STANFORD ENGINEERING

ACSS 2018 December 18, 2018

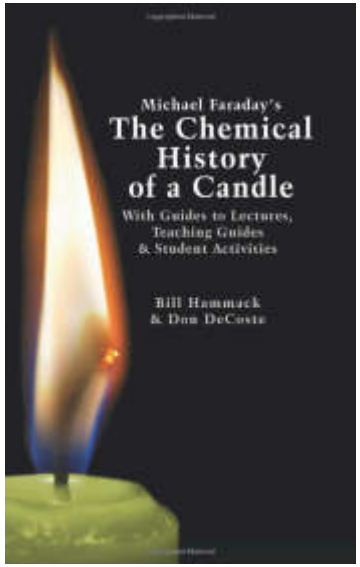
Soot Chemistry and the Evolution of Particles in Flames

Hai Wang

Stanford University

Some Key Review Papers

1. Palmer, H.B. and Cullis, C.F., 1965. The formation of carbon from gases. In *Chemistry and physics of carbon*, 1, pp.265-325., Marcel Dekker: New York.
2. Haynes, B.S. and Wagner, H.G., 1981. Soot formation. *Progress in Energy and Combustion science*, **7**, 229-273.
3. Calcote, H.F., 1981. Mechanisms of soot nucleation in flames—a critical review. *Combustion and Flame*, **42**, 215-242.
4. Glassman, I., 1989, Soot Formation in Combustion Processes. *Symposium (international) on combustion*, **22**, 295-311.
5. H. Bockhorn, 1994, Soot formation in combustion: mechanisms and models," Springer-Verlag, Berlin (a collection of papers).
6. Kennedy, I.M., 1997. Models of soot formation and oxidation. *Progress in Energy and Combustion Science*, **23**, 95-132.
7. Richter, H. and Howard, J.B., 2000. Formation of polycyclic aromatic hydrocarbons and their growth to soot—a review of chemical reaction pathways. *Progress in Energy and Combustion Science*, **26**, 565-608.
8. Frenklach, M., 2002. Reaction mechanism of soot formation in flames. Physical chemistry chemical Physics, **4**, 2028-2037.
9. D'Anna, A., 2009. Combustion-formed nanoparticles. *Proceedings of the Combustion Institute*, **32**, 593-613.
10. Wang, H., 2011. Formation of nascent soot and other condensed-phase materials in flames. *Proceedings of the Combustion Institute*, **33**, 41-67.



A series of six lectures on the chemistry and physics of flames given by Michael Faraday at the Royal Institution in 1848

Outline

1. **Why soot interests us?**
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6. The processes of soot formation
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8. Some unresolved questions about soot formation

Soot and Civilization

https://www.pinterest.com/pin/324892560597771403

Fire made us?

https://www.theemotionmachine.com/origin-of-us-campfires-bedrock-human-civilization

https://www.alternet.org/environment/how-fire-made-us-human

http://blog.world-mysteries.com/strange-artifacts/prehistoric-cave-paintings

Lampblack (soot) used in prehistoric cave paintings (35,00 -10,000 ybp)

G. Nelson Eby, http://faculty.umb.edu/nelson_eby/Forensic%20Geology/PowerPoint%20Presentations.htm

World's oldest tattoos (Tyrolean iceman, Ötzi) were etched in soot (c. 3,300 BC)

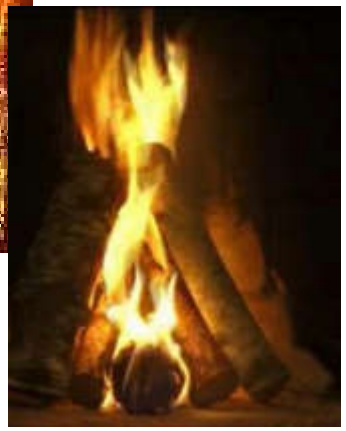
http://www.newscientist.com/article/dn17469-worlds-oldest-tattoos-were-made-of-soot.html/.Ufjc4xYSM54

Soot is ubiquitous in flames

http://www.historyforkids.org/learn/science/fire.htm

http://upload.wikimedia.org/wikipedia/commons/1/1c/Candle-flame-no-reflection.jpg

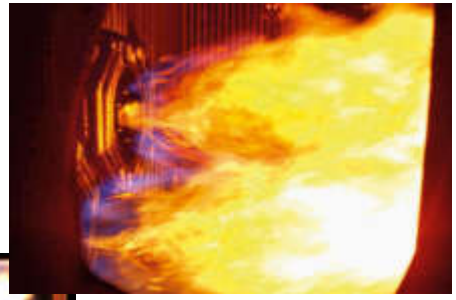
www.alaska-in-pictures.com



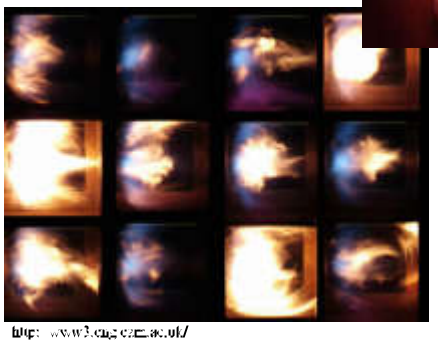
www.bidorbuy.co.za

https://abstract.desktopnexus.com/wallpaper/1323916

http://www.truckstrend.com/how-to/engine/0703dp-bosch-diesel-injection-system/



http://www.stek.insight-online.com/gm960-gas-analyzer-stop-boiler-wall-corrosion



http://www3.engineer.ac.uk/photocomp/2009/is262_1.jpg

Soot-Like materials may even be abundant in interstellar media

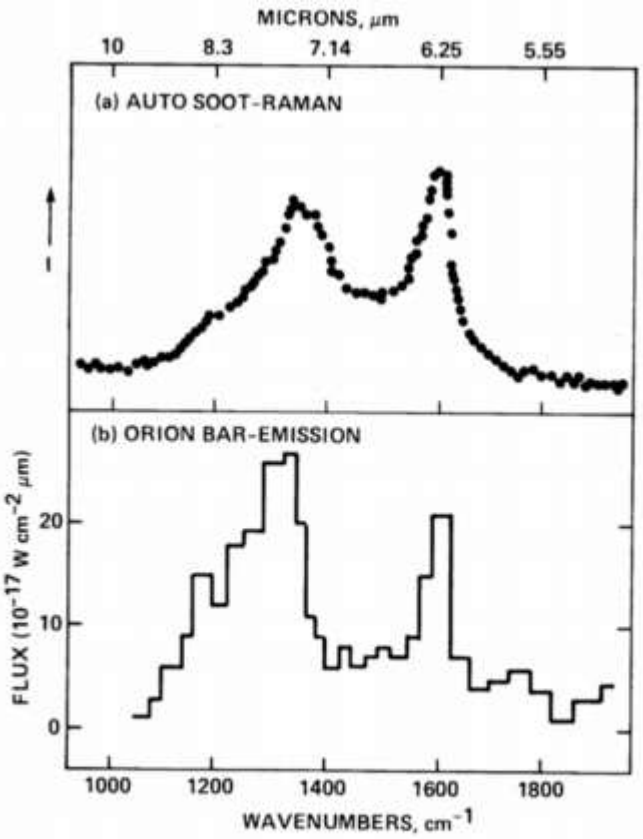
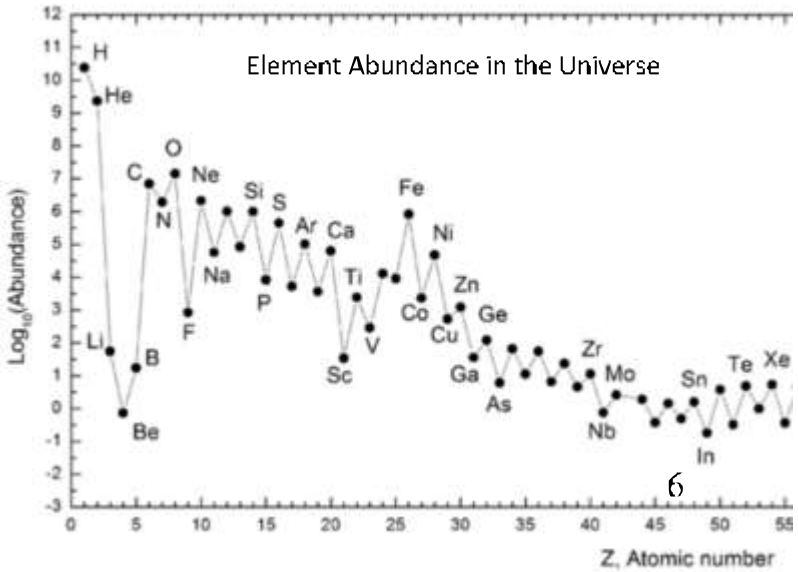


FIG. 1.—(*a*) Raman spectrum from 5 to 10 μm of auto exhaust, adapted from Rosen and Novakov (1978). (*b*) Spectrum from 5 to 10 μm of the Orion bar (Bregman *et al.* 1984).

Allamandola; Tielens & Baler ApJ 290; 1985



Soot as Particulate Air Pollutants

http://farm1.static.flickr.com/216/499969453_44089c6c1d.jpg

http://www.spacemart.com/images/cruise-ship-smoke-stack-emission-bg.jpg]

http://www.parks.ca.gov/pages/491/images/sierra_3_steam_locomotive.jpg

http://www.sfgate.com/blogs/images/sfgate/green/2009/06/03/diesel-smoke.jpg

https://www.momscleanairforce.org/a-sooty-mess-in-ohio/

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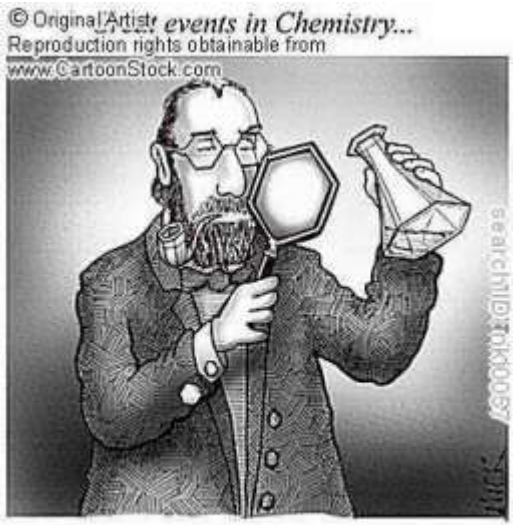
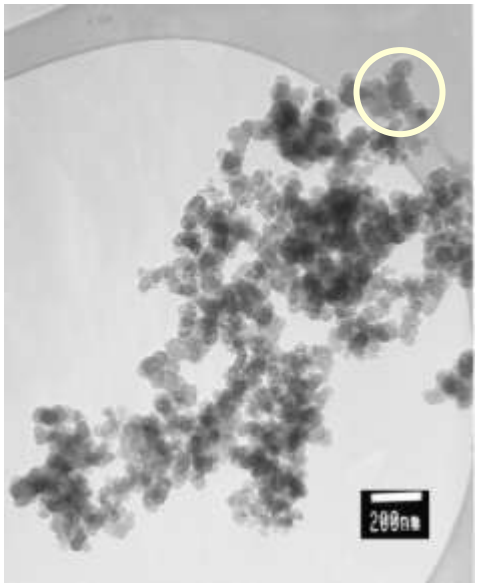
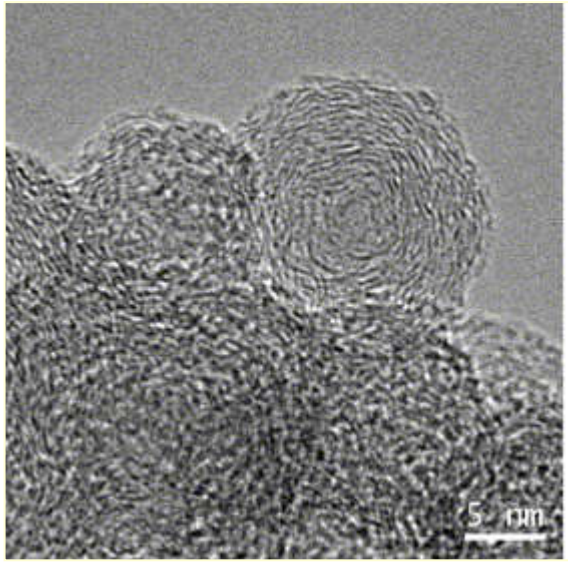
Soot Microstructures/Composition/Morphology



