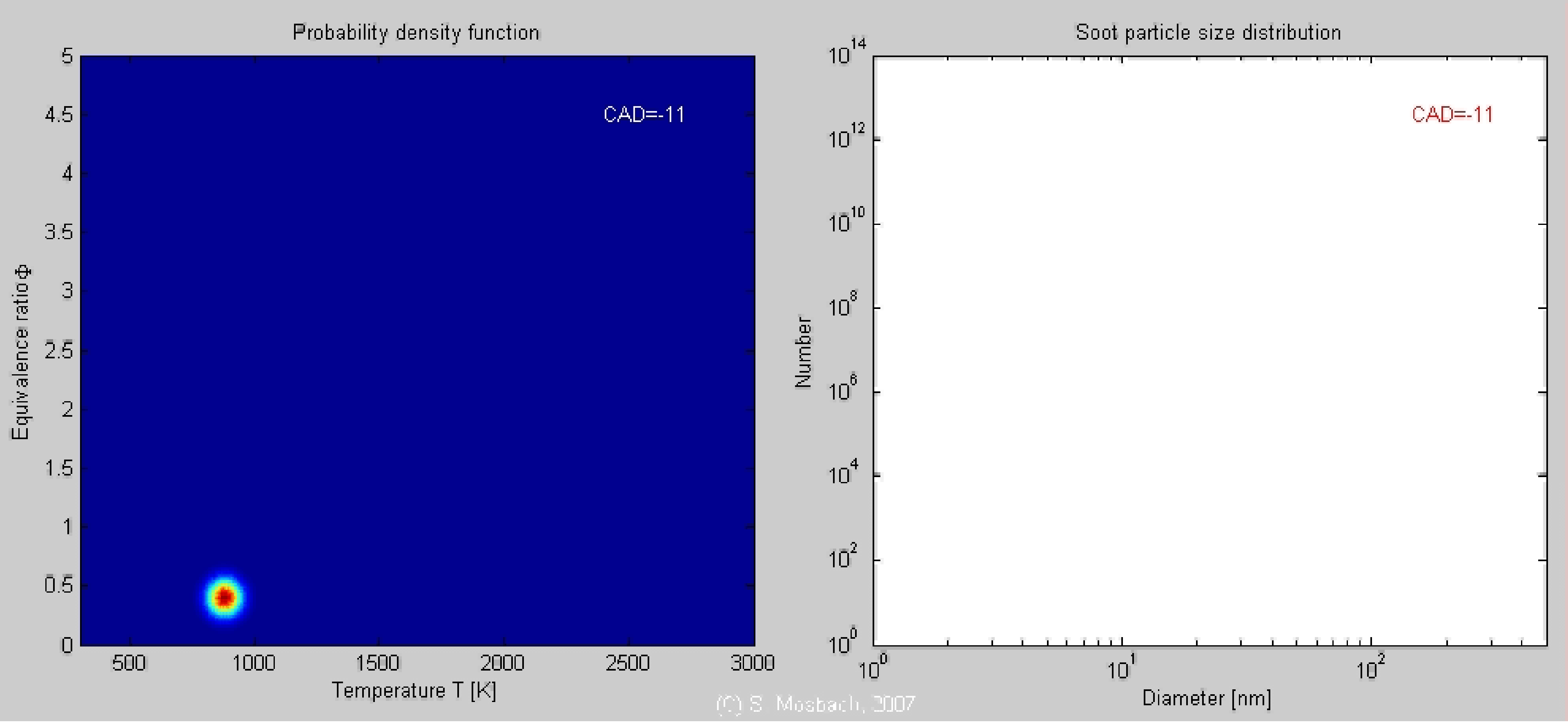
Partially stratified HCCI engine



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