Computational modelling in chemical engineering

From science to technology

Dr Markus Kraft
Computational Modelling Group
Cambridge, 16 July 2008

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UNIVERSITY OF CAMBRIDGE

Research in the Department

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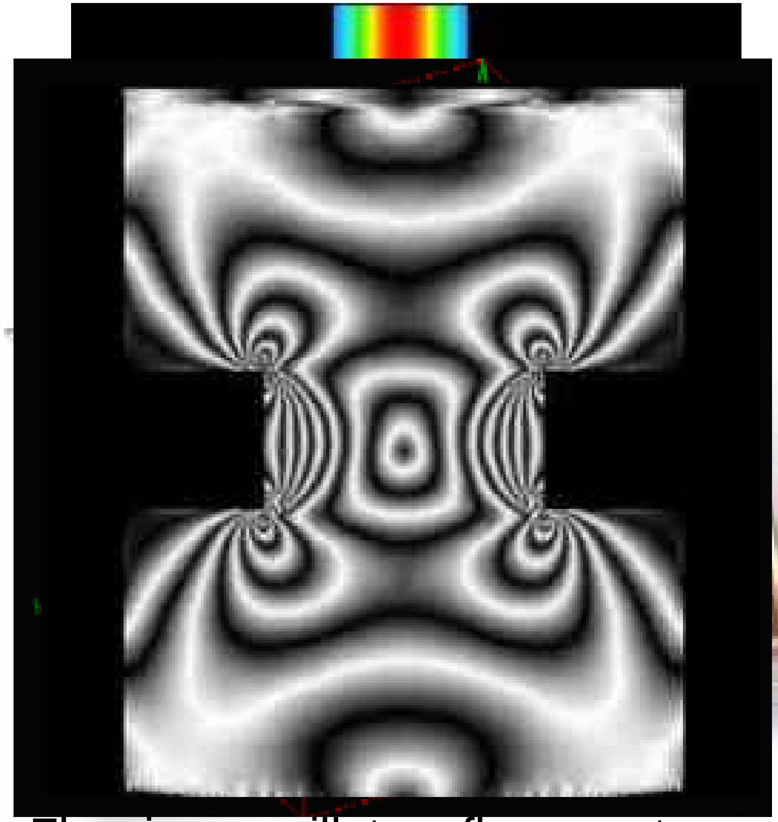
Modelling



Flow in a oscillatory flow reactor.

Pom-Pom equation for high pressure homogeniser

Operation of a DNS of a flame kernel.

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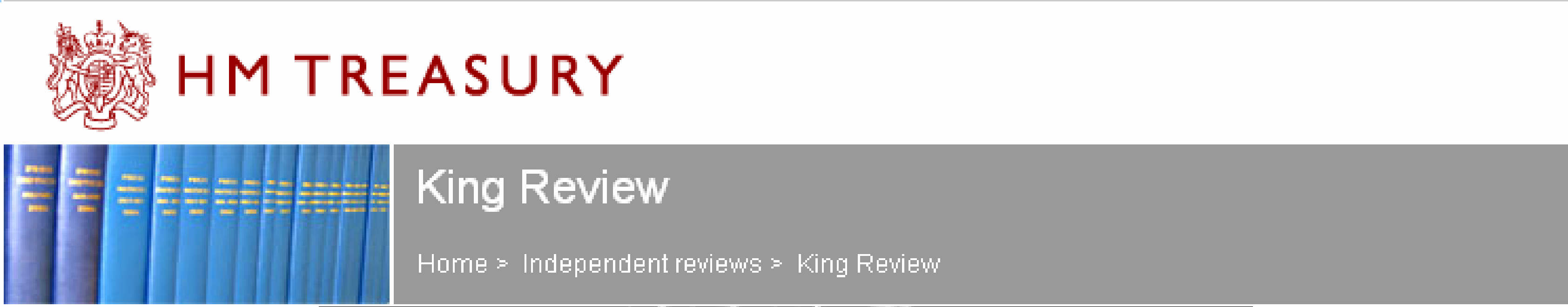
Engine optimisation



- **Increase Efficiency**
  - reduce carbon dioxide
- **Reduce Emission**
  - soot,NOx, unburnt hydrocarbons

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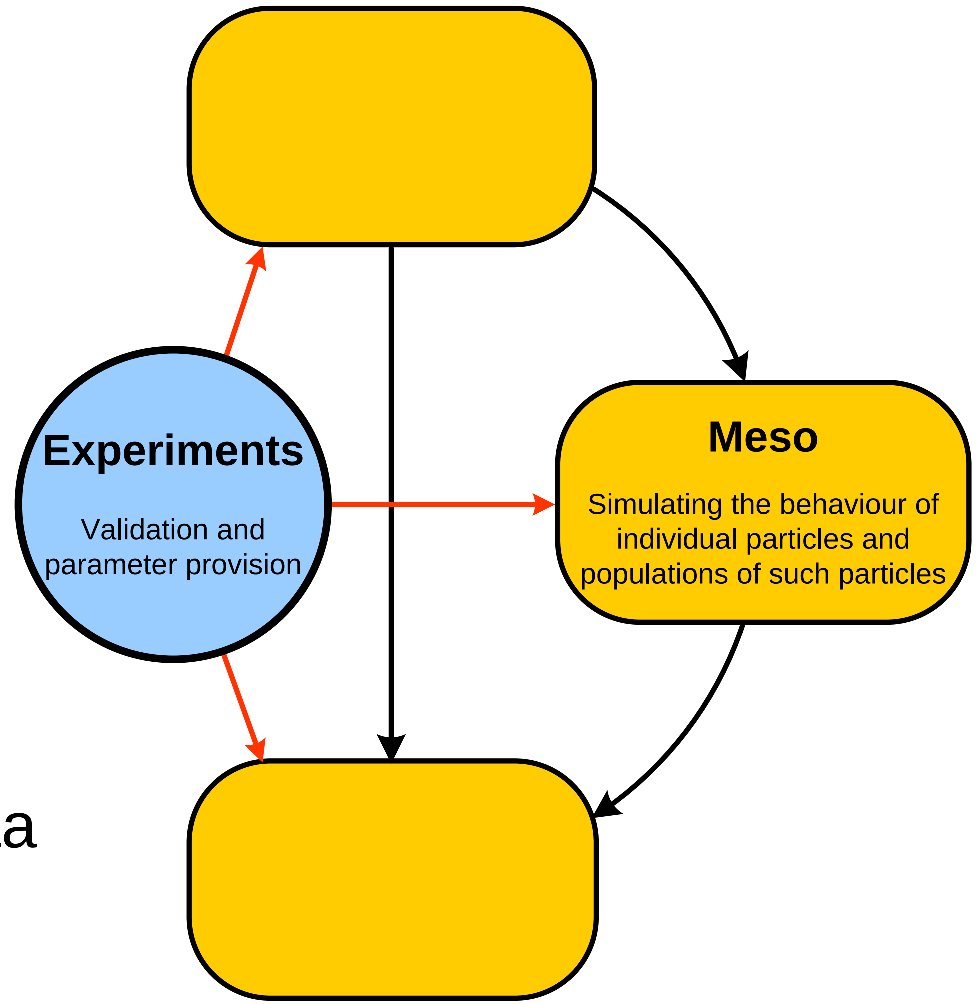
Hierarchy of scales

- Modelling takes place across a hierarchy of scales
- *Micro*- and *meso*-scale modelling directly feeds into *macro*-scale models of industrial processes
- All models validated against experimental data



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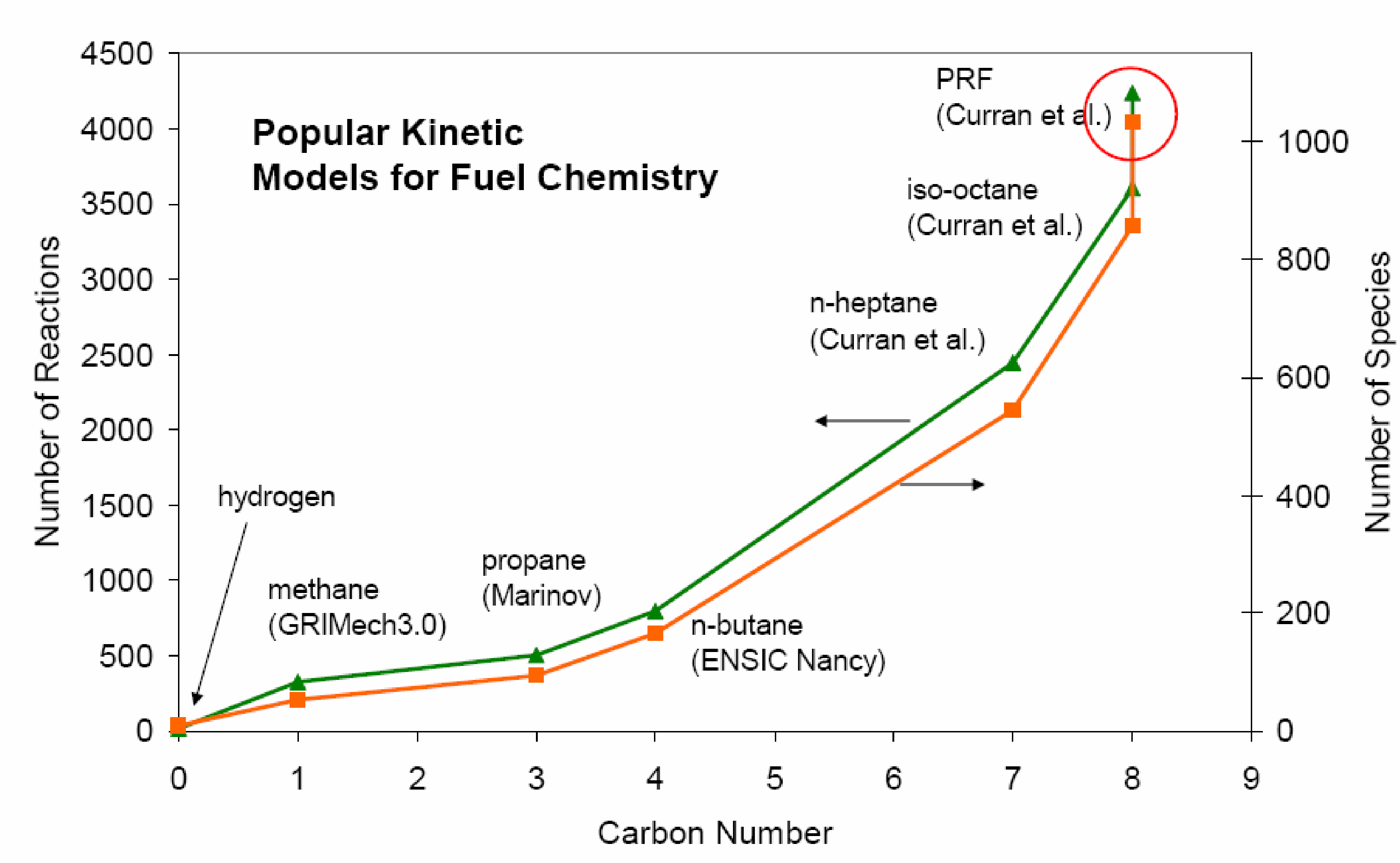
Chemistry can be complex