1865: Kekulé, moments before his brilliant insight into the structure of benzene.



http://www.asn.u-bordeaux.fr/images/soot.jpg

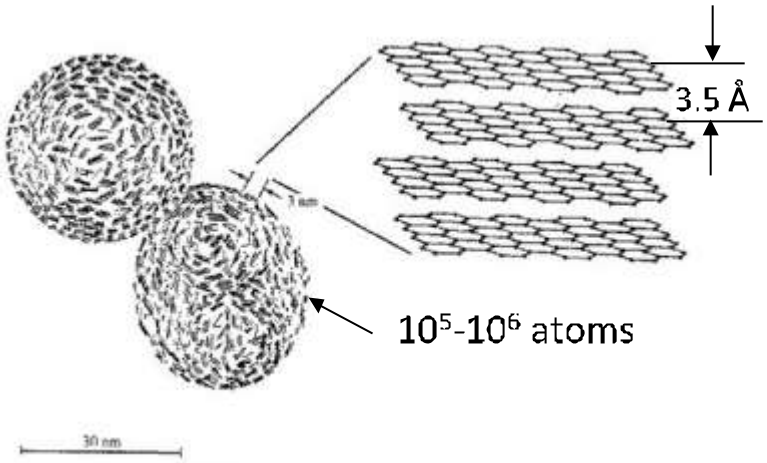


Courtesy: Boehman

Mature soot:

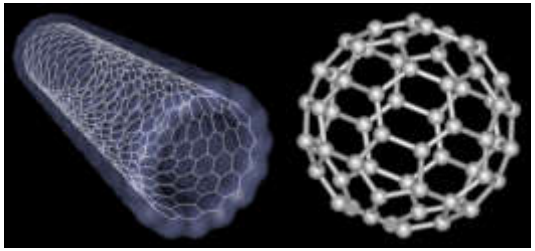
C/H ~ 8/1

ρ = 1.8 g/cc

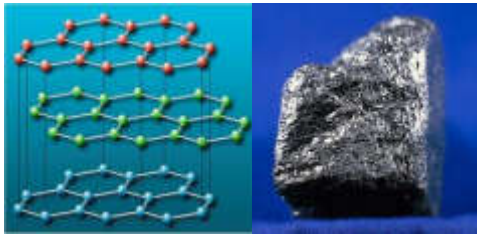


http://www.atmos.umd.edu/~pedro/soot2.jpg

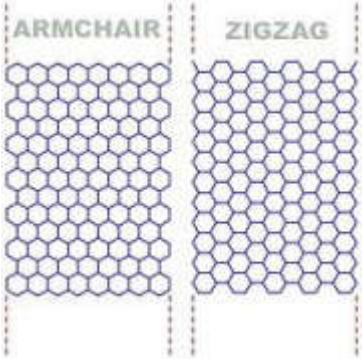
Soot: From Structure to Materials

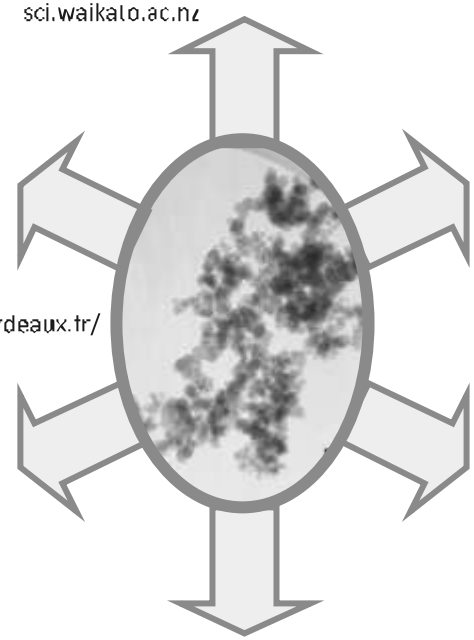


daneshema.com

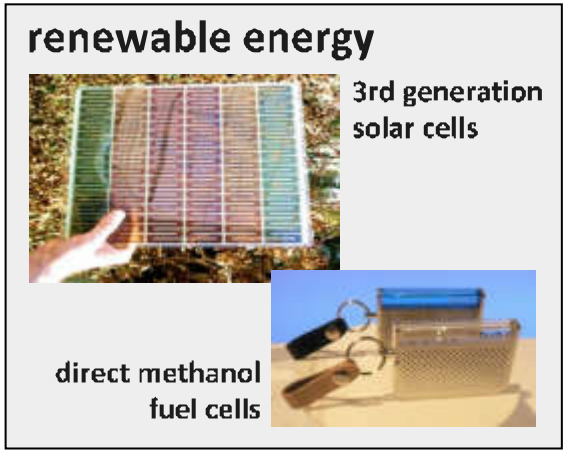


sci.waikato.ac.nz





http://www.asn.u-bordeaux.fr/images/soot.jpg



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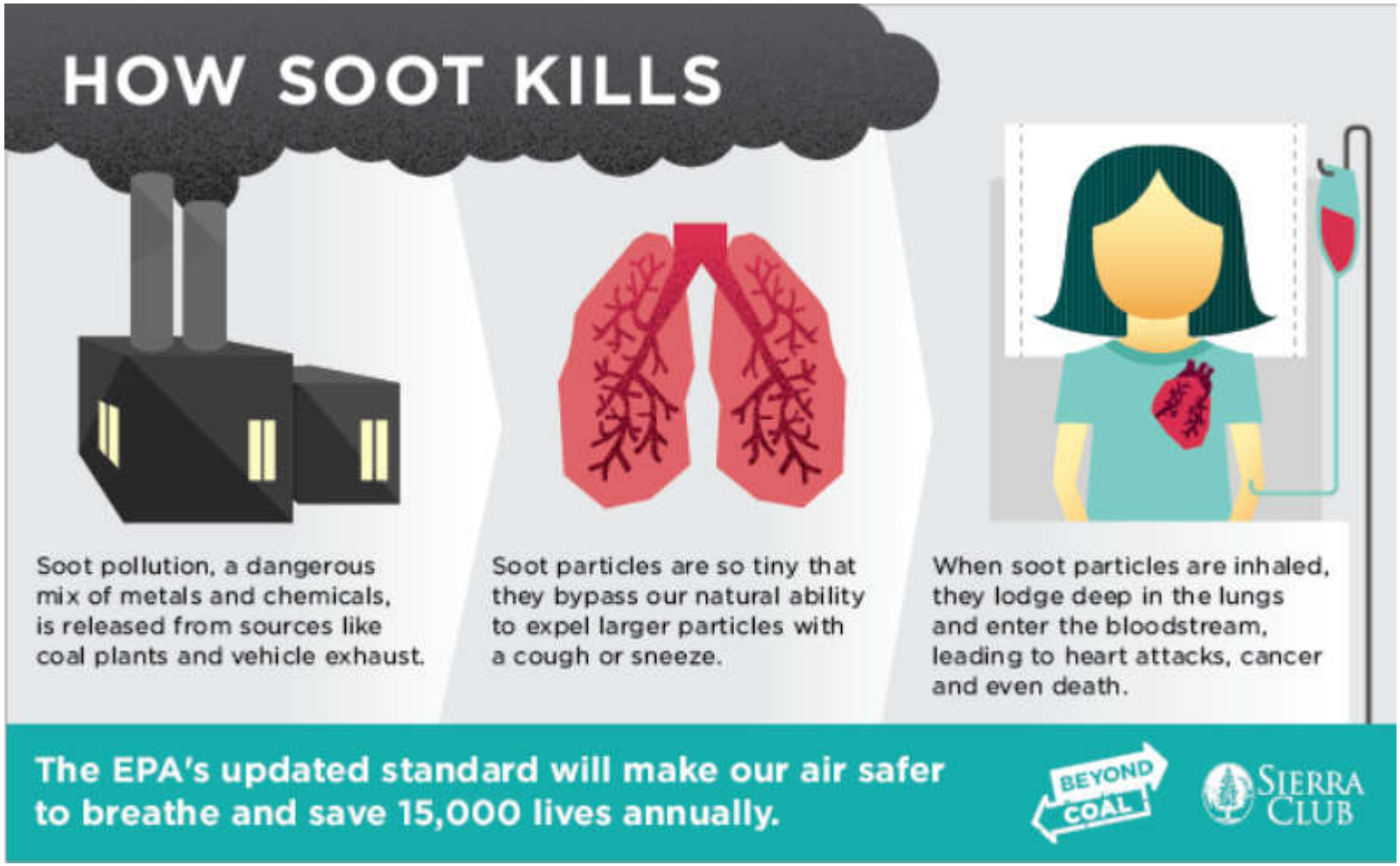
Soot and Human Health Effects