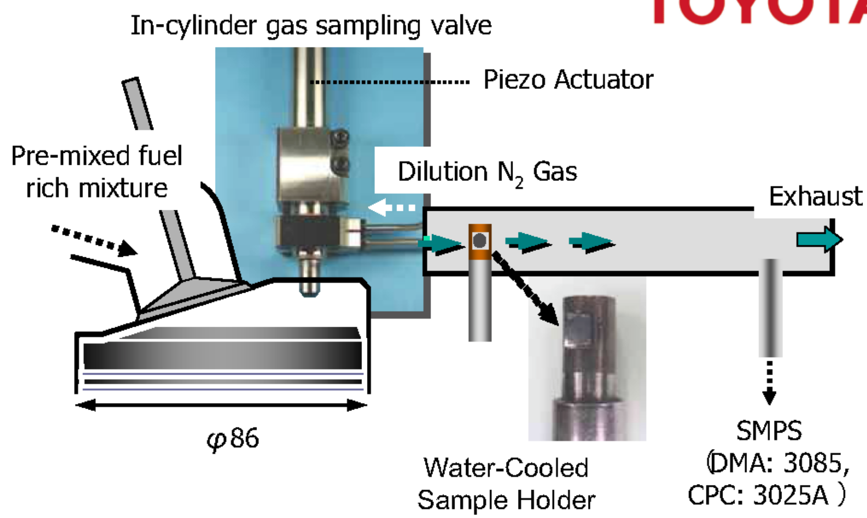
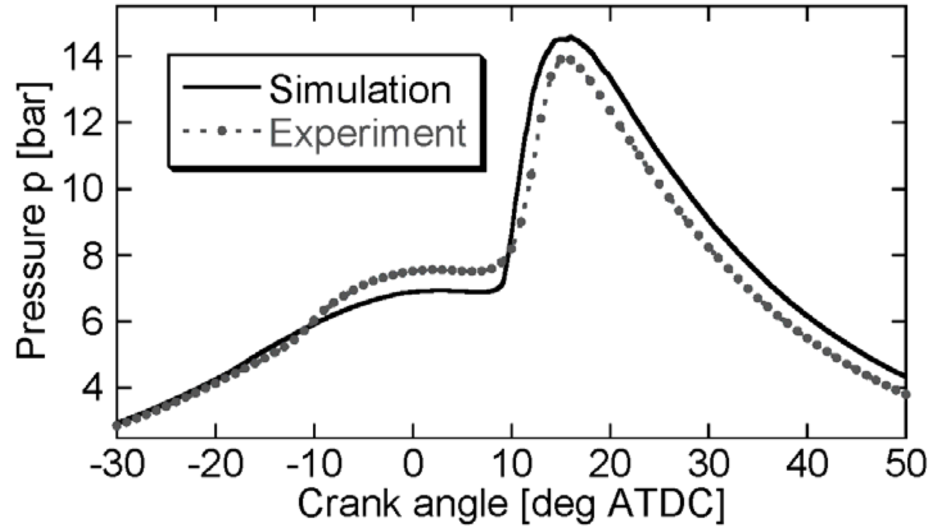
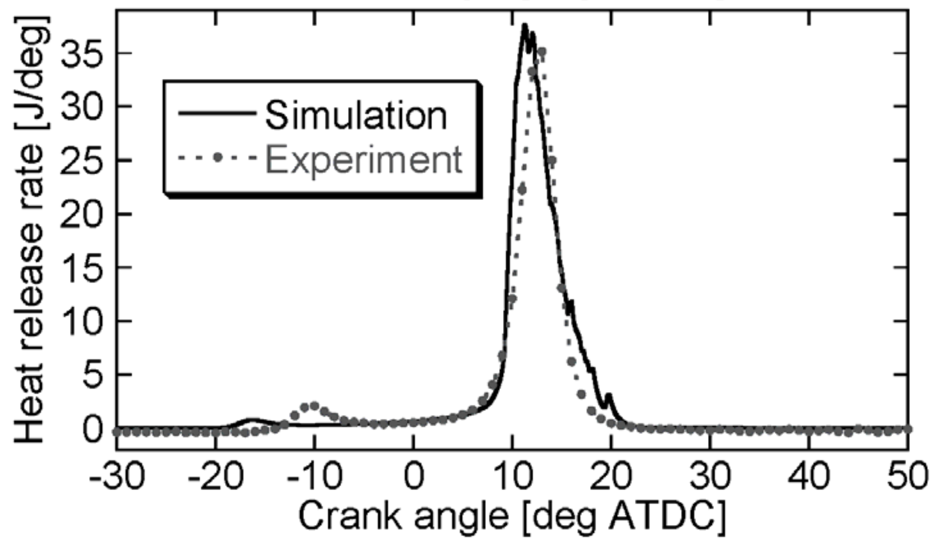
Soot in engines!