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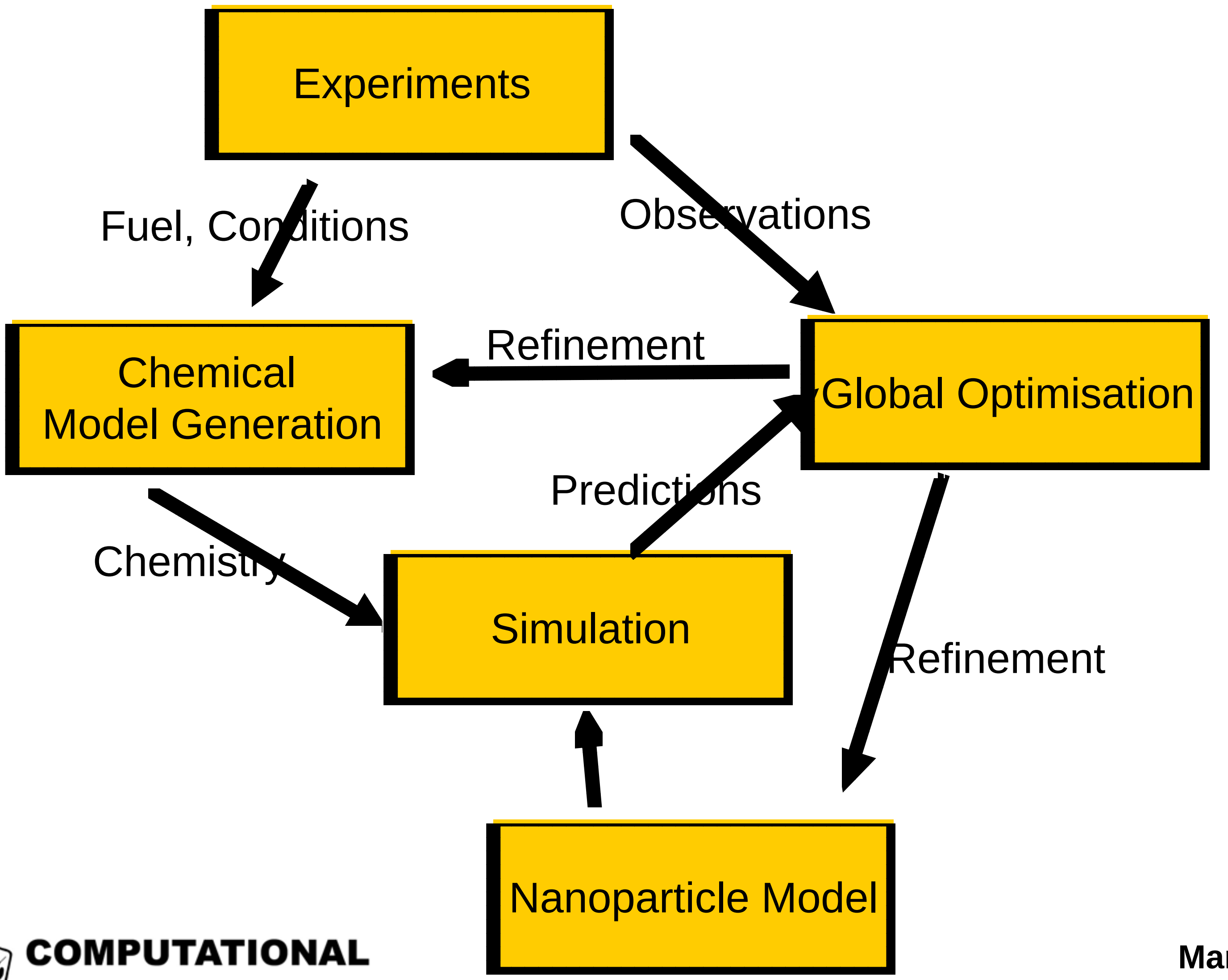
Automated pipedream:



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Solution: machine-readable data

- XML: Extensible Markup Language
  - General purpose
  - Human-readable
  - Machine-readable
  - Standardised
  - Libraries and functions exist in most programming languages

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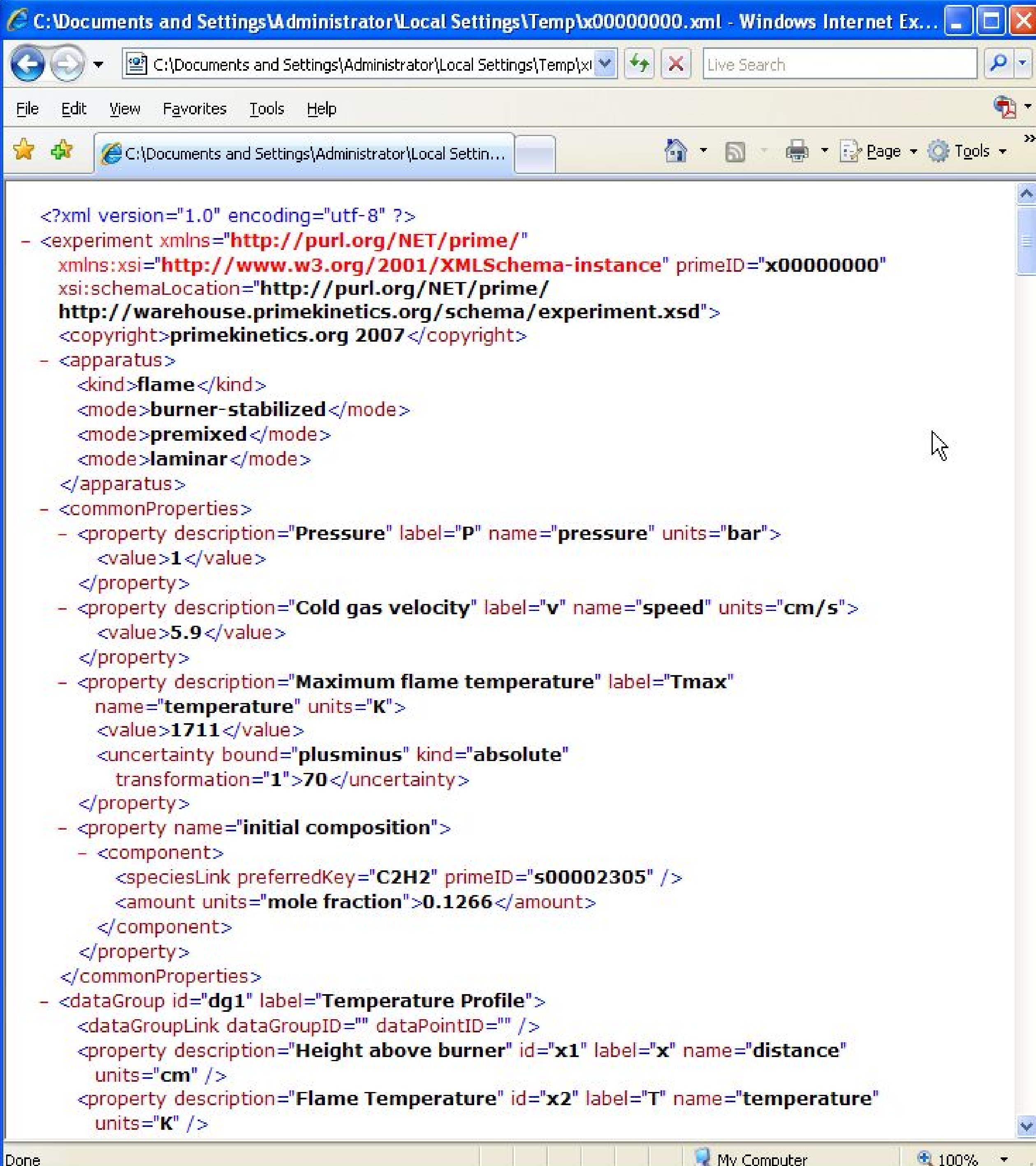
- XML Generated by GUI

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    xsi:schemaLocation="http://purl.org/NET/prime/
    http://warehouse.primekinetics.org/schema/experiment.xsd">
    <copyright>primekinetics.org 2007</copyright>
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      <mode>laminar</mode>
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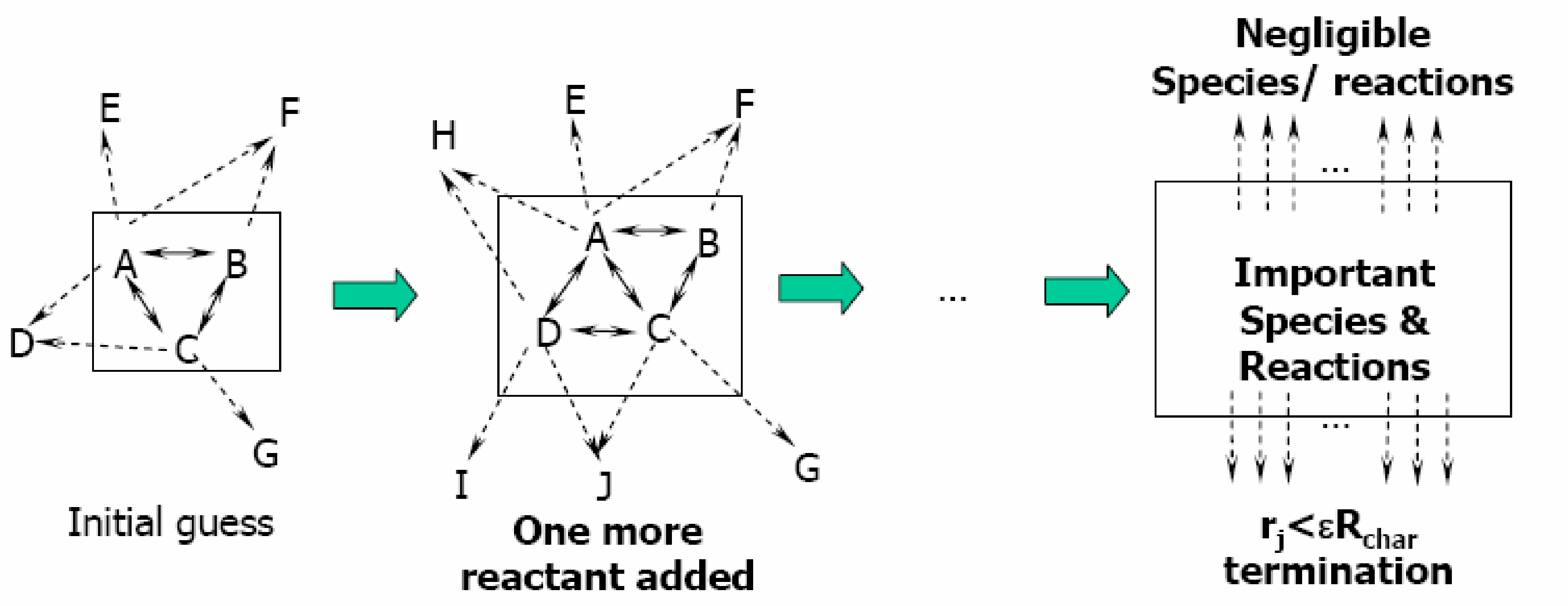
Reaction mechanism generation



- Iteratively add reactions/species until all reactions leading to new species are negligible

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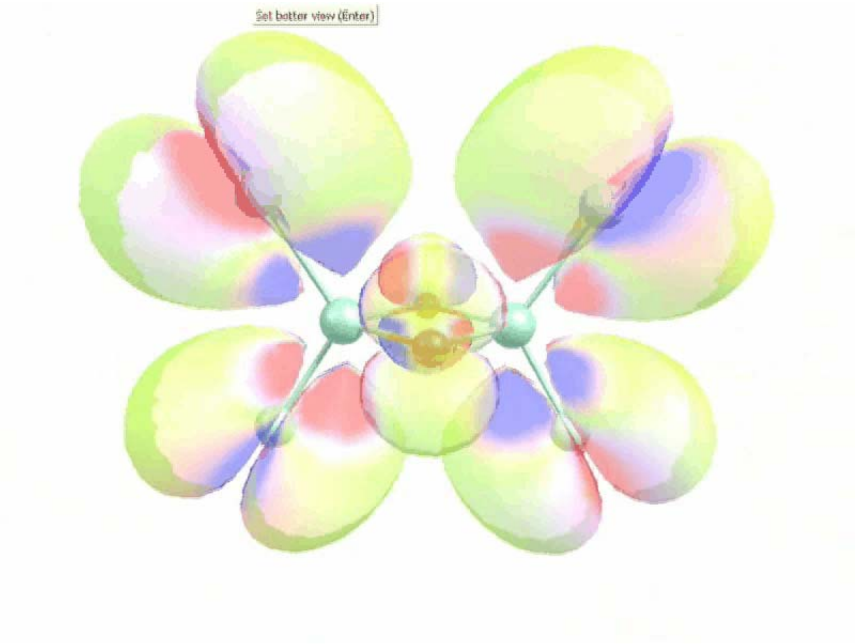
Quantum calculations



- Electronic energy
- Geometry optimisation
- Rotational constants
- Vibrational frequencies
- Find temperature variation of C_p, H, S through Statistical Mechanics