Soot and Climate Change

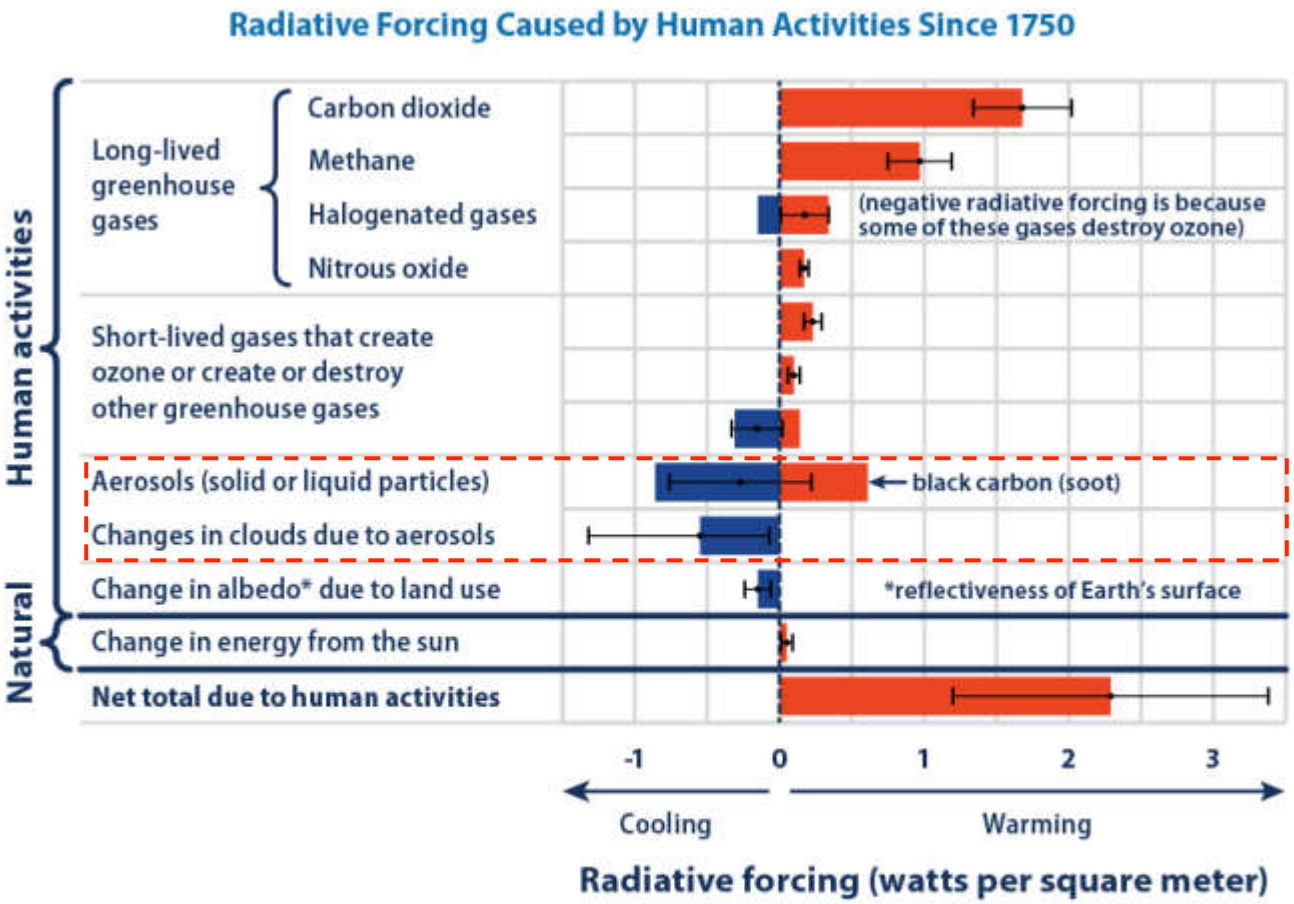
- Soot deposition responsible for 95% polar ice melting

- Dirty snow reduces ice albedo

- Brown clouds causes regional warming

- Contrail related cloud albedo

Soot and Climate Change



Data source: IPCC (Intergovernmental Panel onClimate Change). 2013. Climate change 2013: The physical science basis. Working Group I contribution to the IPCC Fifth Assessment Report. Cambridge, United Kingdom: Cambridge University Press. www.ipcc.ch/report/ar5/wg1.

For more information, visit U.S. EPA's "Climate Change Indicators in the United States" at www.epa.gov/climate-indicators.

A Key Intellectual Driving Force behind Research into Soot Formation

"A major break-through in understanding carbon formation will have been achieved when it becomes possible in at least one case to account for the entire course of nucleation and growth of carbon on the basis of a fundamental knowledge of reaction rates and mechanisms."

Palmer & Cullis, 1965

A Key Intellectual Driving Force behind Research into Soot Formation

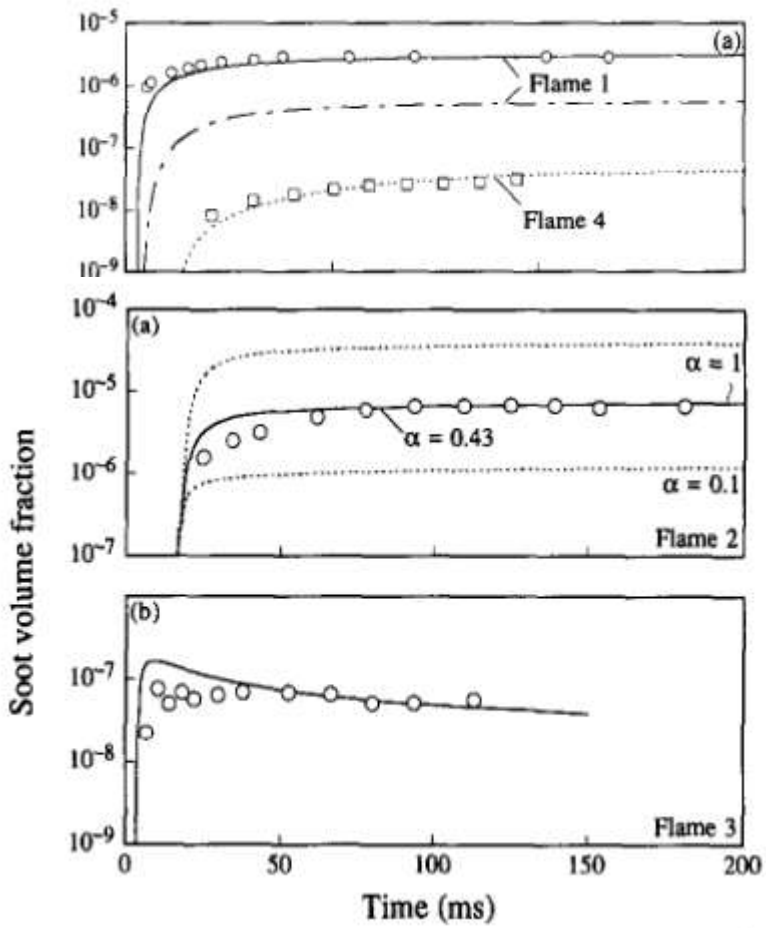
Earlier efforts at modeling soot formation

Frenklach, **Wang**, "Detailed mechanism and modeling of soot particle formation," *Proc. Combust. Inst.* 23 (1990) 1559.

Frenklach, **Wang**, "Detailed modeling of soot particle nucleation and growth," in: *Soot Formation in Combustion: Mechanisms and Models of Soot Formation*, Bockhorn, Ed. Springer-Verlag, Berlin, 1994, pp. 162-190.

Wang, Frenklach "A detailed kinetic modeling study of aromatics formation in laminar premixed acetylene and ethylene flames," *Combust. Flame*, 110 (1997) 173.

Bockhorn ed. *Soot Formation in Combustion: Mechanisms and Models of Soot Formation,* Springer-Verlag, Berlin, 1994.

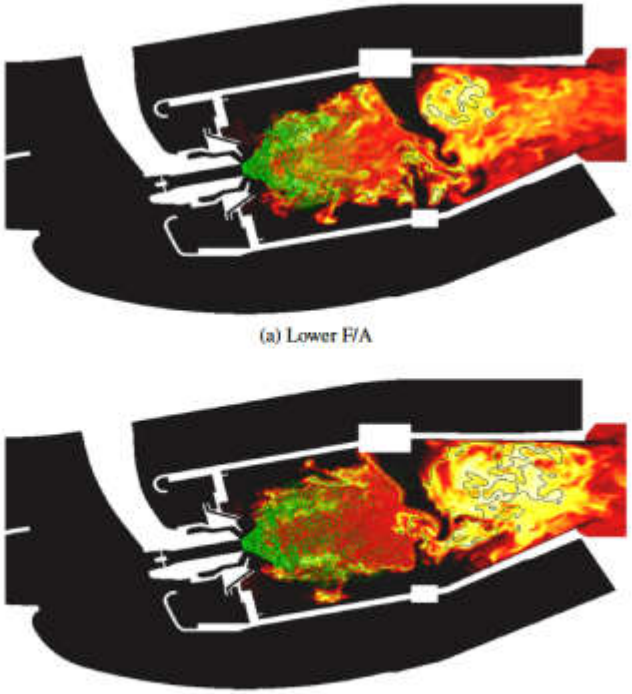


Data: Jander & Wagner, Simulation: Kazakov, Wang, Frenklach (1994)

Practical driving force behind research into soot formation

Potentially an Engine Design Tool

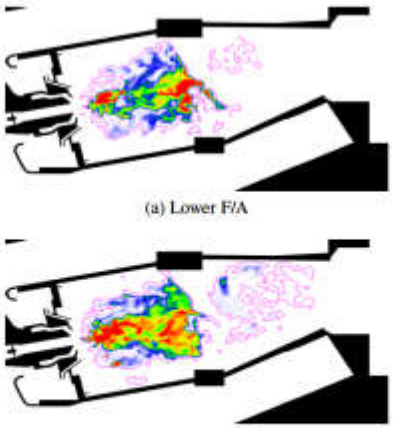
Large eddy simulation of soot evolution in an aircraft combustor.



(a) Lower F/A

(b) Higher F/A

Figure 2: Instantaneous temperature at mid-pitch and the locations of liquid spray parcels (in 3D). The black line is the stoichiometric mixture fraction. The lighter colors correspond to higher temperatures.



(a) Lower F/A

(b) Higher F/A

Figure 3: Instantaneous soot volume fraction at mid-pitch. The magenta line is the stoichiometric mixture fraction. Red regions correspond to the largest soot volume fractions, and the two scales are the same.

Mueller, M.E. and Pitsch, H., 2013. *Physics of fluids*, *25*, 110812.

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Characterizing Particles

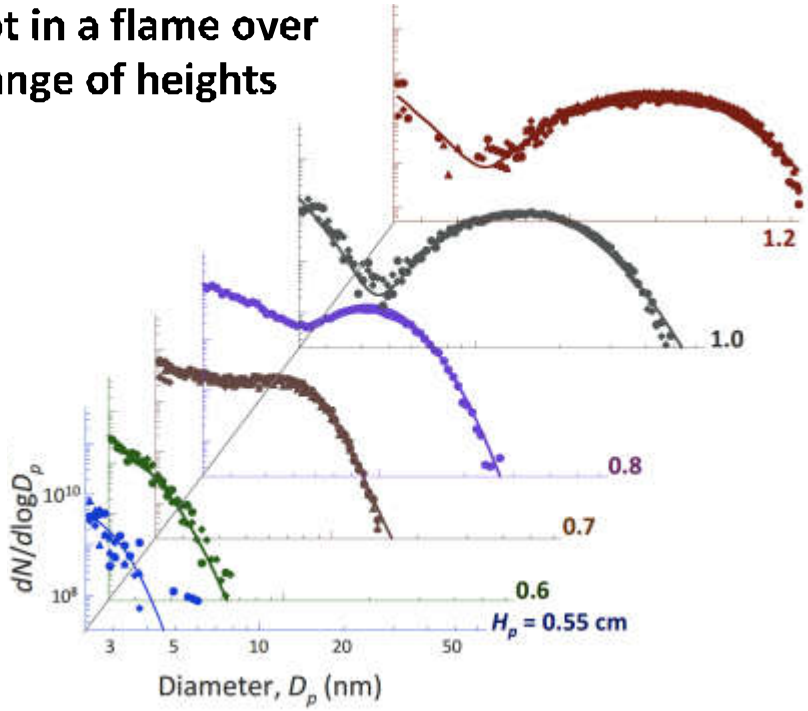
- How many particles?
- How big are they?
- What is the mass/volume?