- HCCI, n-heptane
- Compression ratio 12
- Equivalence ratio 1.93
- Throttled, 20% EGR

TOYOTA







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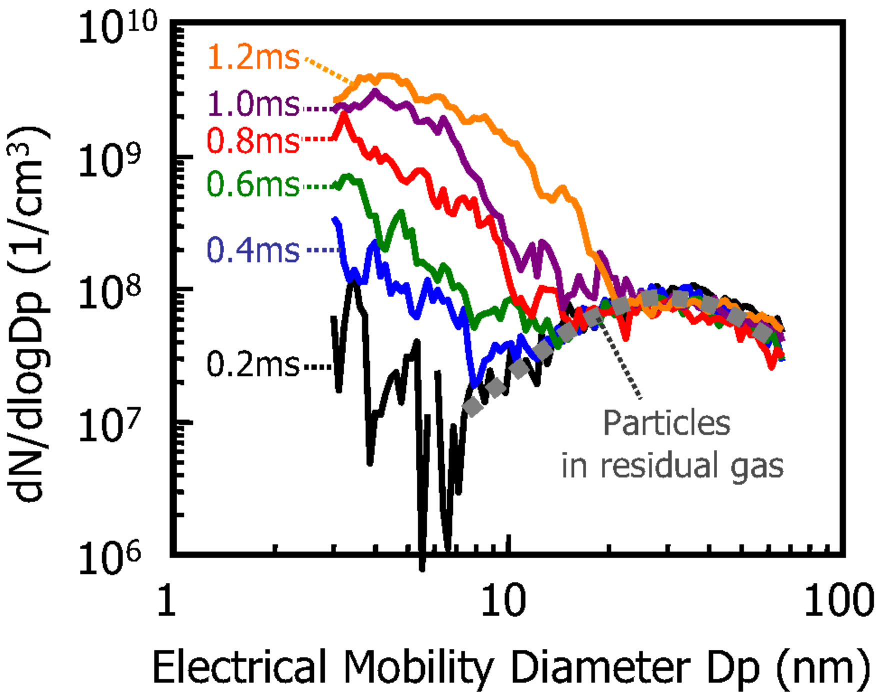
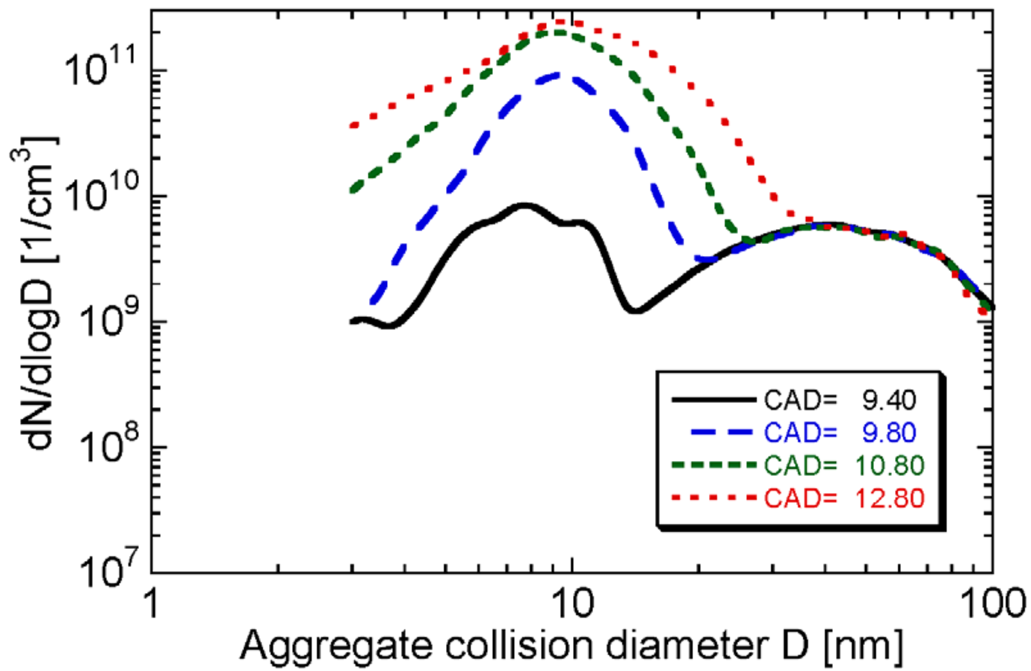
Aggregate size distributions (I)