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Proposed Reactions

Table 3: Reaction mechanism equations

No	Reaction	ΔH°_{298K} [a]	A [b]	n	E_a [a]	Ref.
Thermal Decomposition						
R1	$TiCl_4 + M \rightleftharpoons TiCl_3 + Cl + M$	387	5.40×10^{18}	0	336	[18]
R2	$TiCl_3 + M \rightleftharpoons TiCl_2 + Cl + M$	422	7.70×10^{18}	0	387	[18]
R3	$TiCl_2 + M \rightleftharpoons TiCl + Cl + M$	507	3.20×10^{17}	0	511	[19]
R4	$Ti + Cl \rightleftharpoons TiCl$	-405	1.00×10^{13}	0	0	
R5	$TiCl_2 + Cl_2 \rightleftharpoons TiCl_4$	-567	1.00×10^{13}	0	0	
R6	$TiCl + Cl_2 \rightleftharpoons TiCl_3$	-687	1.00×10^{13}	0	0	
Abstraction and Disproportionation						
R7	$TiCl_3 + Cl_2 \rightleftharpoons TiCl_4 + Cl$	-144	1.00×10^{13}	0	0	
R8	$TiCl_2 + Cl_2 \rightleftharpoons TiCl_3 + Cl$	-180	1.00×10^{13}	0	0	
R9	$TiCl + Cl_2 \rightleftharpoons TiCl_2 + Cl$	-265	1.00×10^{13}	0	0	
R10	$Ti + Cl_2 \rightleftharpoons TiCl + Cl$	-162	1.00×10^{13}	0	0	
R11	$TiCl_4 + TiCl \rightleftharpoons TiCl_3 + TiCl_2$	-121	1.00×10^{13}	0	0	
R12	$TiCl_4 + Ti \rightleftharpoons TiCl_3 + TiCl$	-18	1.00×10^{13}	0	0	
R13	$TiCl_2 + TiCl \rightleftharpoons TiCl_3 + Ti$	-17	1.00×10^{13}	0	0	
R14	$TiCl + TiCl \rightleftharpoons TiCl_2 + Ti$	-103	1.00×10^{13}	0	0	
R15	$Cl + TiO_2Cl_3 \rightleftharpoons Cl_2 + TiO_2Cl_2$	-21	1.00×10^{13}	0	0	
R16	$Cl_2 + Ti_2O_2Cl_3 \rightleftharpoons Cl + Ti_2O_2Cl_4$	-132	1.00×10^{13}	0	0	
R17	$2\,TiCl_3 \rightleftharpoons TiCl_2 + TiCl_4$	35	9.60×10^{12}	0	35	[18] [d]
R18	$TiCl_3 + TiCl \rightleftharpoons 2\,TiCl_2$	-85	1.00×10^{13}	0	0	
Oxidation						
R19	$TiCl_3 + O_2 \rightleftharpoons TiO_2Cl_3$	-151	1.00×10^{13}	0	0	
R20	$TiOCl_3 + ClO \rightleftharpoons TiO_2Cl_3 + Cl$	-22	1.00×10^{13}	0	0	
R21	$TiO_2Cl_3 + TiCl_3 \rightleftharpoons 2\,TiOCl_3$	-67	1.00×10^{13}	0	0	
R22	$TiOCl_2 + Cl \rightleftharpoons TiOCl_3$	-138	1.00×10^{13}	0	0	
R23	$TiOCl_3 + O \rightleftharpoons TiO_2Cl_3$	-291	1.00×10^{13}	0	0	
R24	$TiO_2Cl_2 + Cl \rightleftharpoons TiO_2Cl_3$	-221	1.00×10^{13}	0	0	
R25	$TiO_2Cl_2 + Cl \rightleftharpoons TiCl_3 + O_2$	-71	1.00×10^{13}	0	0	
R26	$TiOCl_3 + O \rightleftharpoons TiCl_3 + O_2$	-140	1.00×10^{13}	0	0	
R27	$TiCl_2 + O_2 \rightleftharpoons TiOCl_2 + O$	-144	1.00×10^{13}	0	0	
R28	$TiO_2Cl_2 + O \rightleftharpoons TiOCl_2 + O_2$	-291	1.00×10^{13}	0	0	
R29	$TiCl_3 + ClO \rightleftharpoons TiCl_4 + O$	-118	1.00×10^{13}	0	0	
R30	$TiCl_2 + ClO \rightleftharpoons TiCl_3 + O$	-153	1.00×10^{13}	0	0	
R31	$TiCl + ClO \rightleftharpoons TiCl_2 + O$	-239	1.00×10^{13}	0	0	
R32	$Ti + ClO \rightleftharpoons TiCl + O$	-136	1.00×10^{13}	0	0	
R33	$TiCl_3 + O \rightleftharpoons TiOCl_2 + Cl$	-220	1.00×10^{13}	0	0	
R34	$TiCl_3 + Cl_2O \rightleftharpoons TiCl_4 + ClO$	-243	1.00×10^{13}	0	0	
R35	$TiCl_3 + ClO \rightleftharpoons TiOCl_3 + Cl$	-89	1.00×10^{13}	0	0	
R36	$TiO_2Cl_2 + Cl \rightleftharpoons TiOCl_2 + ClO$	-62	1.00×10^{13}	0	0	
Cl/O Chemistry						
R37	$O + O_2 + M \rightleftharpoons O_3 + M$	-107	1.84×10^{21} [c]	-2.8	0	[20]
R38	$ClOO + M \rightarrow Cl + O_2 + M$	24	1.69×10^{14}	0	15.13	[20]
R39	$Cl + O_2 + M \rightarrow ClOO + M$	24	8.68×10^{21} [c]	2.9	0	[20]
R40	$Cl + O_3 \rightleftharpoons ClO + O_2$	-161	1.75×10^{13}	0	2.18	[21]
R41	$Cl_2O + Cl \rightleftharpoons Cl_2 + ClO$	-99	3.73×10^{13}	0	-1.09	[21]
R42	$Cl + O_2 \rightleftharpoons ClO + O$	229	8.79×10^{14}	0	230.5	[22]
R43	$O + Cl_2 \rightleftharpoons ClO + Cl$	-26	4.46×10^{12}	0	13.73	[23]
R44	$2\,Cl + M \rightleftharpoons Cl_2 + M$	-243	2.23×10^{14} [c]	0	-7.53	[22]
Dimerisation and dimer reactions						
R45	$2\,TiOCl_2 \rightleftharpoons Ti_2O_2Cl_4$	-357	1.00×10^{13}	0	0	
R46	$TiO_2Cl_2 + TiCl_3 \rightleftharpoons Ti_2O_2Cl_4 + Cl$	-370	1.00×10^{13}	0	0	
R47	$TiO_2Cl_2 + TiOCl_2 \rightleftharpoons Ti_2O_3Cl_3 + Cl$	-130	1.00×10^{13}	0	0	
R48	$TiOCl_2 + TiOCl_3 \rightleftharpoons Ti_2O_2Cl_4 + Cl$	-219	1.00×10^{13}	0	0	
R49	$Ti_2O_3Cl_3 + TiOCl_2 \rightleftharpoons Ti_3O_4Cl_4 + Cl$	-184	1.00×10^{13}	0	0	
R50	$Ti_2O_3Cl_2 + Cl \rightleftharpoons Ti_2O_3Cl_3$	-196	1.00×10^{13}	0	0	
R51	$Ti_2O_2Cl_4 + TiCl_3 \rightleftharpoons Ti_2O_2Cl_3 + TiCl_4$	-12	1.00×10^{13}	0	0	

[a] $kJ\,mol^{-1}$ [b] $cm^3\,mol^{-1}\,s^{-1}$ [c] $cm^6\,mol^{-2}\,s^{-1}$ [d] estimate

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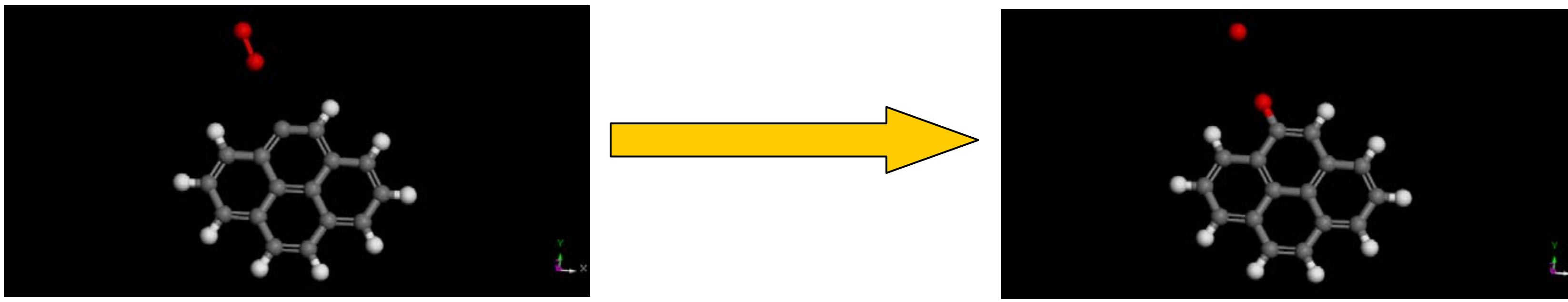
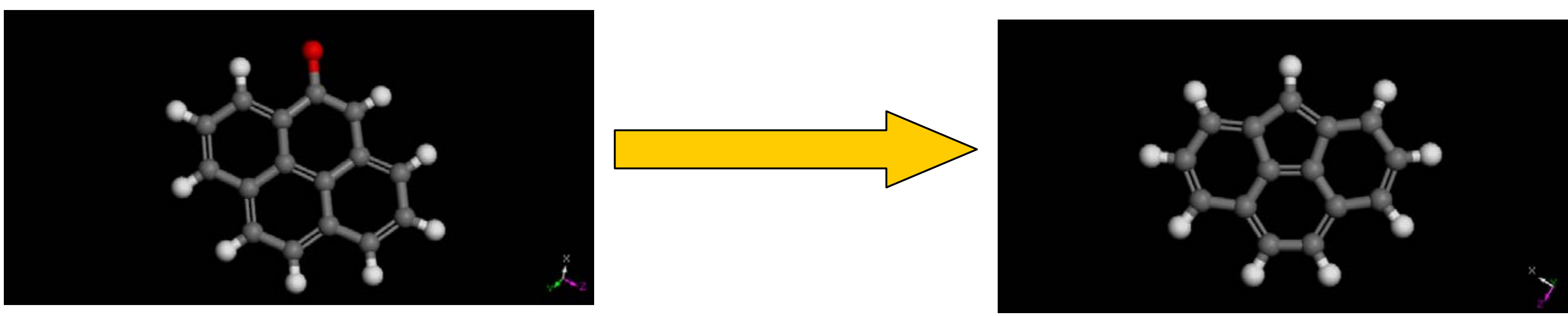
Oxidation processes in PAHs

Investigated reactions:

Oxidation process:



Decomposition process:



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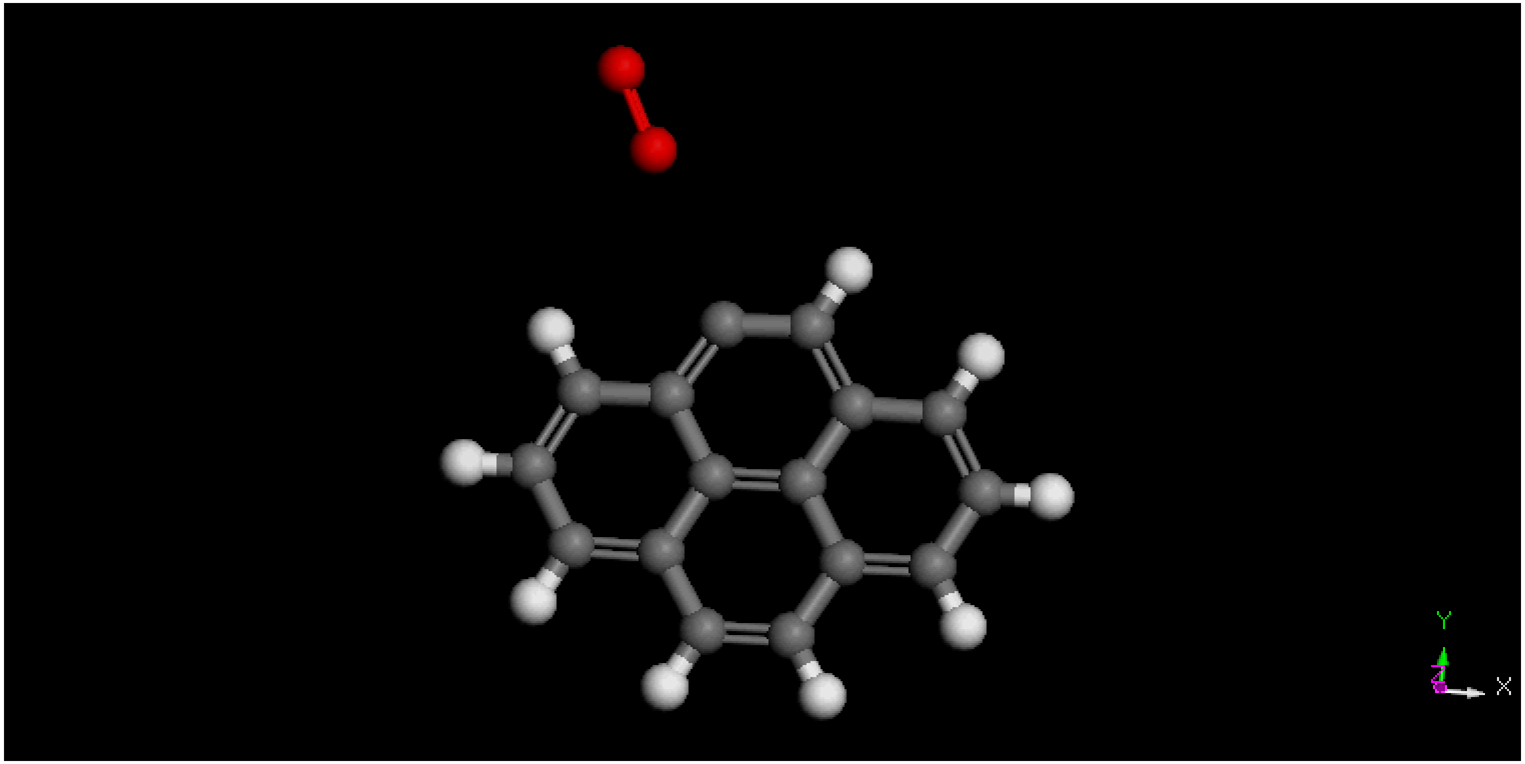
Pyrene oxidation pathway