- How are the size distributed?
- What do they look like?
- What are they made of (surface versus bulk)?

Characterizing Particles

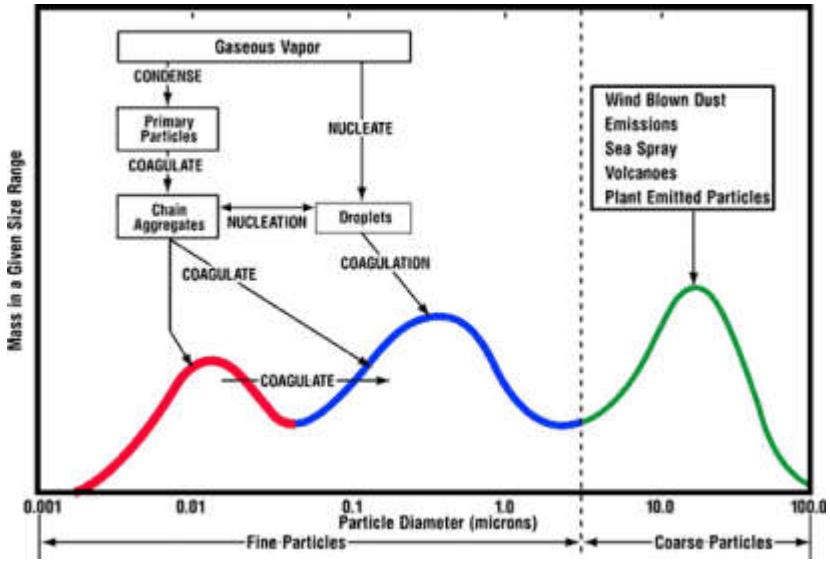
- **In Flames**
  - Number density, N (cm^{-3})
  - Diameter, D_p (nm)
  - Volume fraction, f_v (volume of soot / volume of gas)
  - Particle size distribution function, dN/dD_p or $dN/d\log D_p$

Soot in a flame over a range of heights



Bimodal with a truncated tail

Atmospheric aerosols



Trimodal, indicative of different sources.

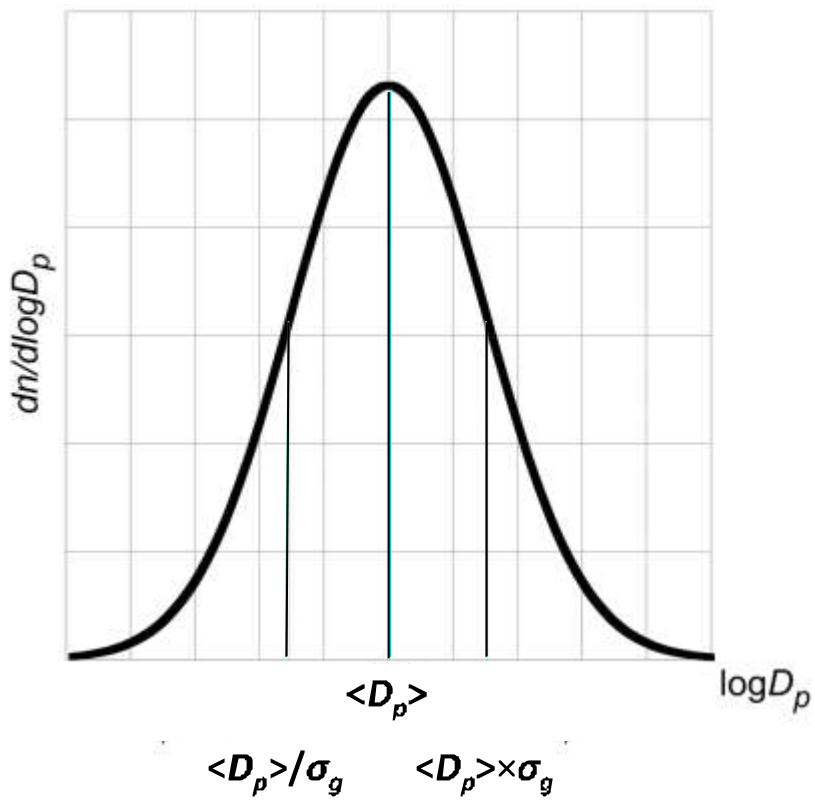
Characterizing Particles

- The lognormal particle size distribution function (PSDF):

$$\frac{dn}{d\log D_p} = \frac{1}{\sqrt{2\pi}\log\sigma_g} e^{-\frac{\left(\log D_p - \log\langle D_p\rangle\right)^2}{2\left(\log\sigma_g\right)^2}}$$

where

- n is the *fractional number* of particles having diameter between $\log D_p$ and $\log D_p + d\log D_p$
- D_p is the diameter
- $\langle D_p \rangle$ is the median diameter
- σ_g geometric standard deviation.



Characterizing Particles

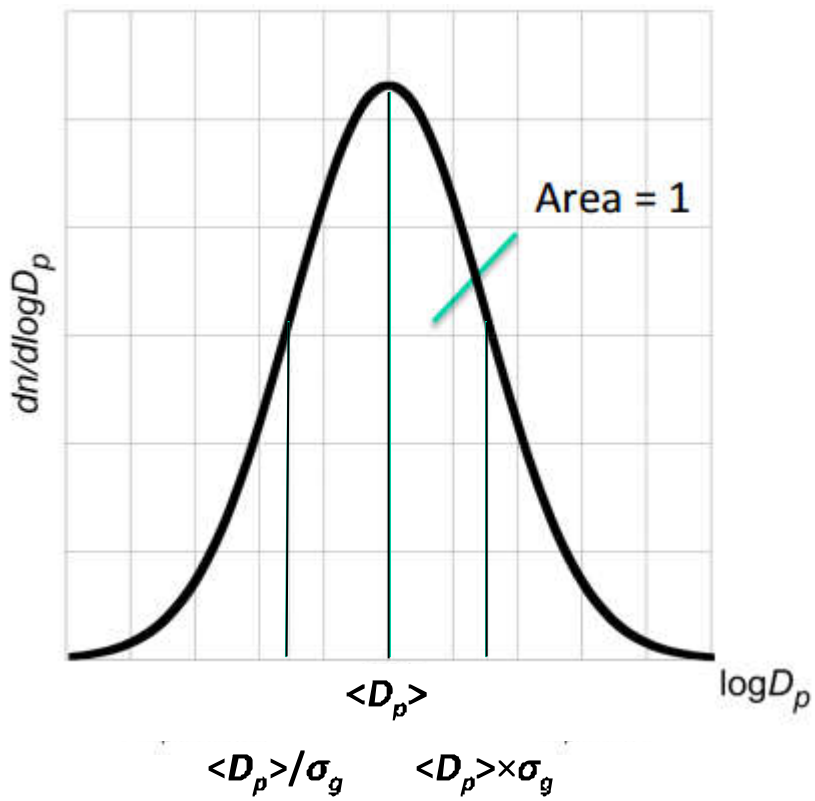
- Lognormal PSDF

$$\frac{dn}{d\log D_p} = \frac{1}{\sqrt{2\pi}\log\sigma_g} e^{-\frac{\left(\log D_p - \log\langle D_p\rangle\right)^2}{2\left(\log\sigma_g\right)^2}}$$

- Multiplying both sides of the equation by the total number of particles *N*

$$\frac{dN}{d\log D_p} = \frac{N}{\sqrt{2\pi}\log\sigma_g} e^{-\frac{\left(\log D_p - \log\langle D_p\rangle\right)^2}{2\left(\log\sigma_g\right)^2}}$$

$$N = N \underbrace{\int_{-\infty}^{\infty} \frac{1}{\sqrt{2\pi}\log\sigma_g} e^{-\frac{\left(\log D_p - \log\langle D_p\rangle\right)^2}{2\left(\log\sigma_g\right)^2}} d\log D_p}_{=1}$$



Characterizing Particles

- Total number (density)

  Zeroth moment

$$N = \int_0^\infty \frac{dN}{dD_p} dD_p = \int_{-\infty}^\infty \frac{dN}{d\log D_p} d\log D_p$$

- Mean diameter

  1st moment

$$\bar{D}_p = \frac{1}{N} \int_0^\infty D_p \frac{dN}{dD_p} dD_p = \frac{1}{N} \int_{-\infty}^\infty D_p \frac{dN}{d\log D_p} d\log D_p$$

- Surface area (density)

  2nd moment

$$S = \int_0^\infty \pi D_p^2 \frac{dN}{dD_p} dD_p = \int_{-\infty}^\infty \pi D_p^2 \frac{dN}{d\log D_p} d\log D_p$$

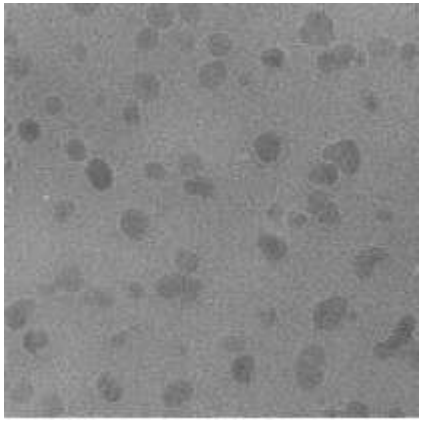
- Volume (fraction)

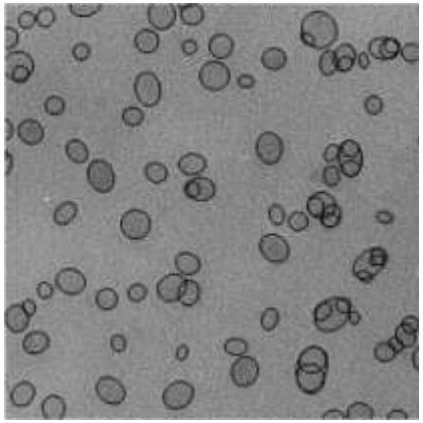
  3rd moment

$$V = \int_0^\infty \frac{\pi}{6} D_p^3 \frac{dN}{dD_p} dD_p = \int_{-\infty}^\infty \frac{\pi}{6} D_p^3 \frac{dN}{d\log D_p} d\log D_p$$

Characterizing Particles

Morphology

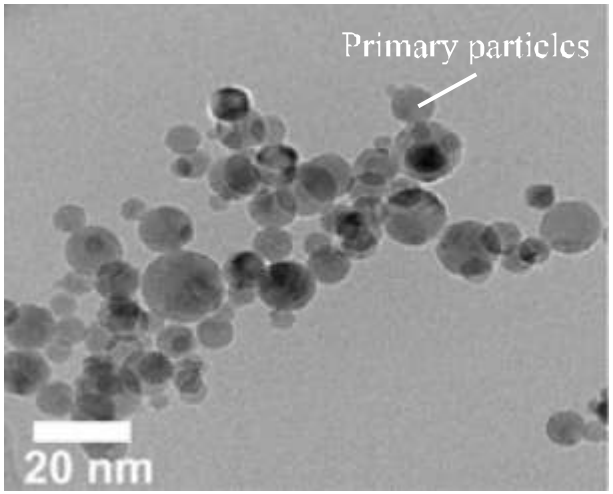




R. Fisker, J.M. Carstensen, M.F. Hansen, F. Bødker and S. Morup, *Journal of Nanoparticle Research* **2**: 267–277, 2000.