Experiment



Simulation



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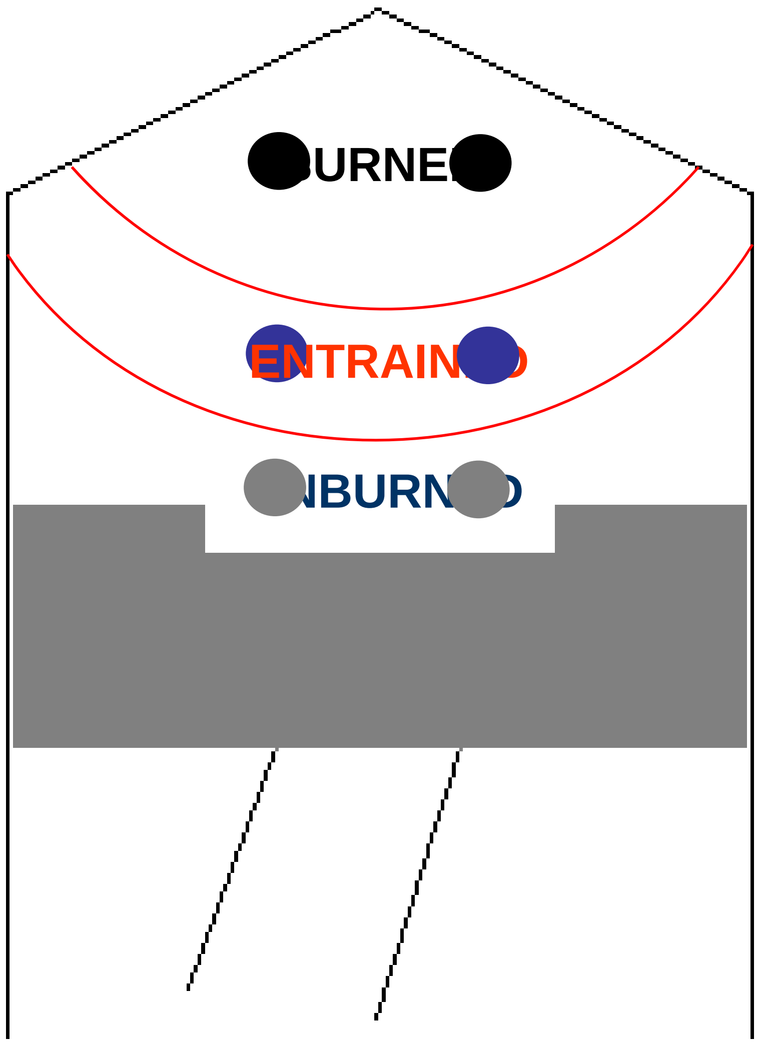
SI Model



- The chemistry of the three zones is calculated with a detailed mechanism containing 157 species and 1552 reactions.
- Mixing occurs within each zone but not between zones.
- When the calculated volume is greater than the particles' volume a new particle is added to the entrained zone.