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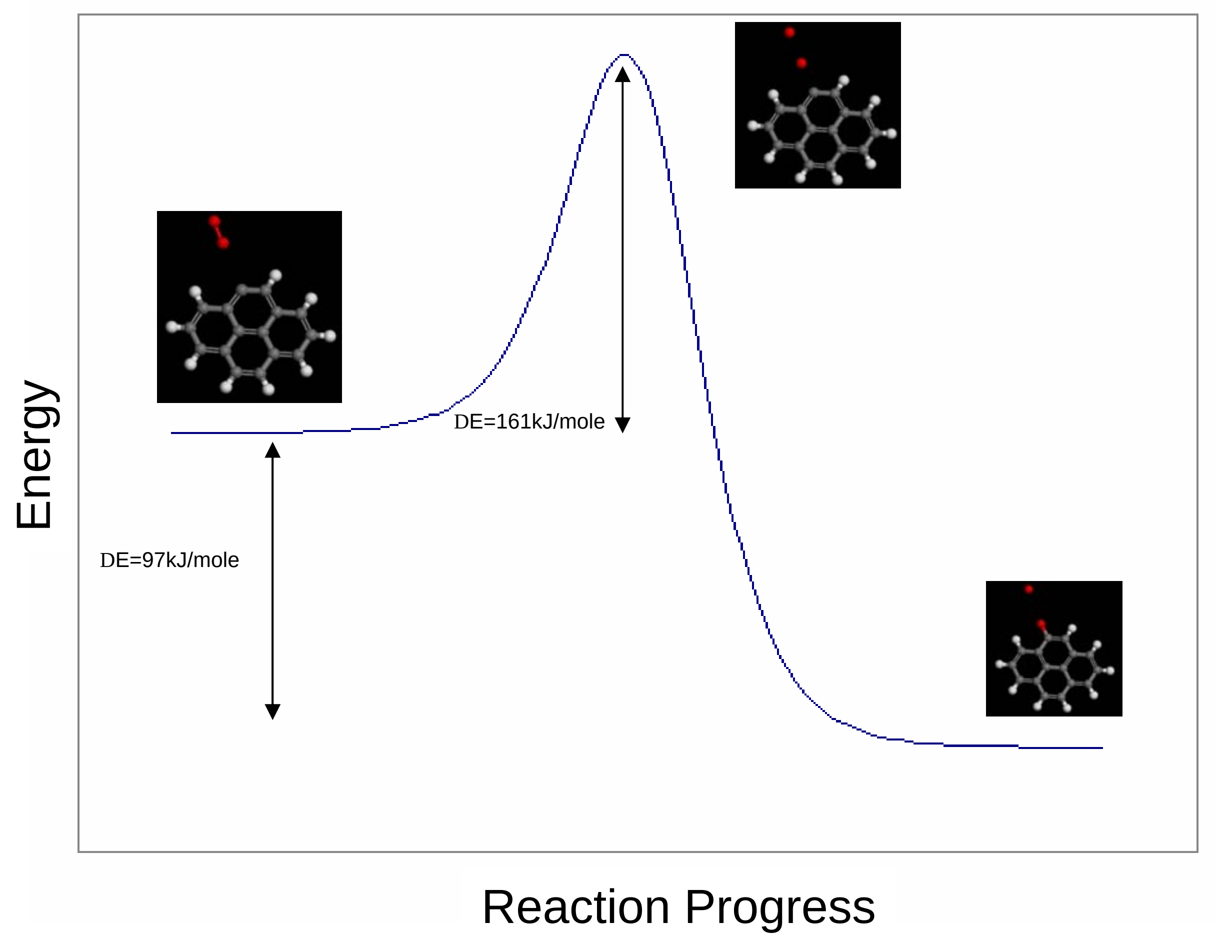
Pyrene oxidation pathway



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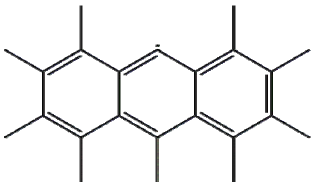
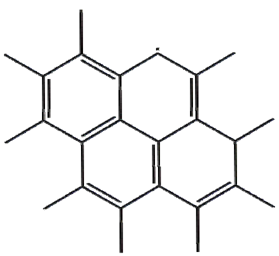
Oxidation rates of different site types

Zigzag next to zigzag (zz)



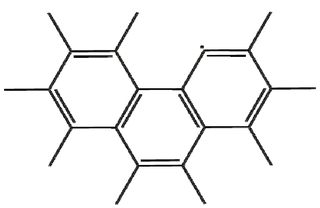
E_{act}=156 kJ/mole

Zigzag next to free edge (zf)

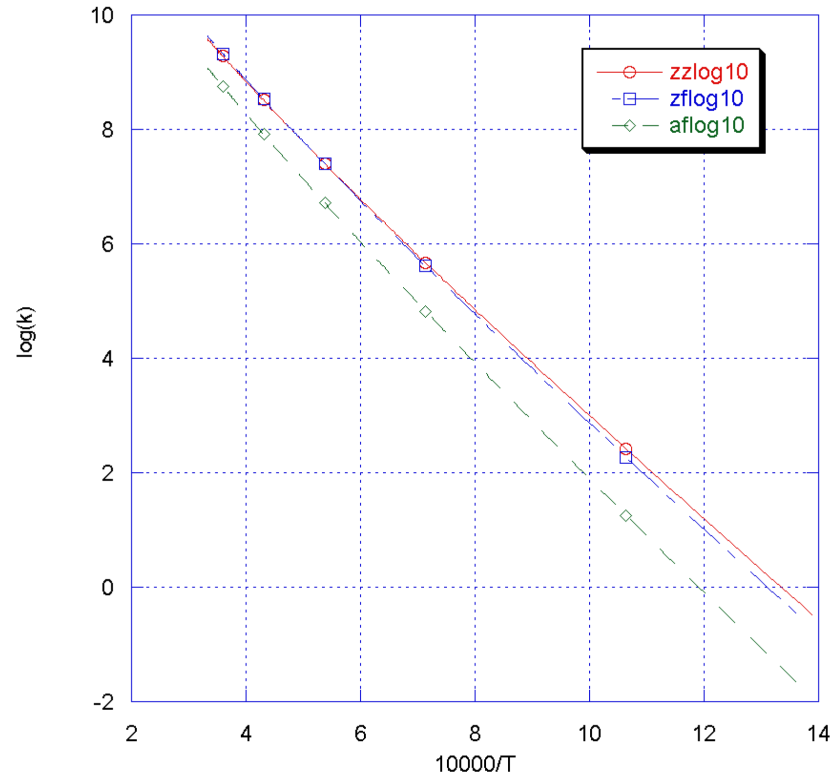


E_{act}=161 kJ/mole

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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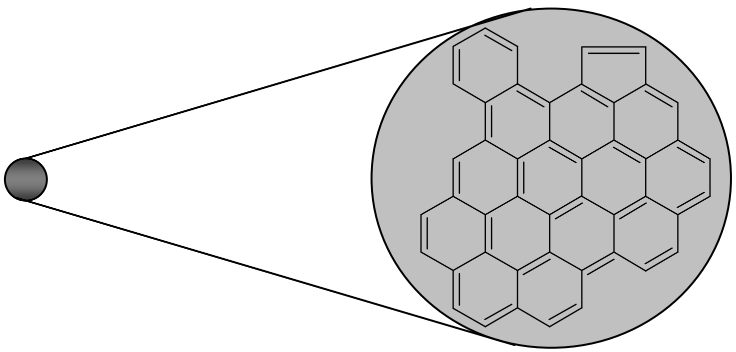
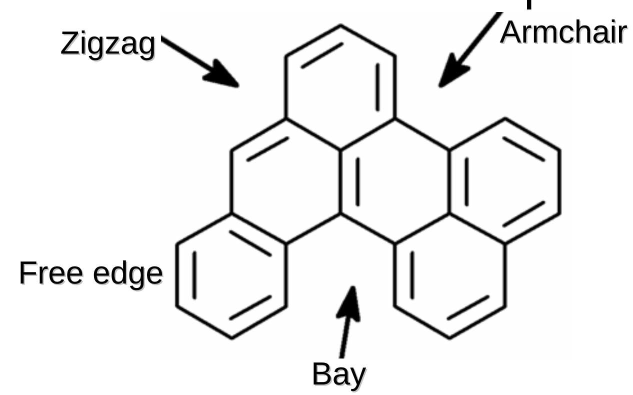
PAH growth model

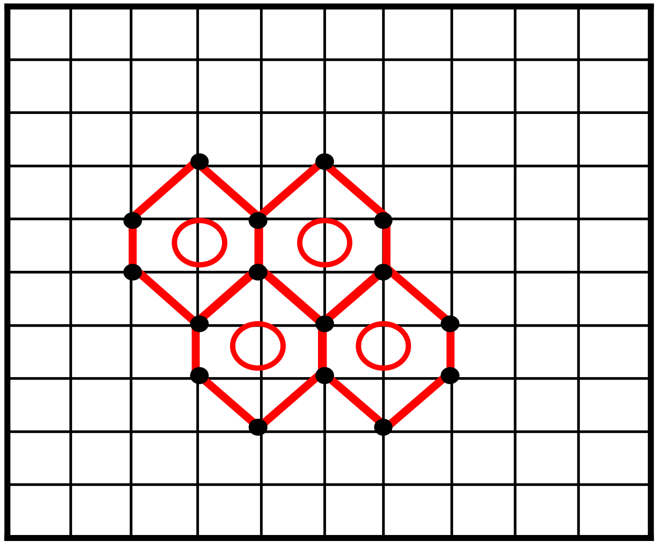
- Soot particle described by its PAH structure.



- PAH growth based on site types and various reaction steps.



- An algorithm developed to track the changing sites with reactions and resulting PAH structure.



A 2-D grid showing a pyrene molecule

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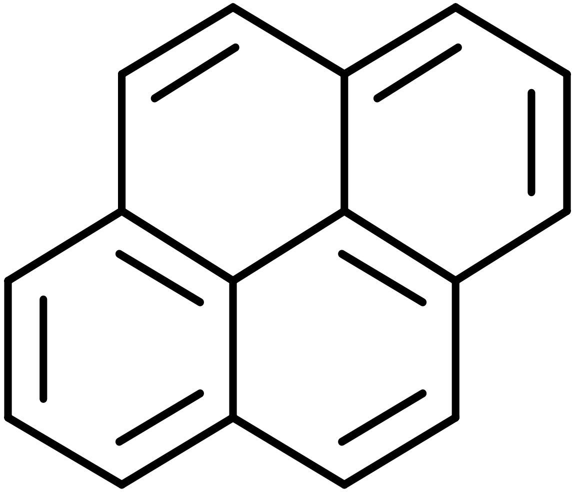
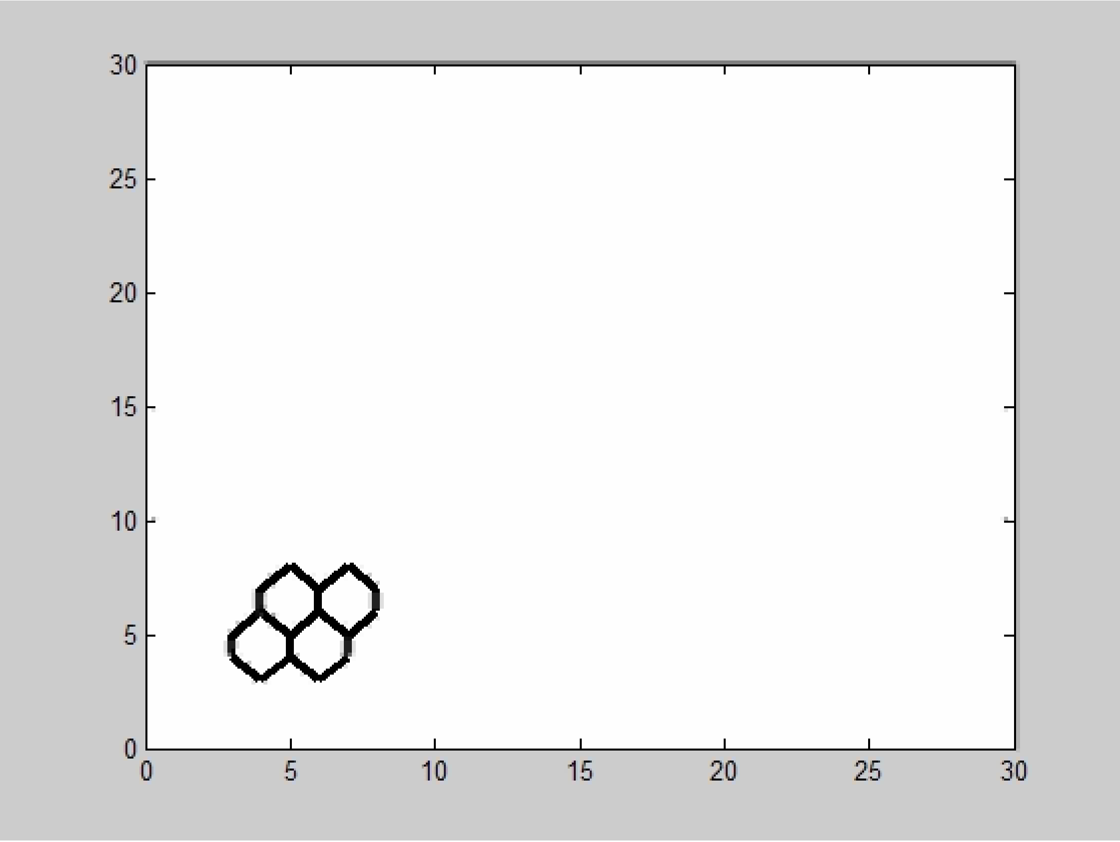
Growth of a PAH molecule