Well defined, segregated particles

- Size distribution
- Shape parameters
  - Aspect ratio
  - Circularity
  - Sphericity
  - ……

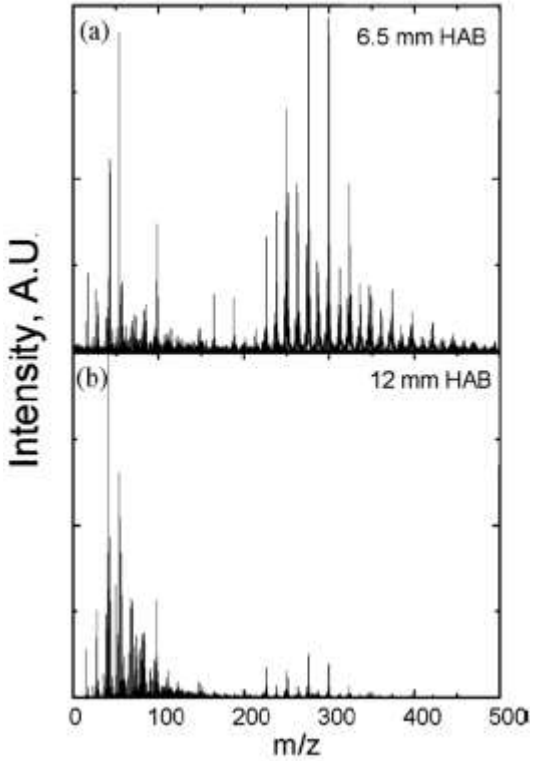


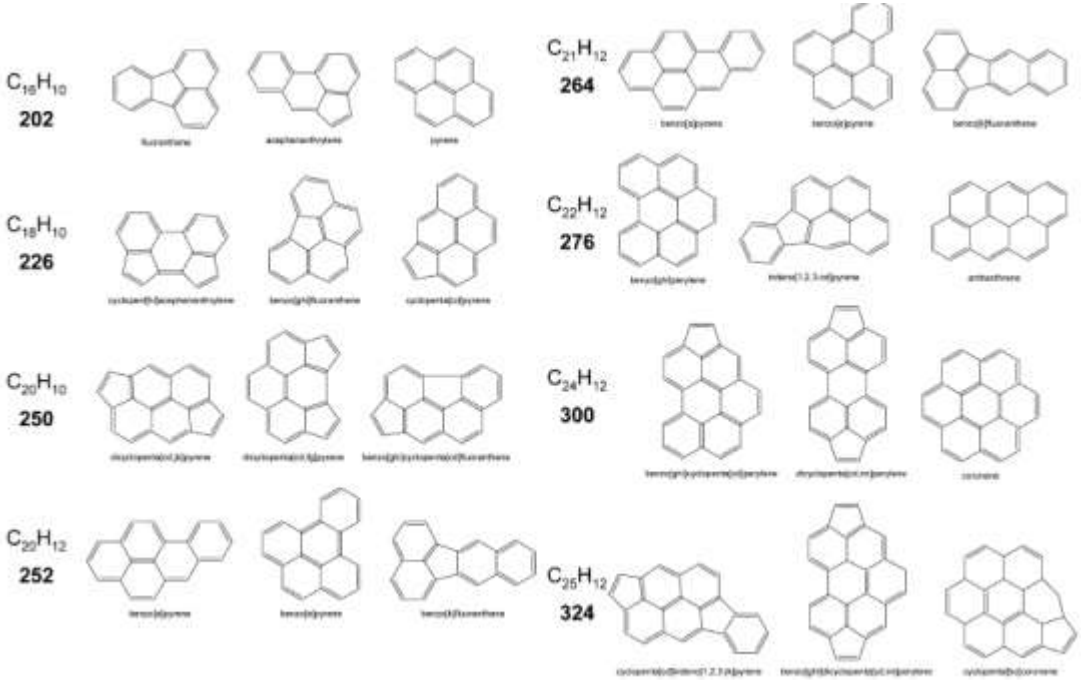
Fractal aggregates with well defined spherical primary particles

- Size distribution of primary particles
- Number of primary particles in an aggregate
- Properties about how compact an aggregate is
  - Radius of gyration
  - Fractal dimension

Characterizing Particles

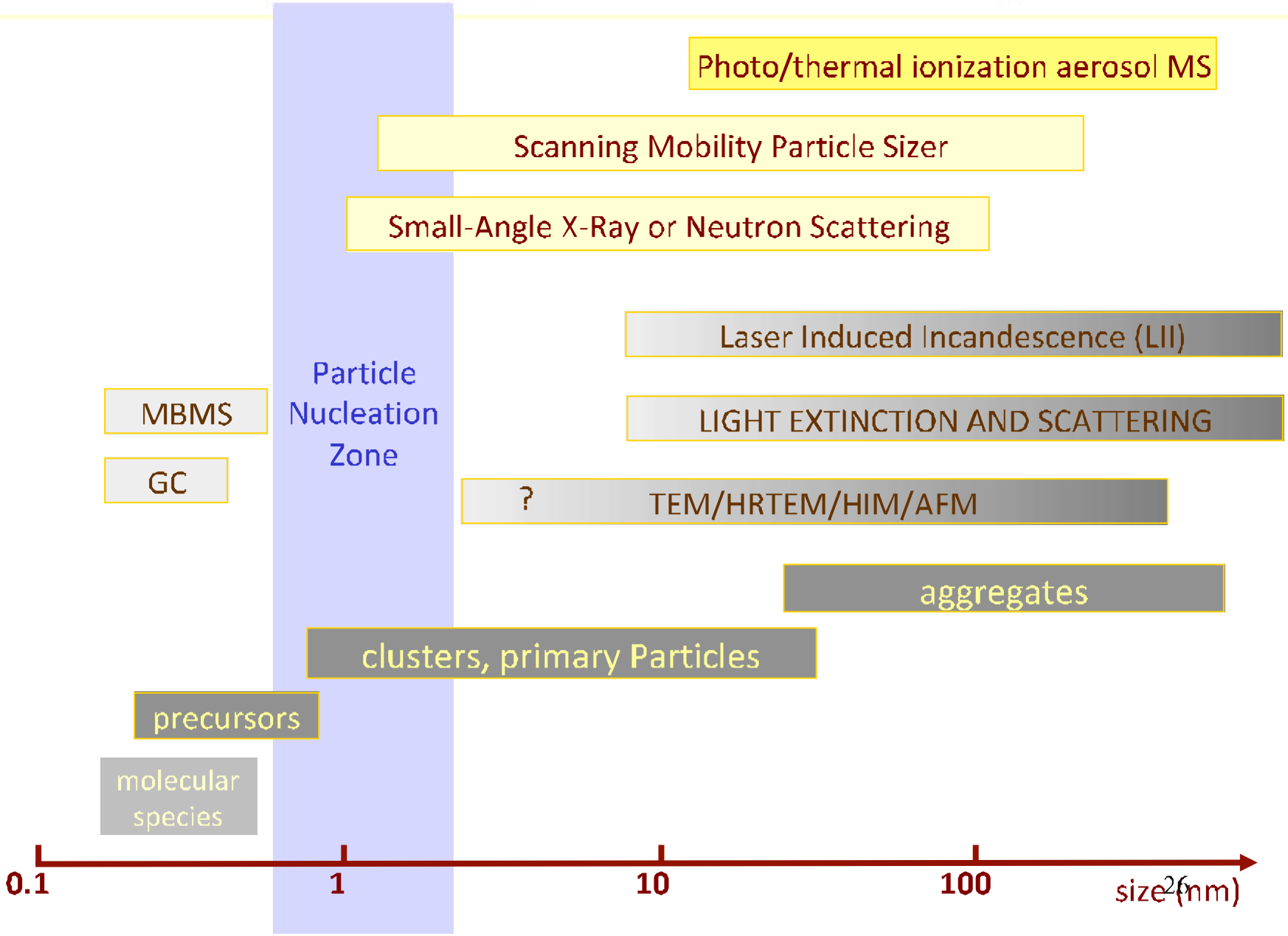
Composition



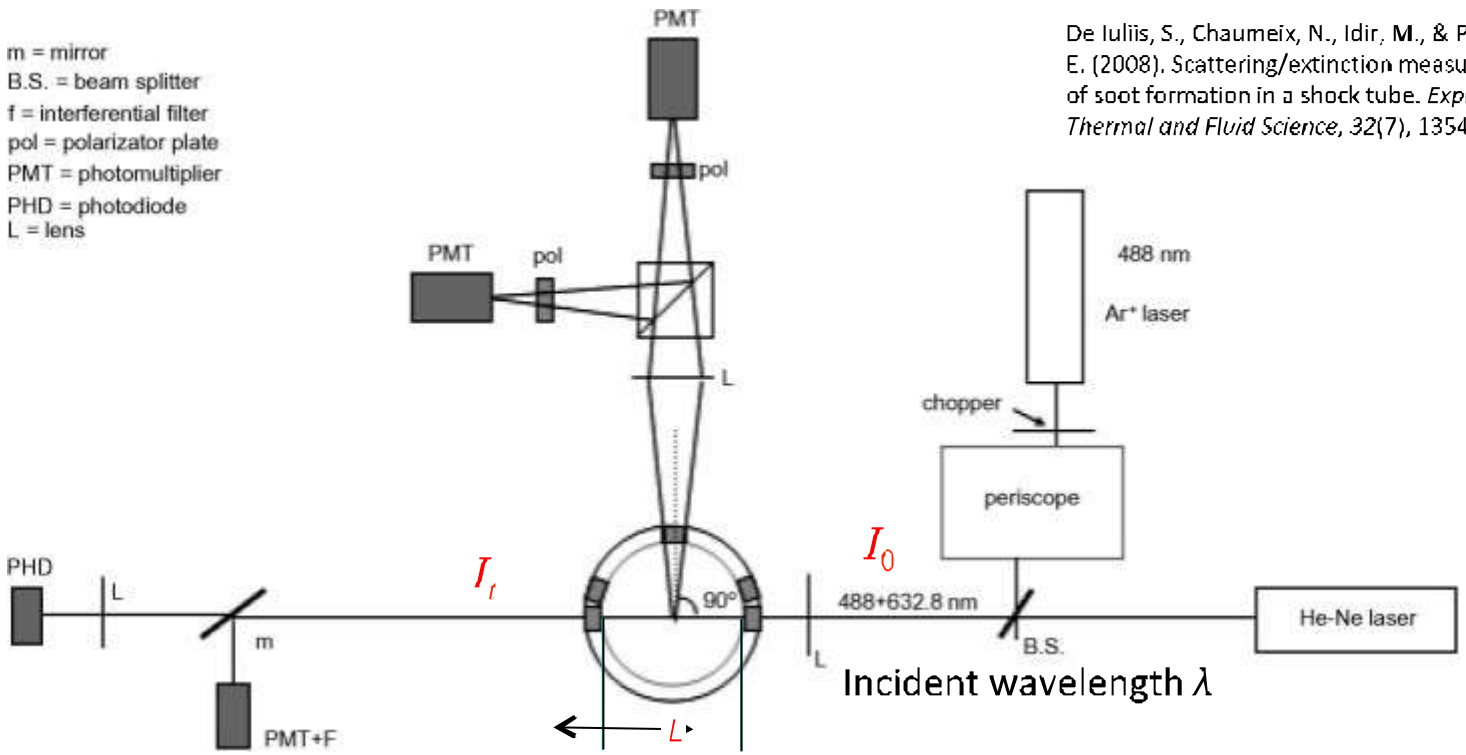


Oktem et al. Combust. Flame (2006)