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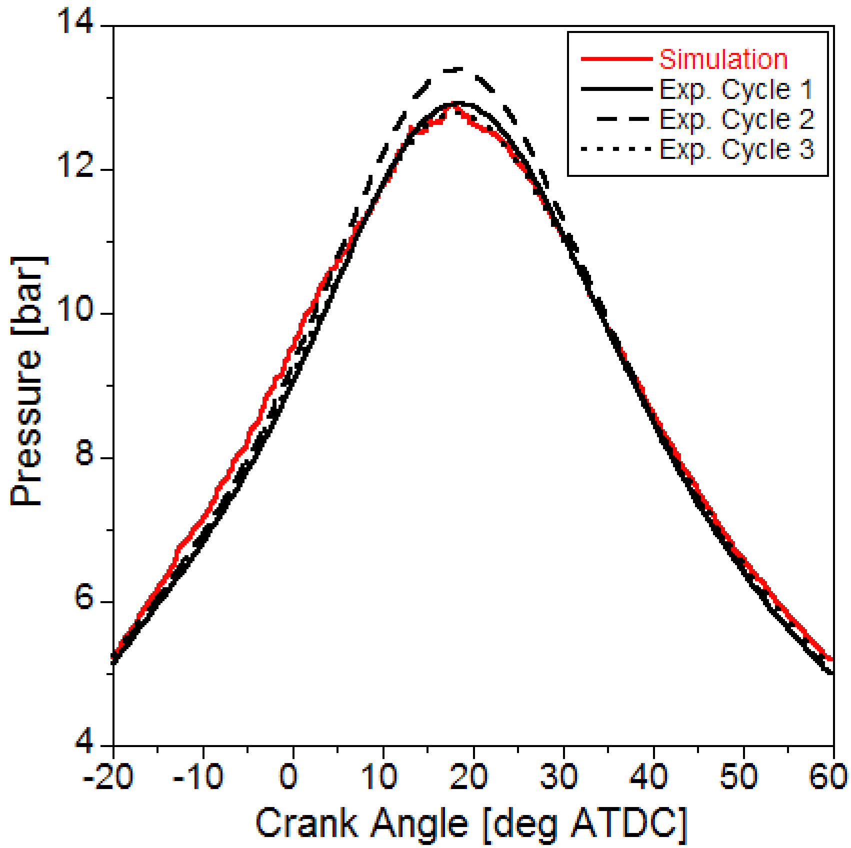
GDI SI Research Engine



Fuel	iso-octane
Bore	89.0 mm
Stroke	90.3 mm
Con. rod length	148.9 mm
Disp. volume	562 cm^3
CR	11.1
Speed	1500 RPM
Air/fuel equiv. ratio	1.0
EGR	15%

	Exp.	Sim.
uHC [ppm]	600	239
CO [ppm]	2700	2541
NO_x [ppm]	-	886

In collaboration with Professor Richard Stone from Oxford University.

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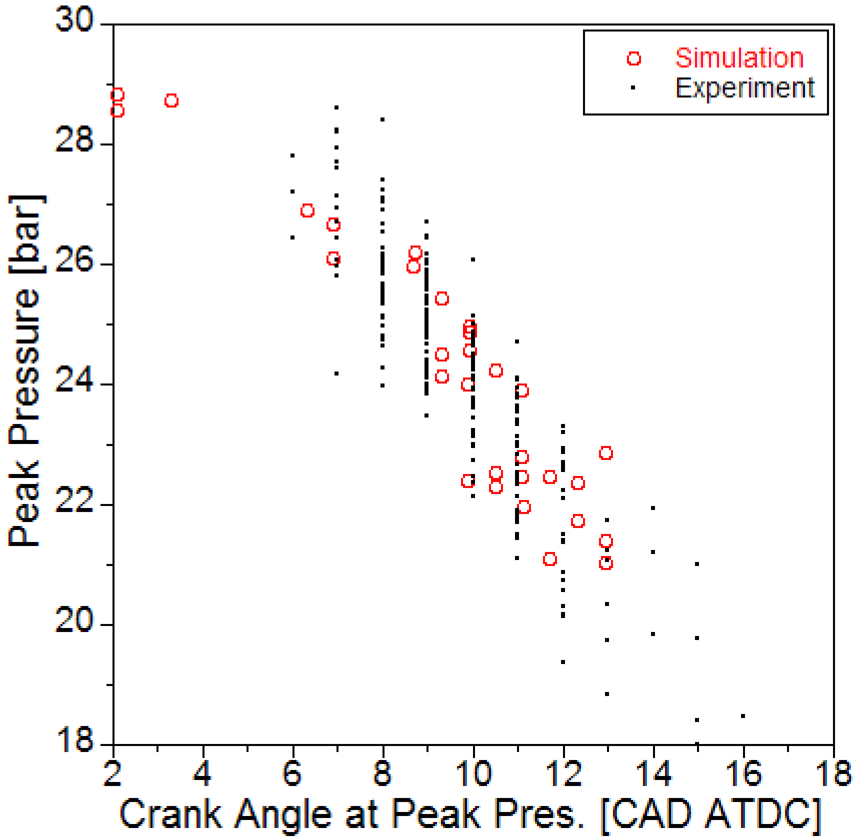
Multi-cycle SI Simulation



- Model coupled to GT-Power for multi-cycle simulation.
- 40 simulated and 200 experimental cycles.
- NO_x emissions:
  - 496 ppm simulation
  - 528 ppm experiment

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DISI Engine

- Late injection produces stratified mixture.
- Fuel rich regions close to spark gap.