Starting structure:
Pyrene





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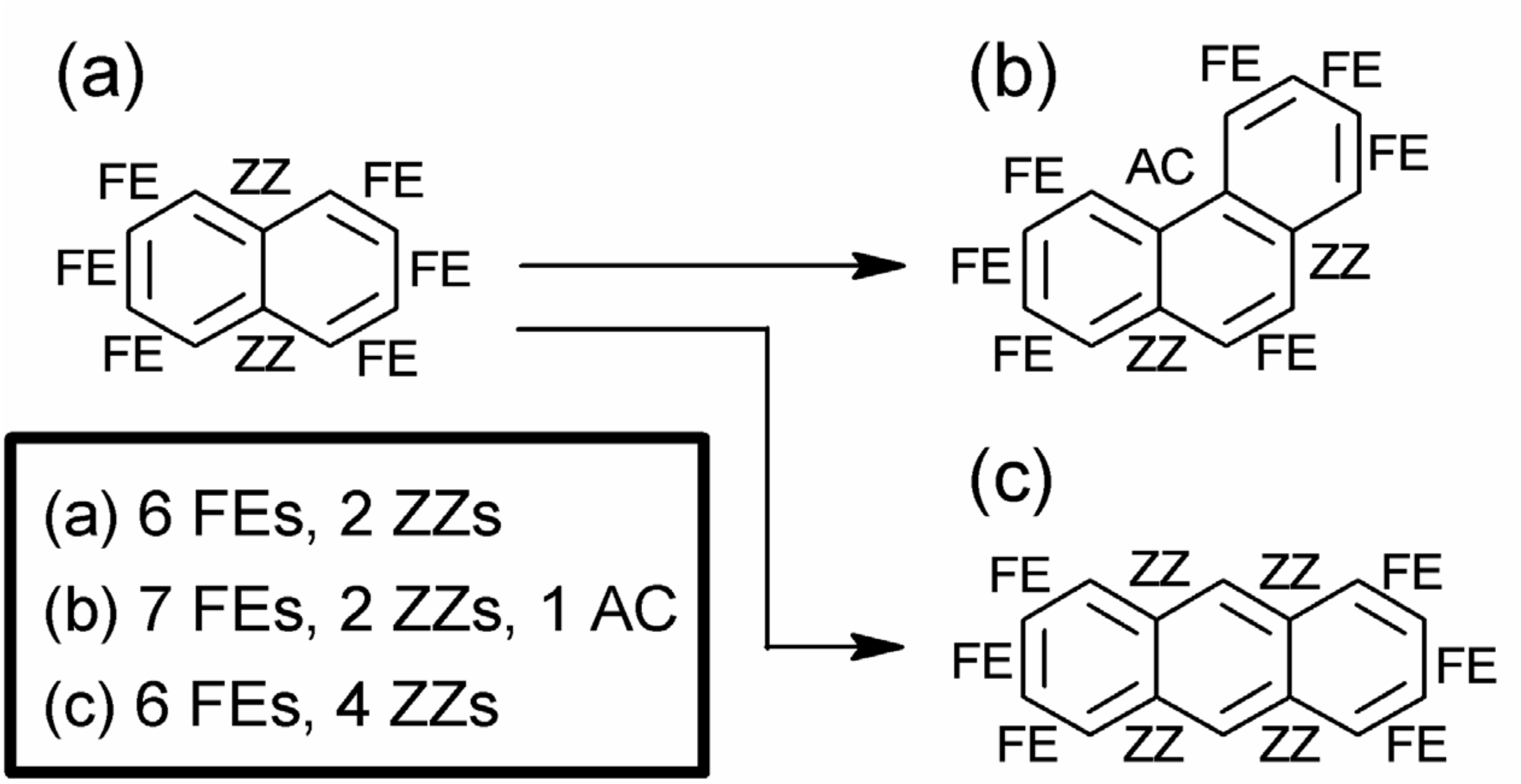
Adding structural information



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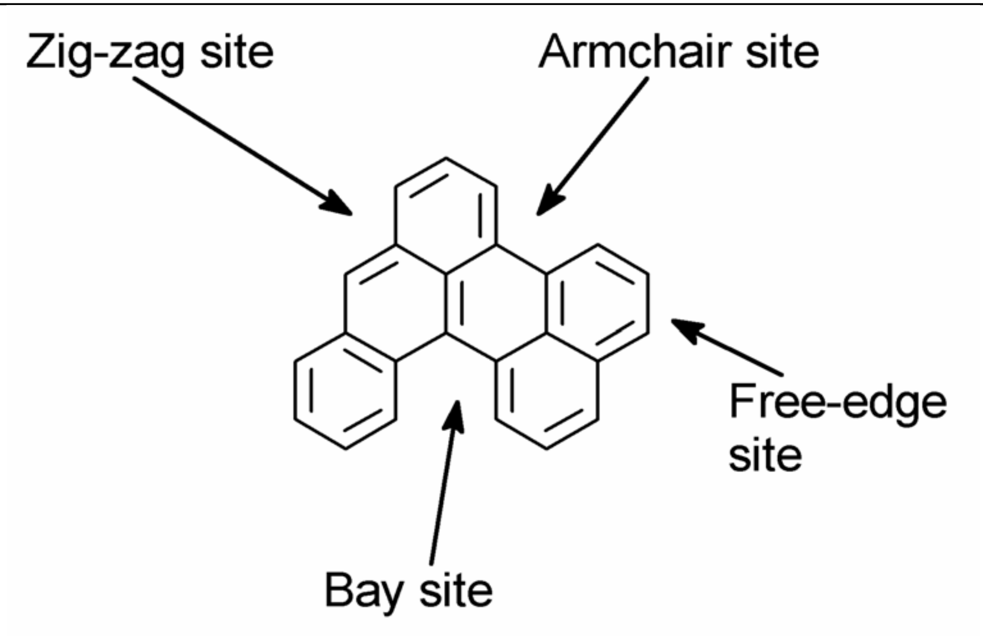
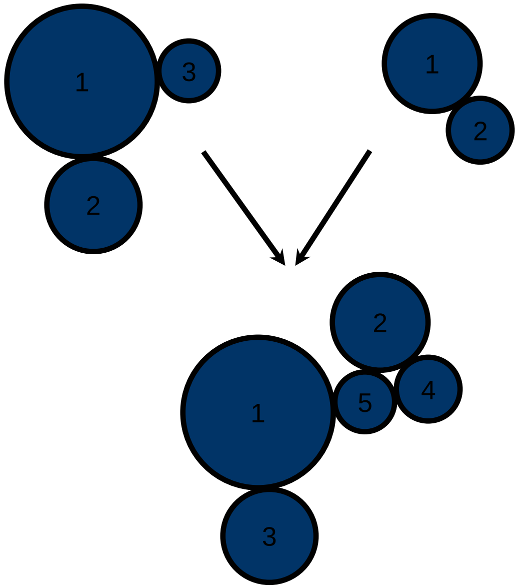
Aromatic site-counting model

Describe soot particles by $9+N$ dimensional type space (ARSC-PP model):

$$E = (C, H, S_a, N_{ed}, N_{zz}, N_{ac}, N_{bay}, N_{R5}, N_{PAH}, PP_{(1\text{-}N)})$$

PP = primary particle list





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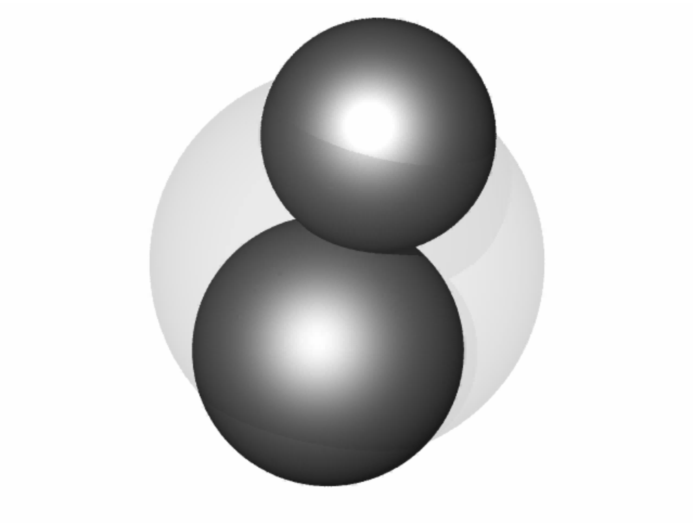
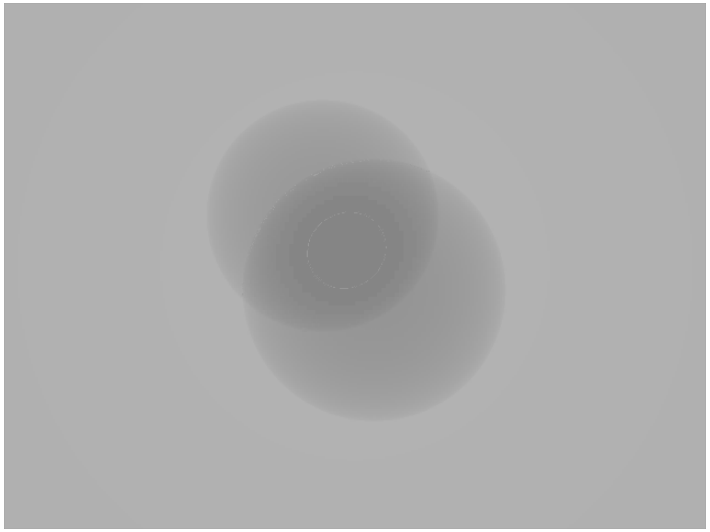
Particle growth