Some Useful Experimental Techniques



Light Extinction and Scattering



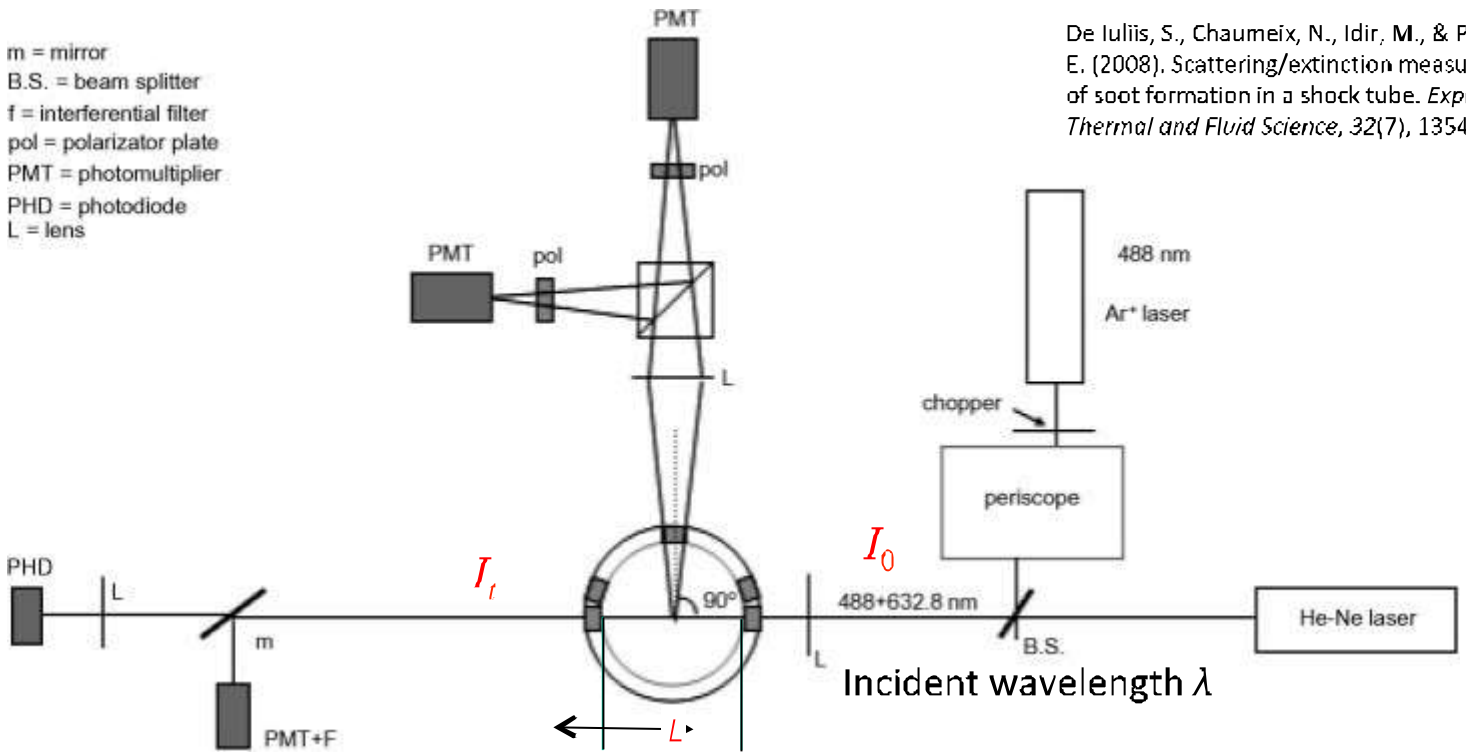
De Iuliis, S., Chaumeix, N., Idir, M., & Paillard, C. E. (2008). Scattering/extinction measurements of soot formation in a shock tube. *Experimental Thermal and Fluid Science*, *32*(7), 1354-1362.

Light extinction (the Beer-Lambert law) $$\frac{I_t}{I_0} = \exp\left(-k_{ext} L\right)$$

The extinction coefficient
(in the Rayleigh region $\pi D_p/\lambda$ <<1): $$k_{ext} = \frac{\pi^3}{\lambda} \mathrm{Im}\left\{\frac{\tilde{n}^2 - 1}{\tilde{n}^2 + 2}\right\} N\left\langle D_p^3 \right\rangle = \frac{6\pi^2}{\lambda} \mathrm{Im}\left\{\frac{\tilde{n}^2 - 1}{\tilde{n}^2 + 2}\right\} f_v$$

The complex refractive index: $$\tilde{n} = m + ki$$
(property of the particle material)

Light Extinction and Scattering



De Iuliis, S., Chaumeix, N., Idir, M., & Paillard, C. E. (2008). Scattering/extinction measurements of soot formation in a shock tube. *Experimental Thermal and Fluid Science*, *32*(7), 1354-1362.

Light scattering in the Rayleigh region:

The scattering coefficient $$Q_{sc} \cong \frac{1}{4}\left(\frac{\pi}{\lambda}\right)^4 \left|\frac{\tilde{n}^2-1}{\tilde{n}^2+2}\right|^2 N\left\langle D_p^6\right\rangle$$

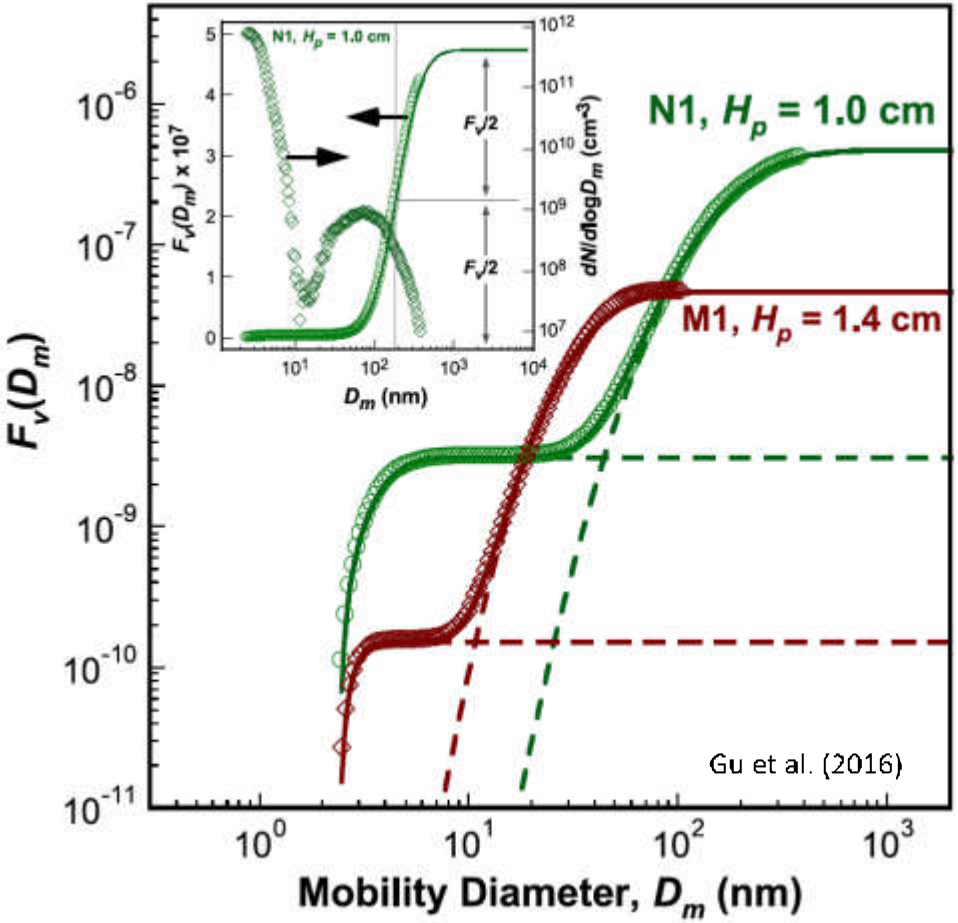
Light Extinction and Scattering

Advantages

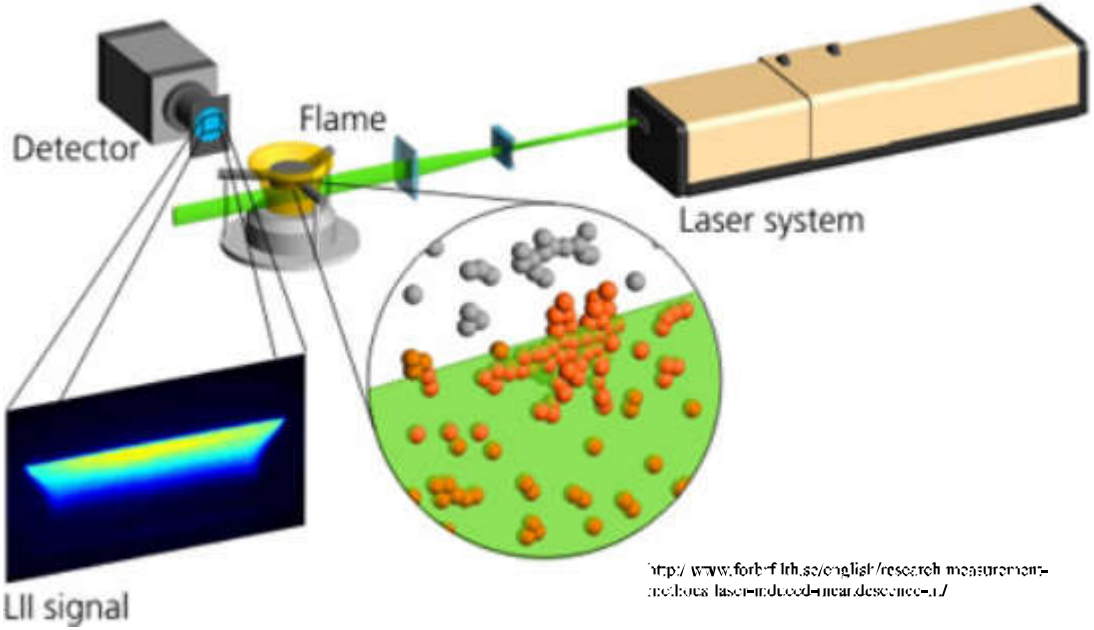
- Simple, easy to set up
- In situ

Disadvantages

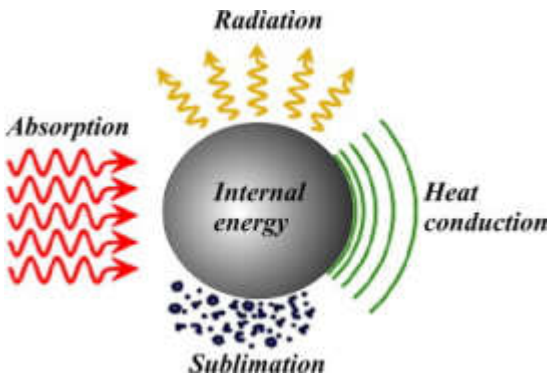
- Line of sight: no spatial resolution)
- Detects big particles only: measures the tail-end of the PSDF.