Image from www.engineforall.com

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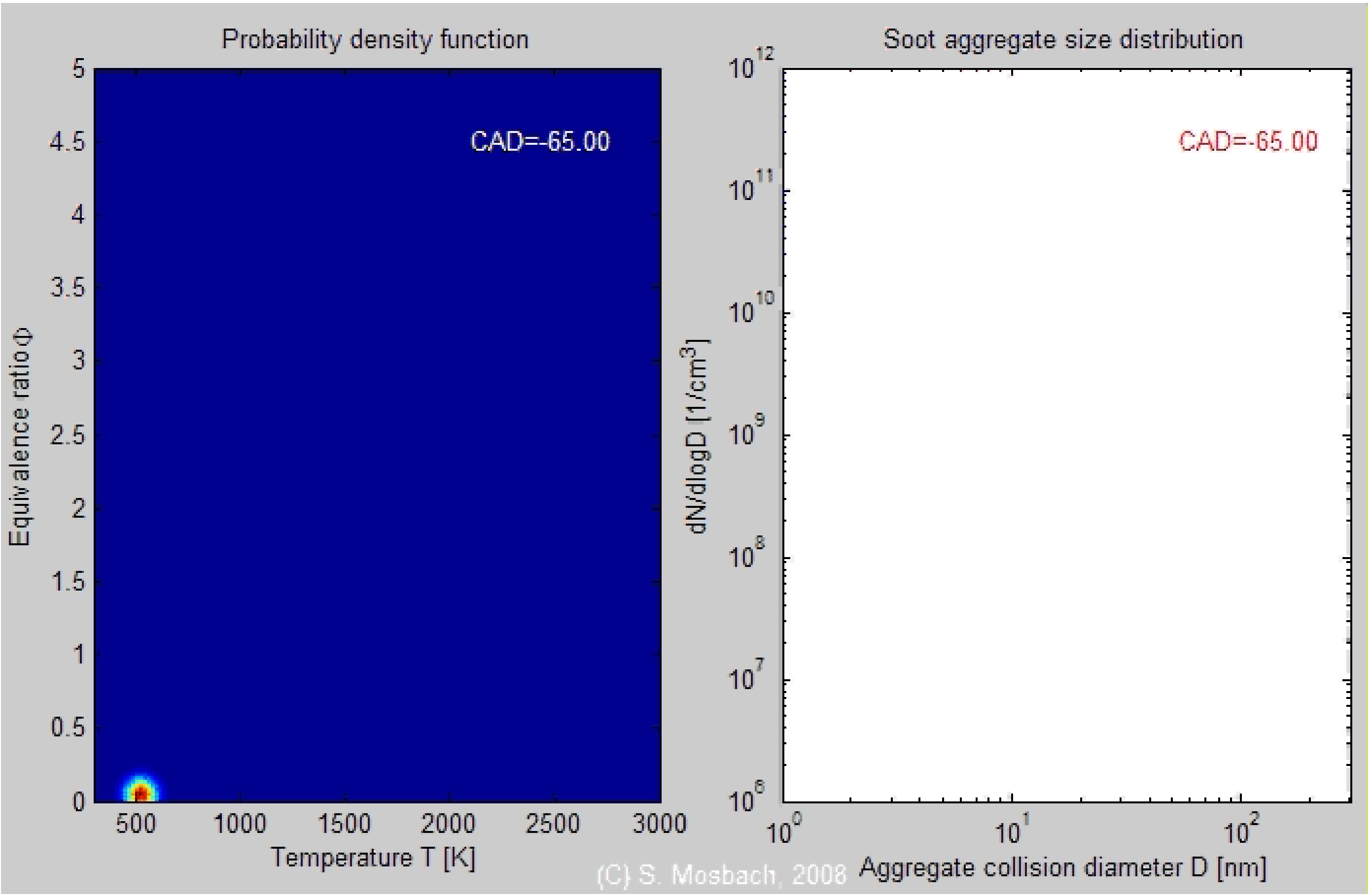
Soot in DISI Engine