Single trajectory of a soot particle





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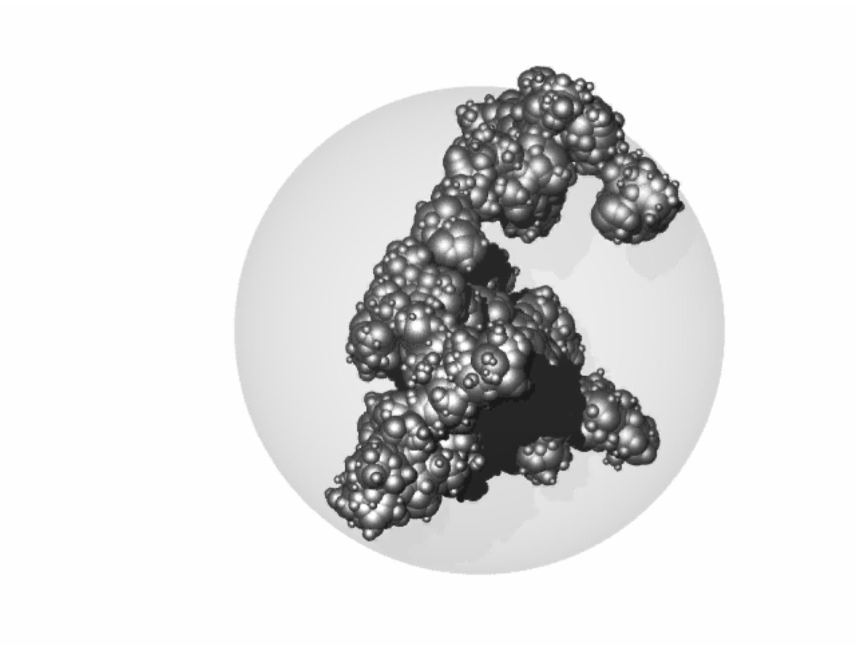
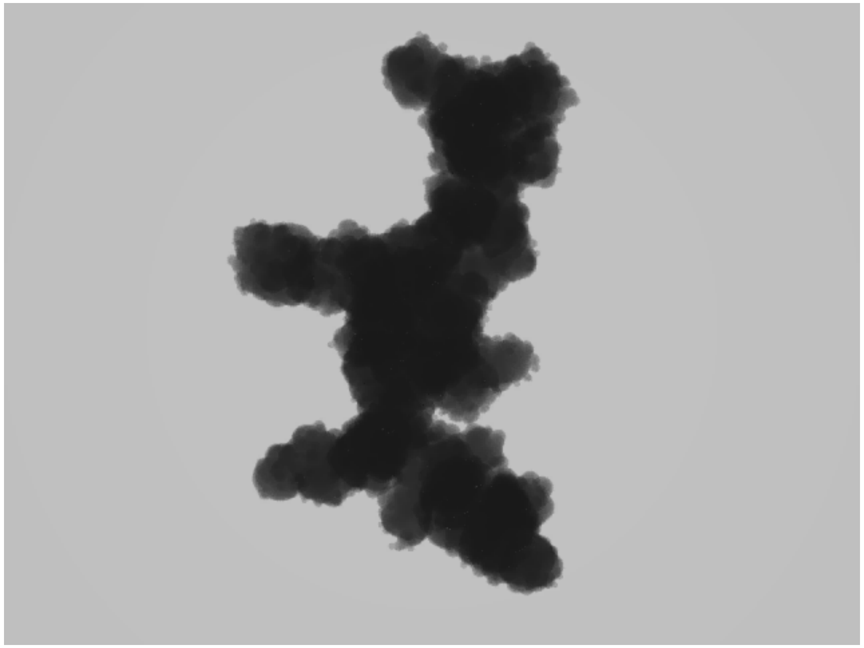
Particle rotation





- Sub Particles: 3172
- No. Carbon atoms: 4.967×10^6
- Surface Area: 2.345×10^{-10} cm^2

- Shape Descriptor: 0.768
- Radius of Gyration: 44.384 nm
- Age: 0.0917 s

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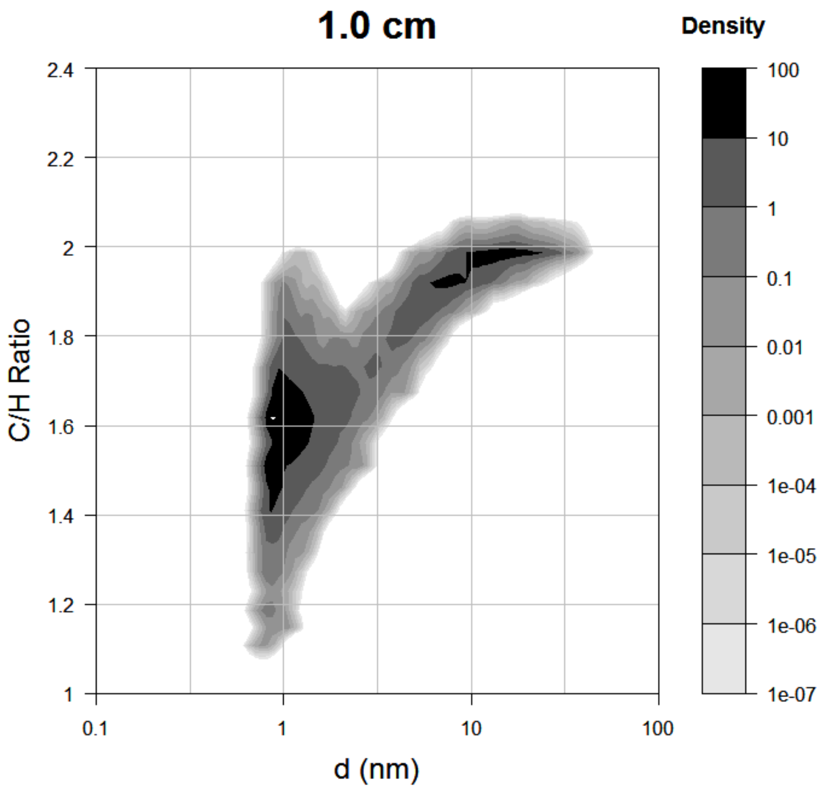
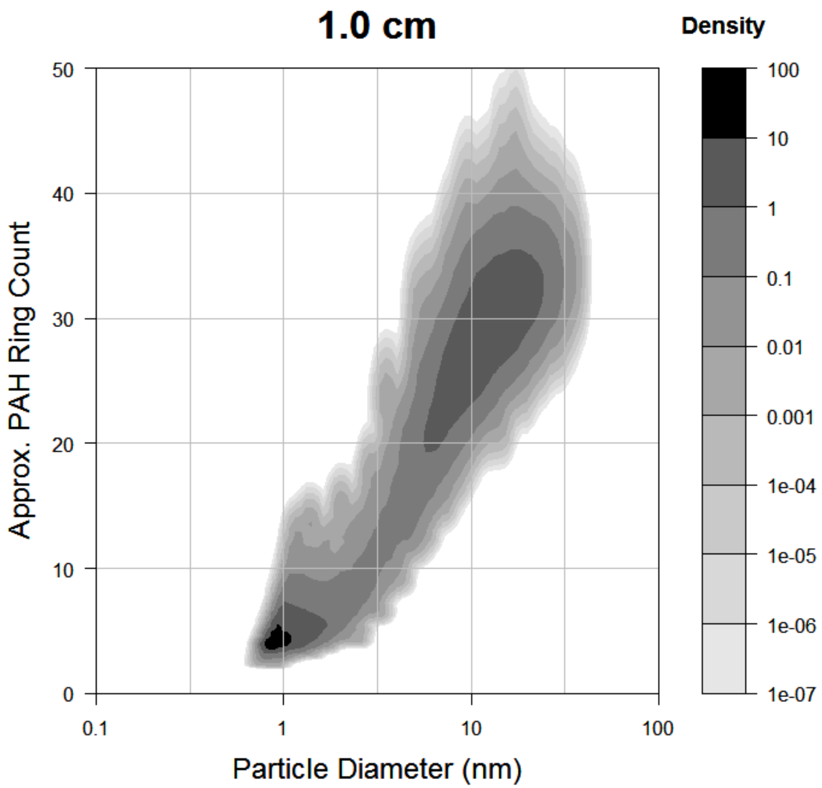
Particle composition





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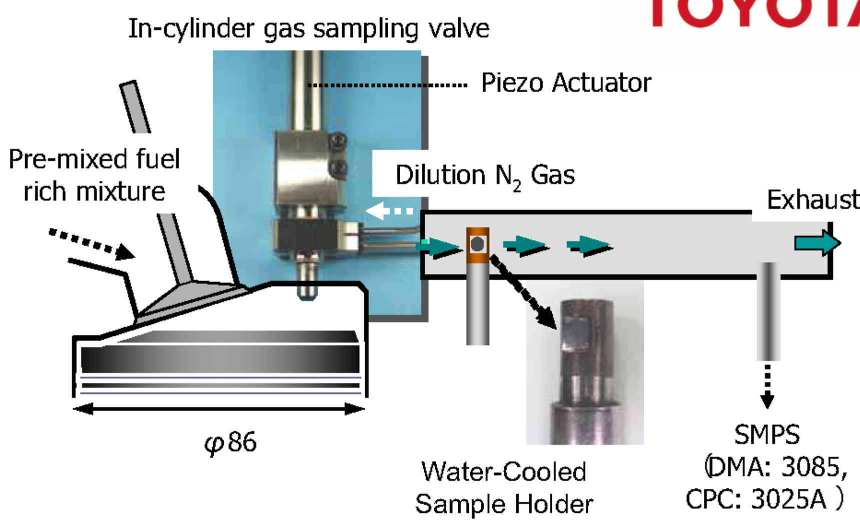
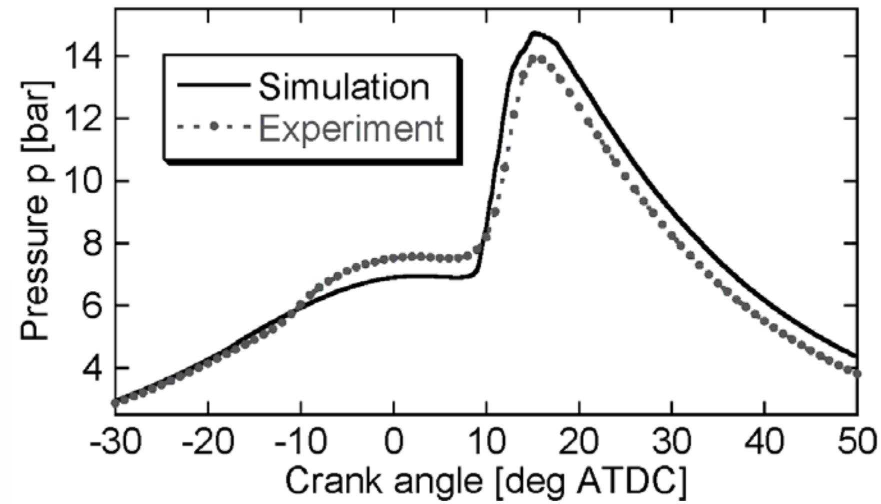
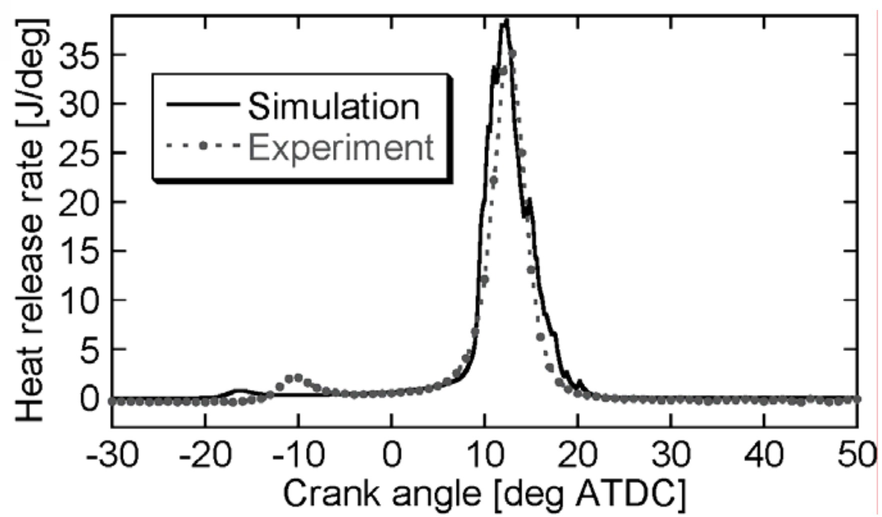
Soot in engines!