Laser Induced Incandescence (LII)



http://www.forbrf.lrh.se/english/research measurement-methods laser-induced-incandescence-li/



Hadef et al. Int. J. Thermal Sci. (2010)

Advantages

- In situ
- Spatially resolved

Disadvantages

- Requires calibration / modeling
- Particle damage by laser

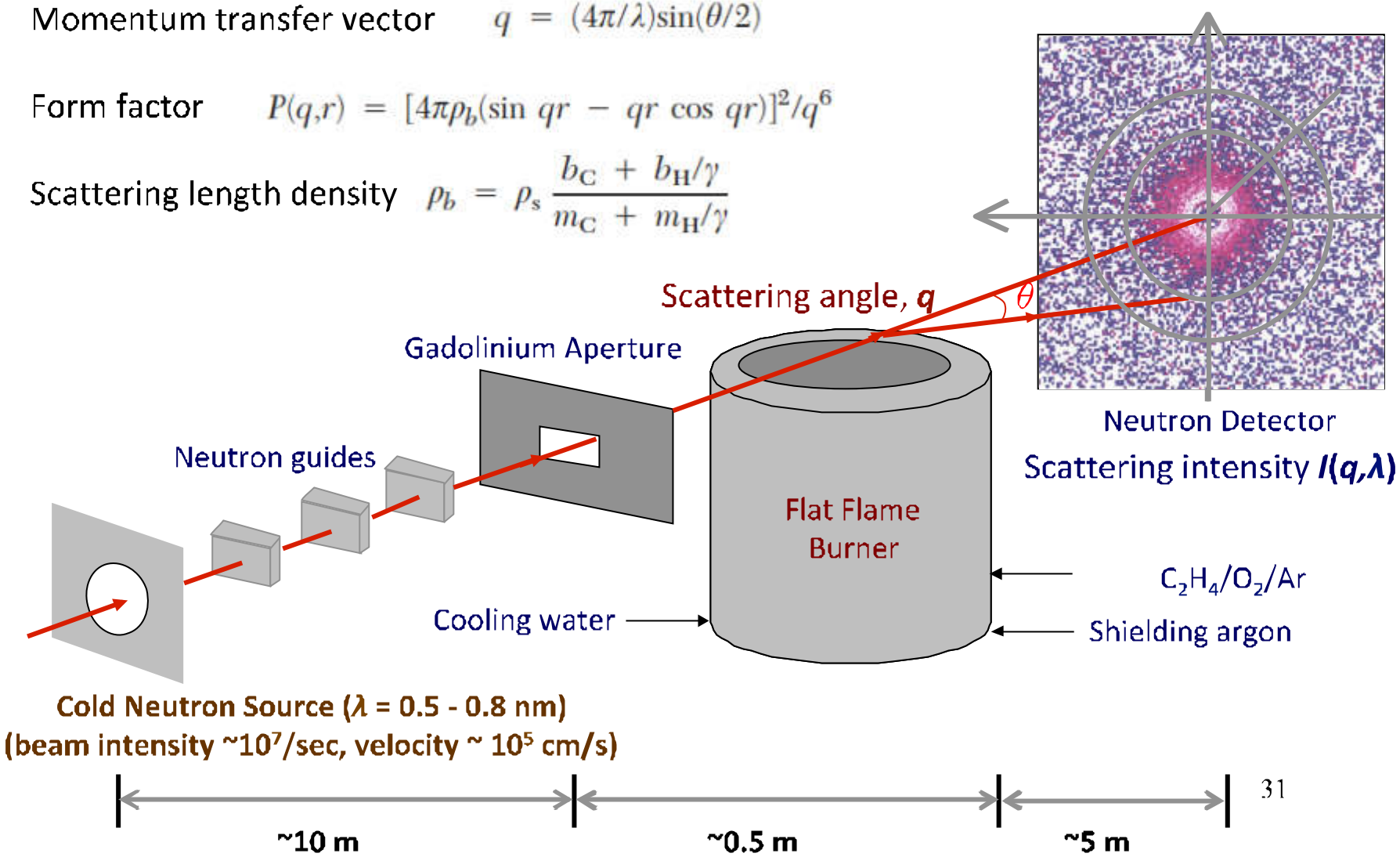
Small-angle Neutron Scattering (SANS)

Scattering intensity $I(q) = \int_r N(r)P(q,r)dr$

Momentum transfer vector $q = (4\pi/\lambda)\sin(\theta/2)$

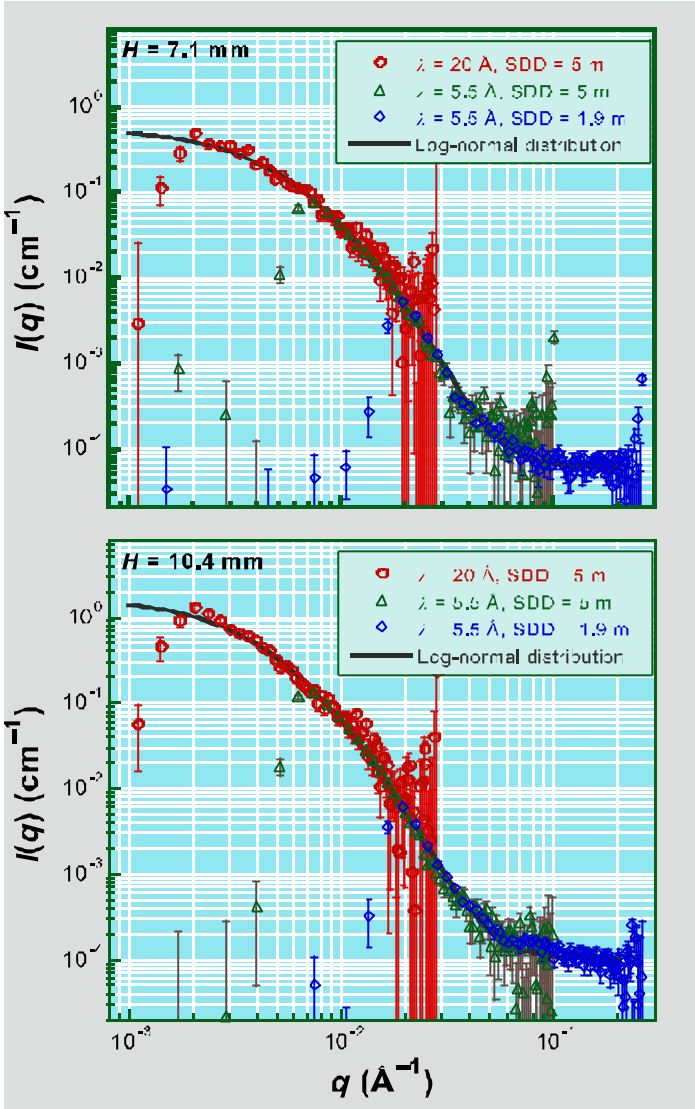
Form factor $P(q,r) = [4\pi\rho_b(\sin qr - qr\cos qr)]^2/q^6$

Scattering length density $\rho_b = \rho_s \dfrac{b_C + b_H/\gamma}{m_C + m_H/\gamma}$

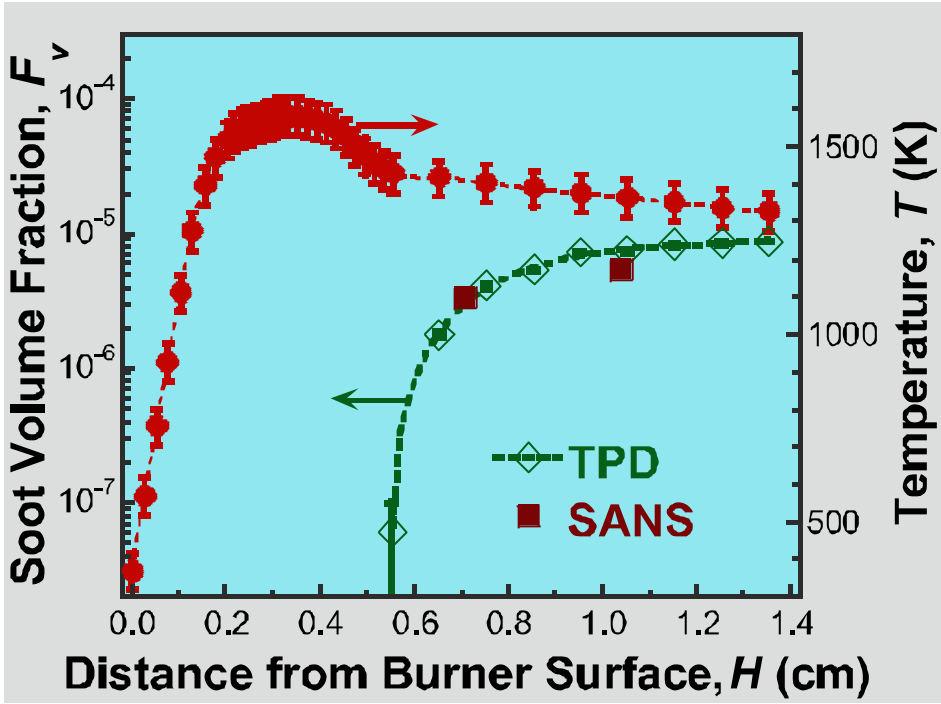


Small-angle Neutron Scattering (SANS)

1 mm spatial resolution



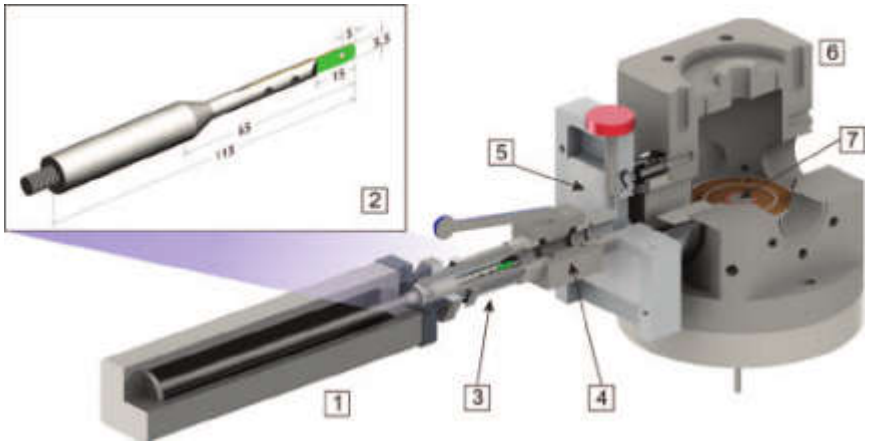
Ultra-Sooty Flame (φ= 4), $f_v \sim 10^{-5}$



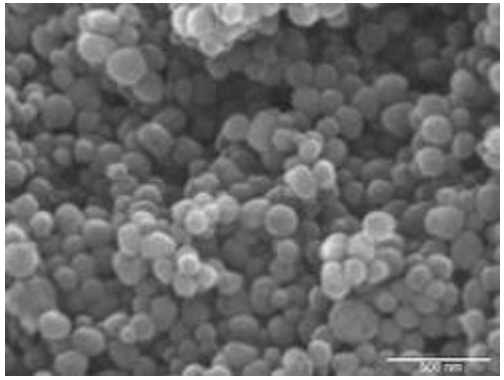
TPD: Thermocouple Particle Densitometry

Thermophoretic Sampling and Imaging Techniques

Leschowski et al. Rev. Sci. Instrum. (2014)