λ = 1.0
EOI = -50 CAD ATDC
Spark = -30 CAD ATDC

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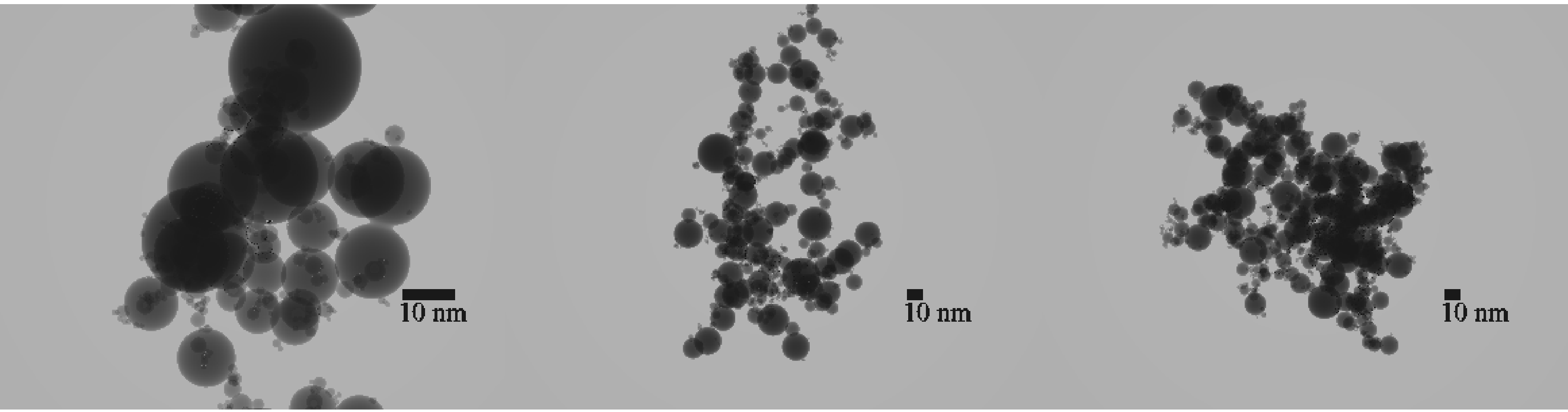
Soot in DISI Engine

2.6 CAD ATDC | 12.6 CAD ATDC | 32.6 CAD ATDC



CAD [deg ATDC]	2.6	12.6	32.6
No. Primaries	492	1315	2083
Coll. Diam [nm]	70	108	137

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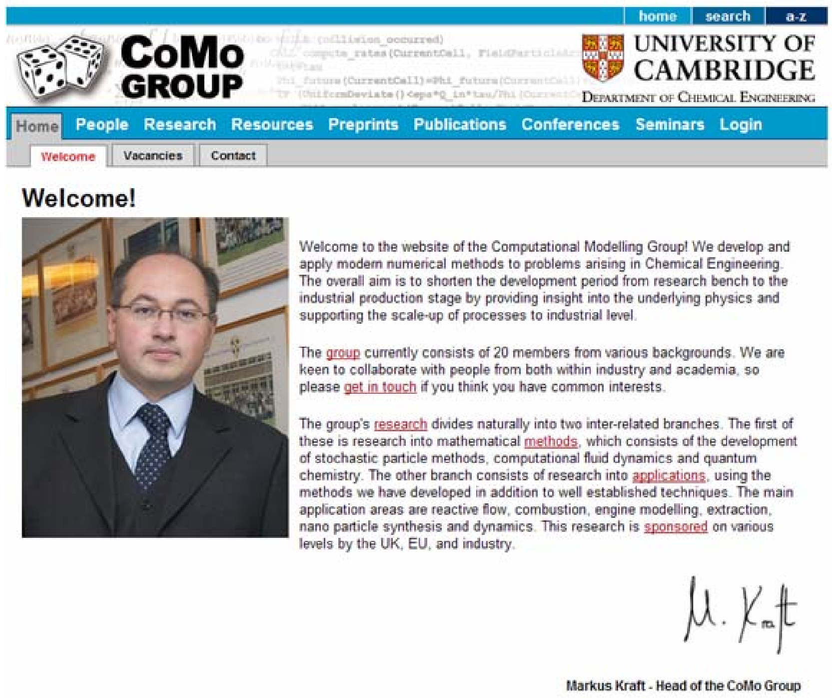
Thank you!

Please visit our website:



http://como.cheng.cam.ac.uk

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