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

TOYOTA







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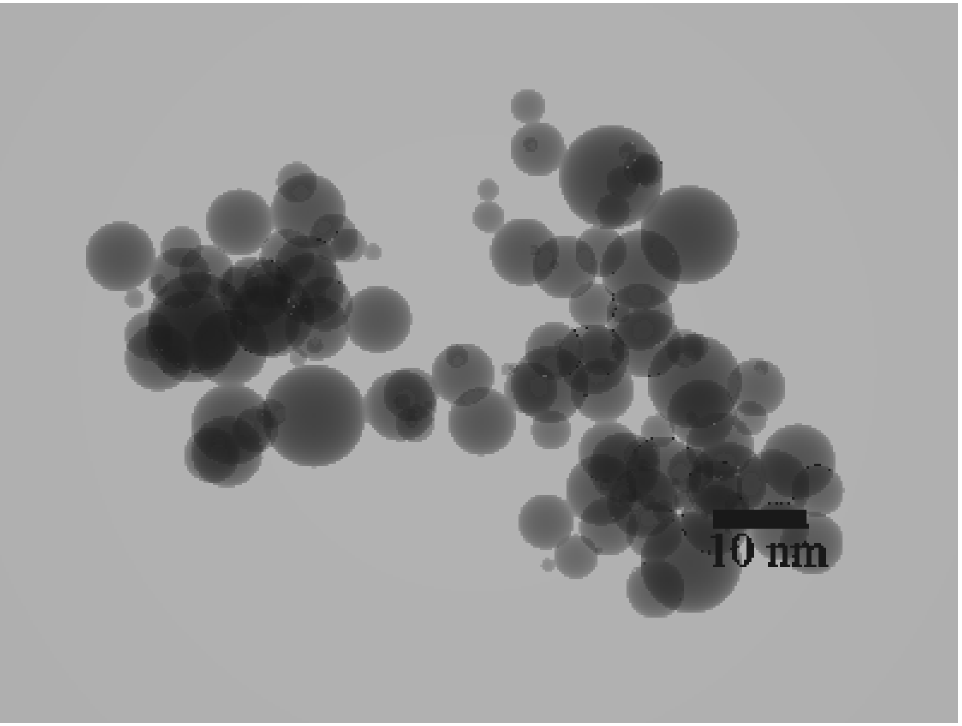
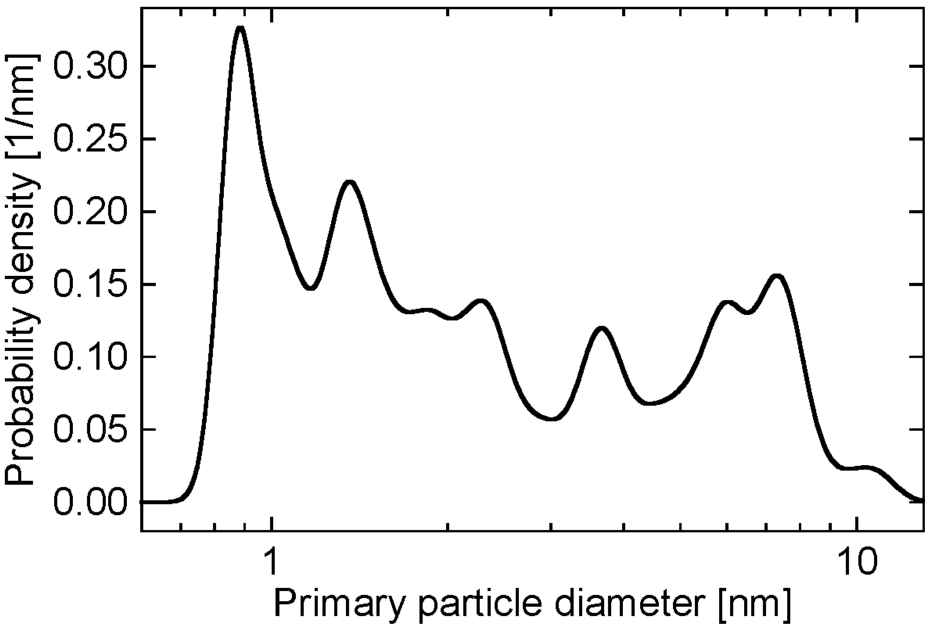
Sampled aggregates (I)

Simulation



Simulation



49.4 CAD ATDC, 129 primaries, coll. diam. 64 nm

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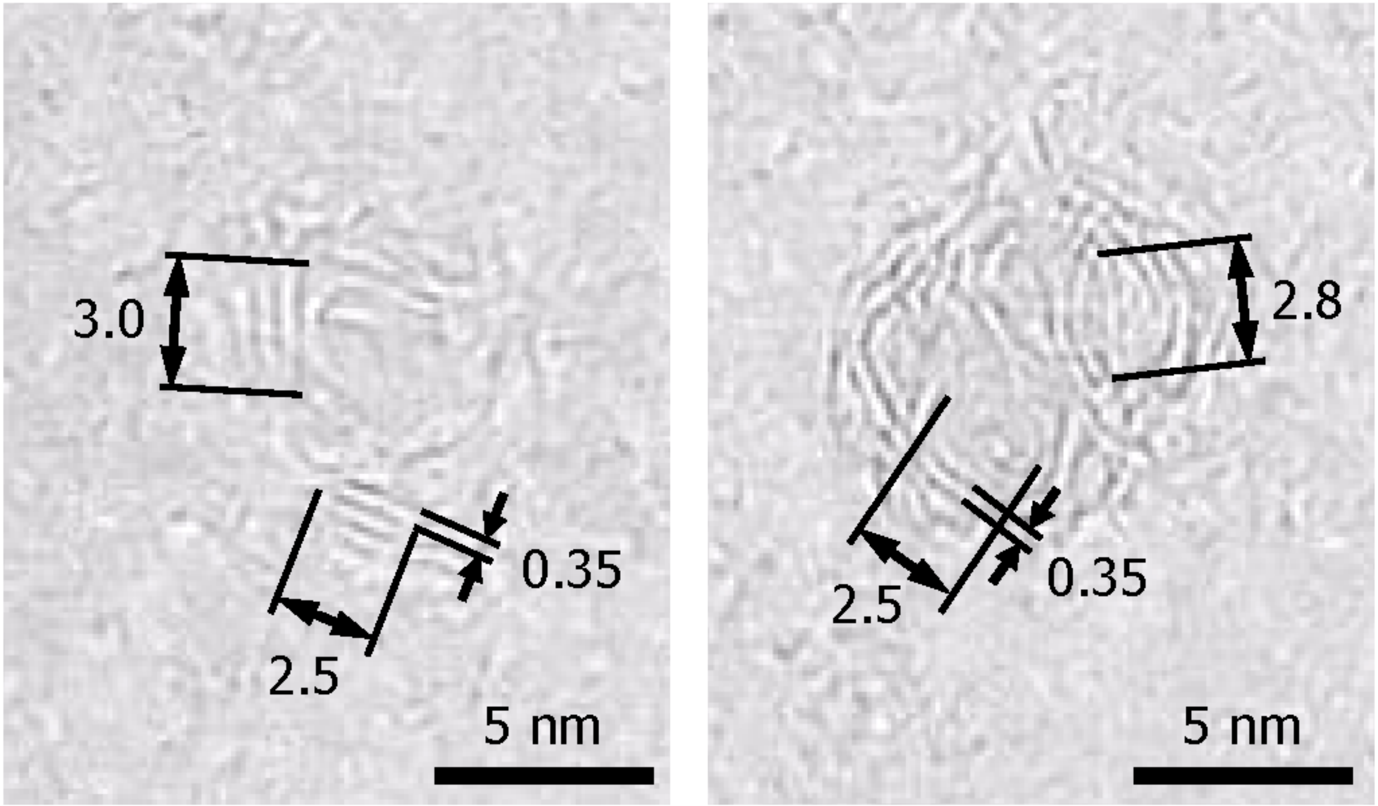
Sampled aggregates (II)

Experiment, sampled at ~46 CAD ATDC



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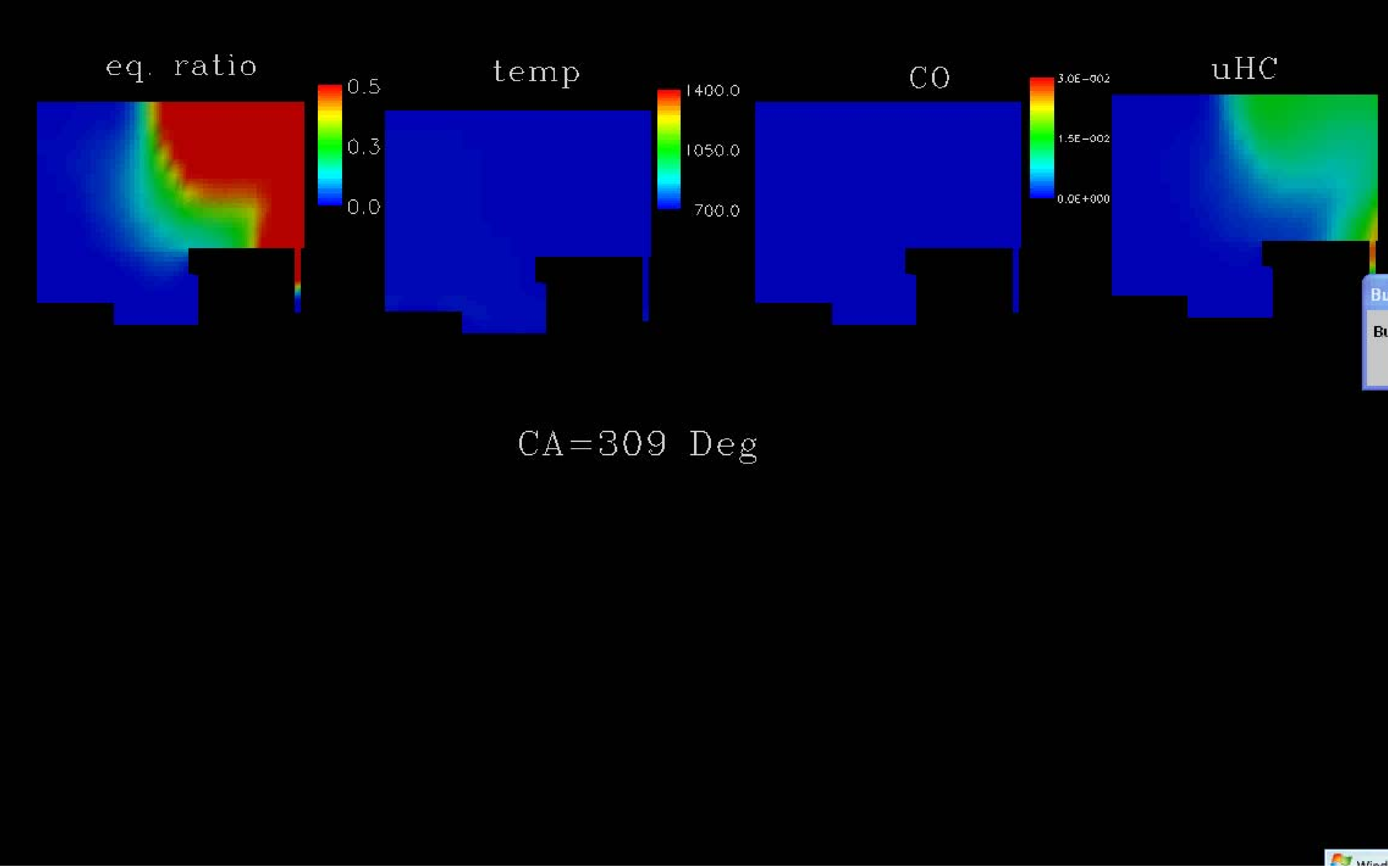

SOI at -100 aTDC, spray cone angle: 100 deg.

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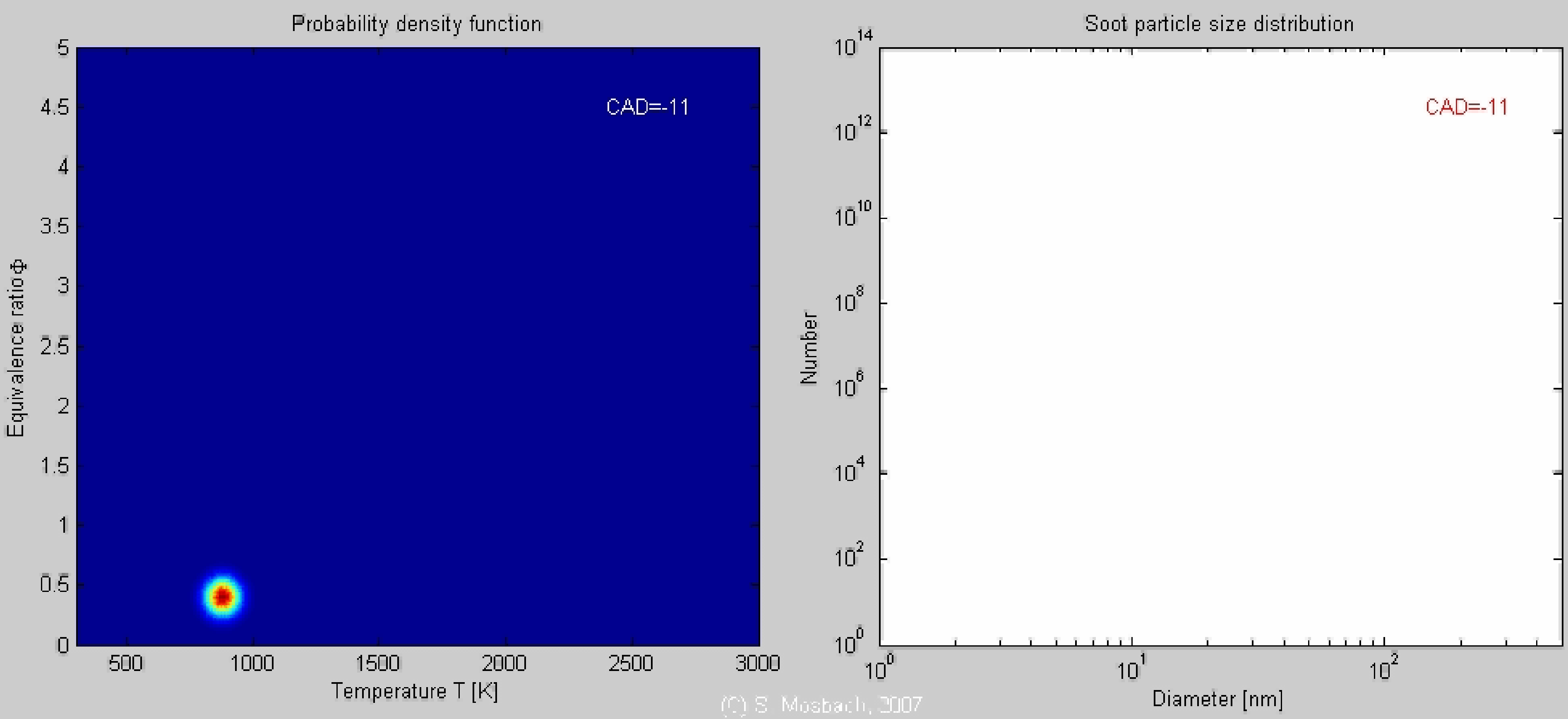
Engine soot model

Soot formation in a partially stratified HCCI engine:



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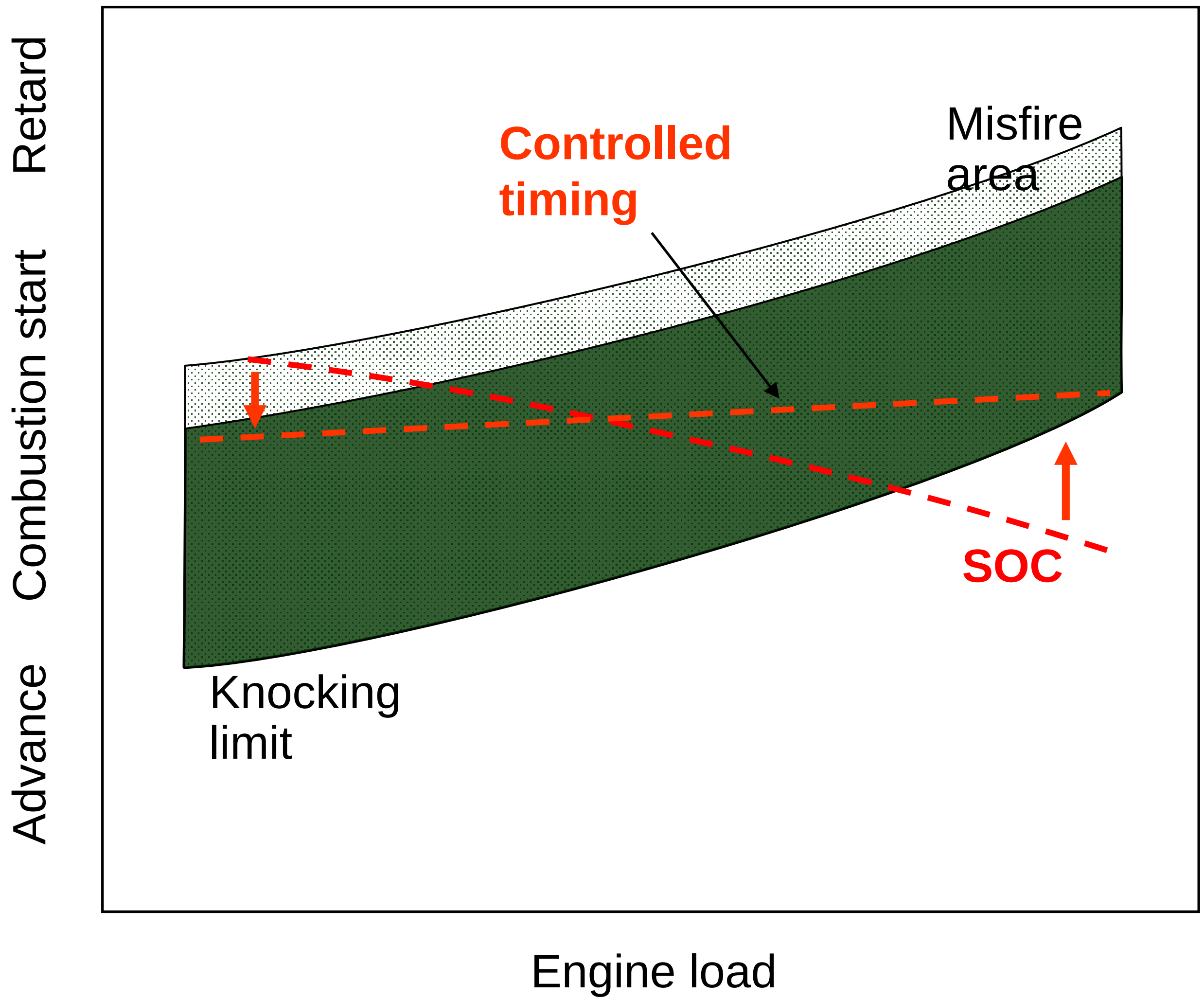
HCCI control problem



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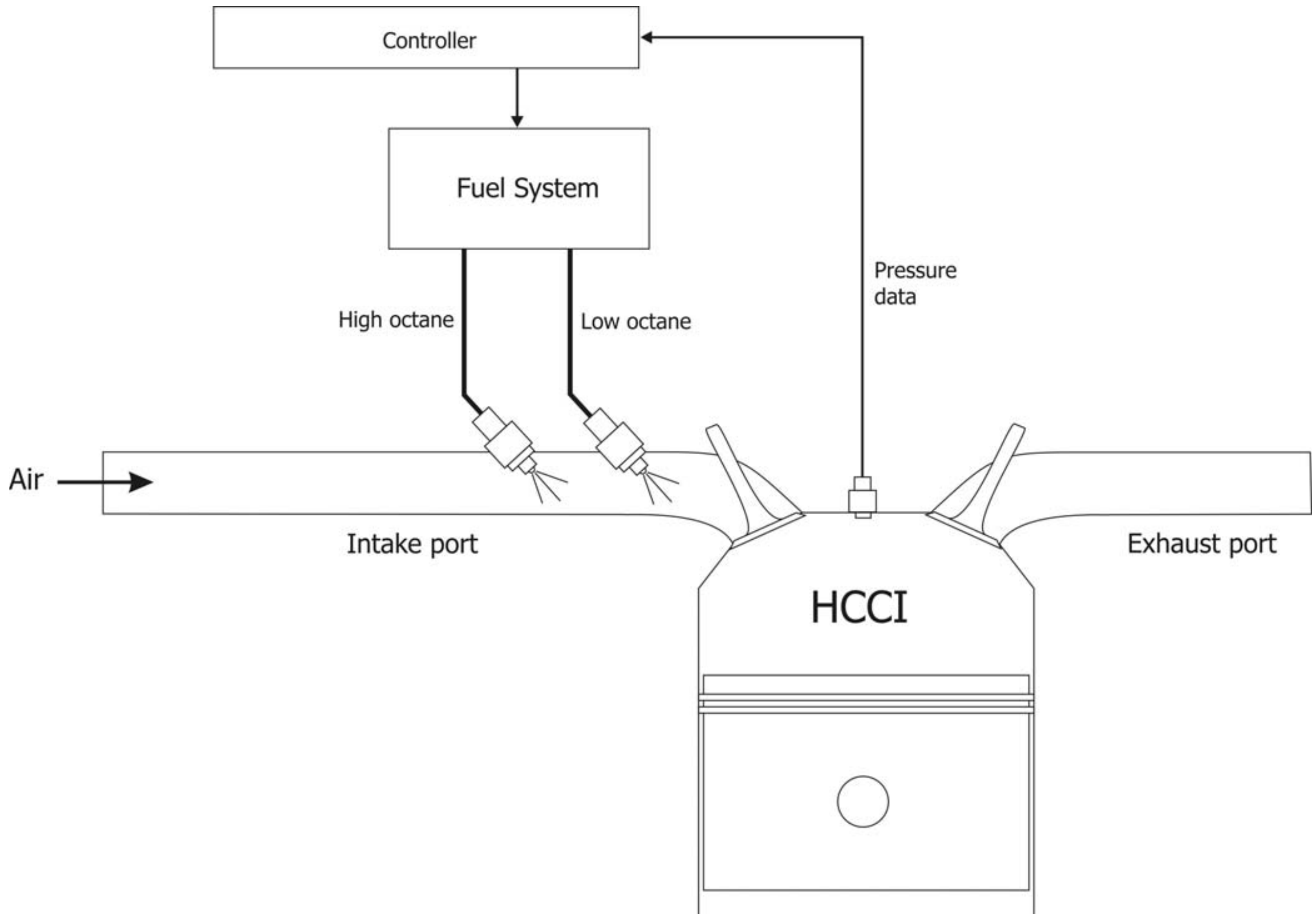
Octane variation strategy



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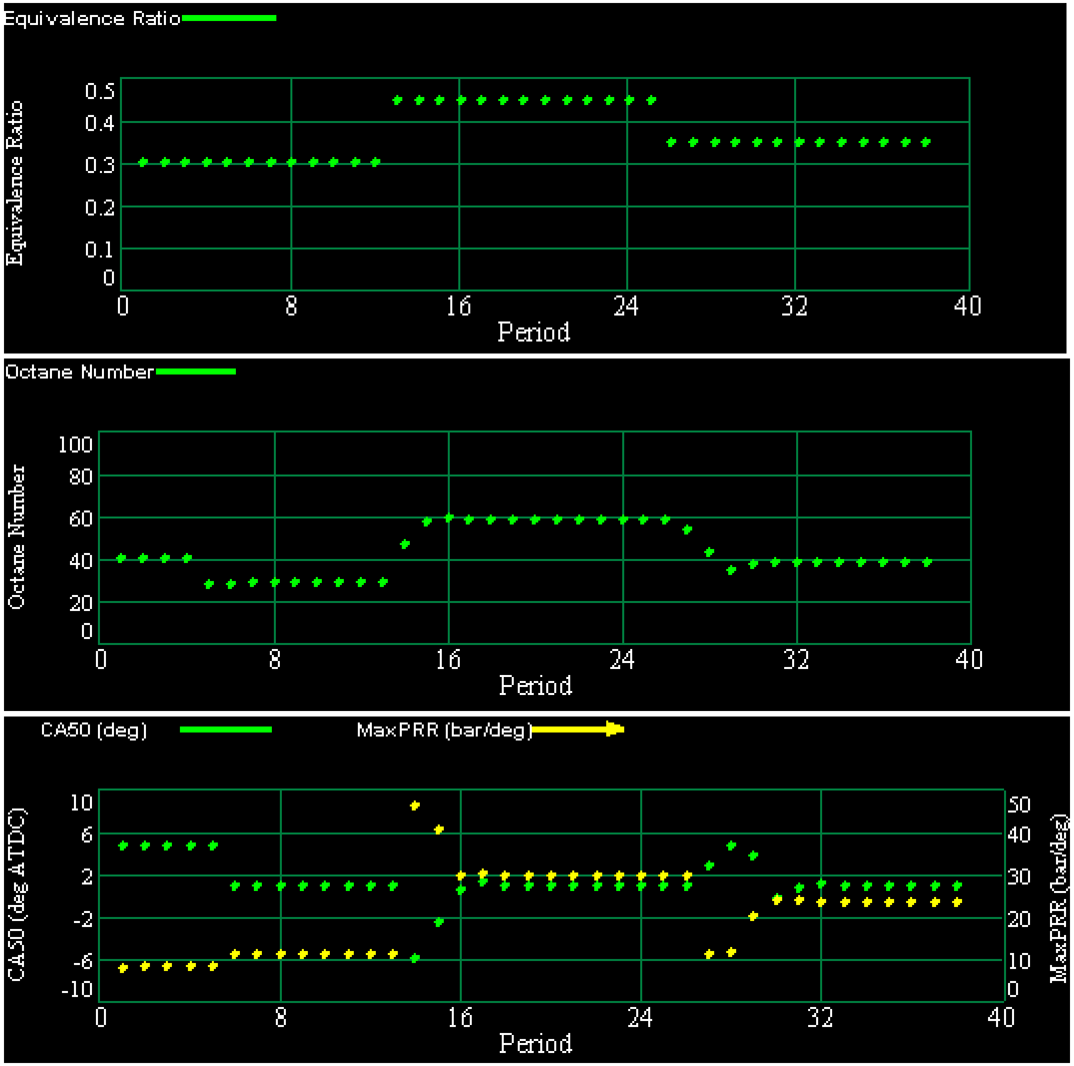
Example: Transient control

- Imposed equivalence ratio profile
- PID controller changes fuel composition (octane number) such that…
- … ignition timing (CA50) is held at a given set point.



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Live simulation…

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Thank you…

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Thank you for your attention.

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