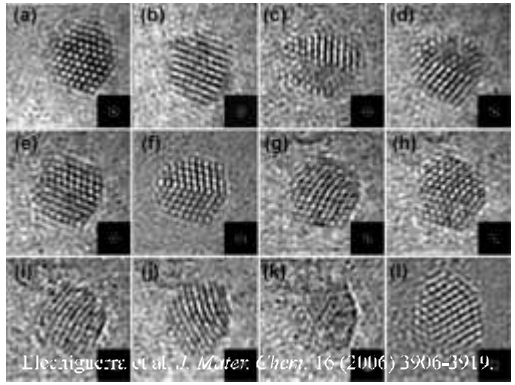


An anteater approach



Scanning electron microscopy

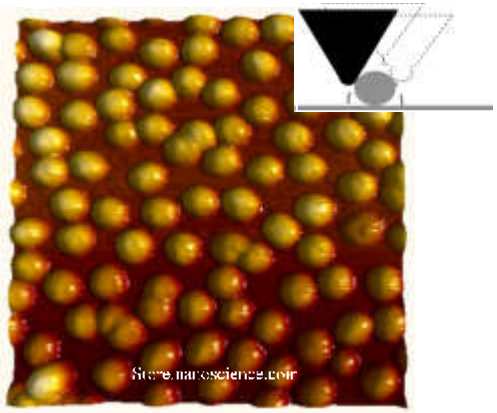
- Scanning a sample with a focused electron beam
- Resolution >~ 1 nm.



Llecaiguerre et al. J. Mater. Chem. 16 (2006) 3906-3919.

Transmission electron microscopy

- a beam of electrons transmitted through an ultra-thin sample, interacting with the specimen.
- Atomic resolution (<1 nm).
- Can damage sample.

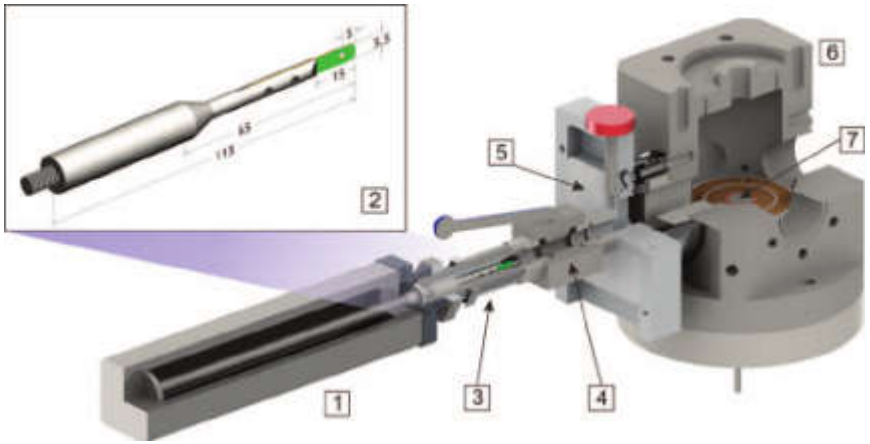


Atomic force microscopy

- scanning a sample using a probe.
- Resolution ~ 1 nm.
- Can be combined with scanning tunneling microscopy
- Strong tip effects

Thermophoretic Sampling and Imaging Techniques

Leschowski et al. Rev. Sci. Instrum. (2014)

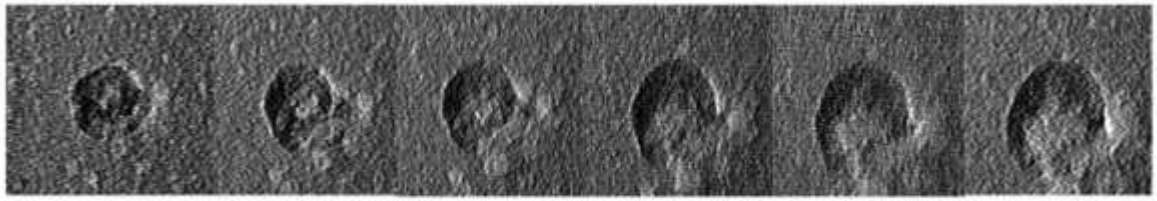


An anteater approach

Advantages

- Can "see" particles
- Resolve distribution

The time history of a young soot particle under TEM electron beam (200 keV)

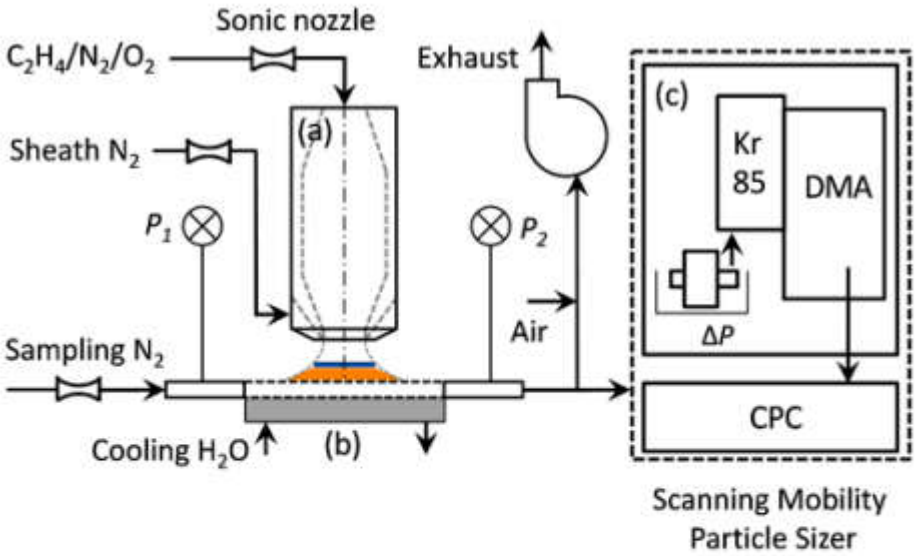


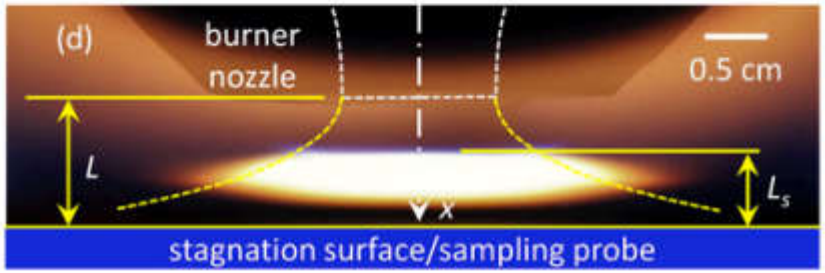
t = 5 min *t* = 10 min *t* = 15 min *t* = 20 min *t* = 25 min *t* = 30 min

Disadvantages

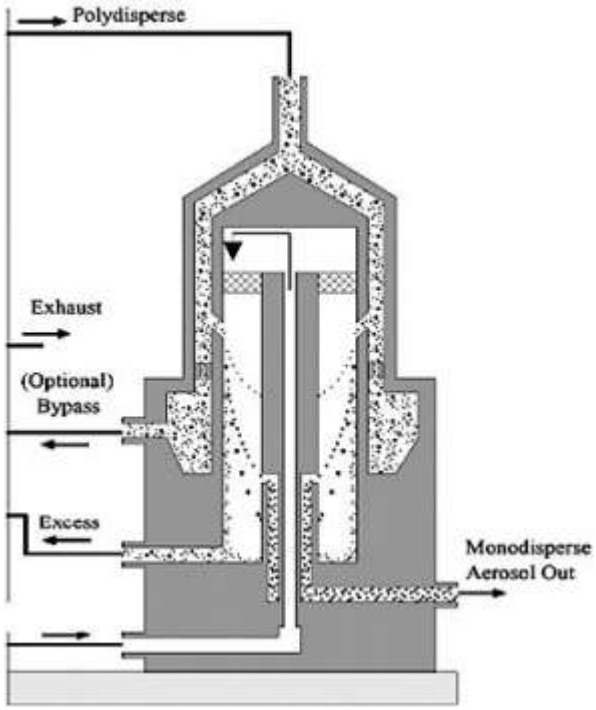
- Ex situ
- Probe disturb the flame
- Particle-substrate interaction can distort the particle
- Beam/probe can damage particles

Scanning Mobility Particle Size (SMPS)



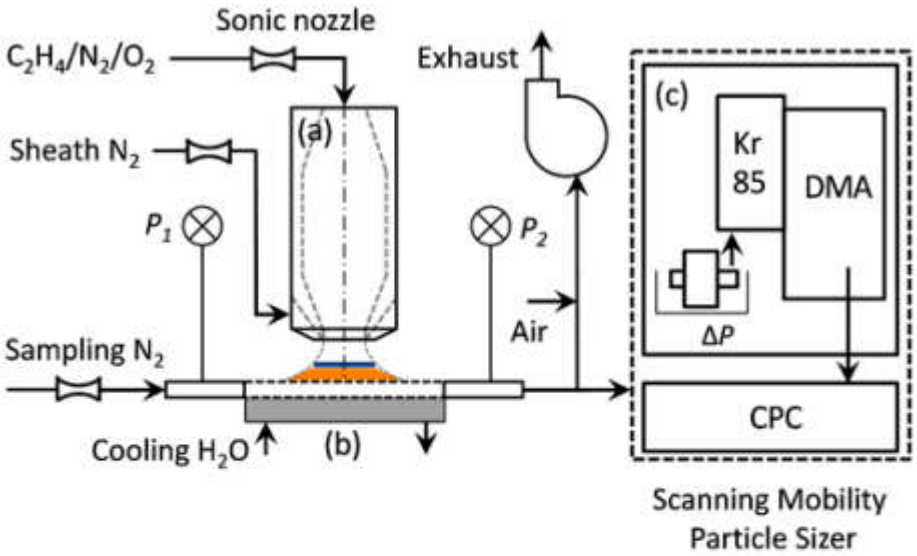


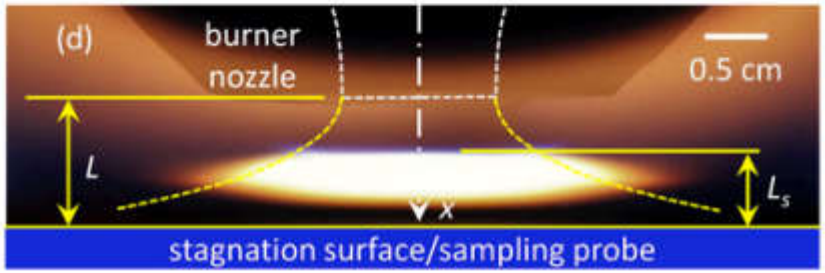
- Dilution probe sampling (dilution ratio > ~1000)
- Aerosol send to SMPS sizing
- SMPS = Differential mobility size (DMA) + Condensation nuclei counter (CNC)

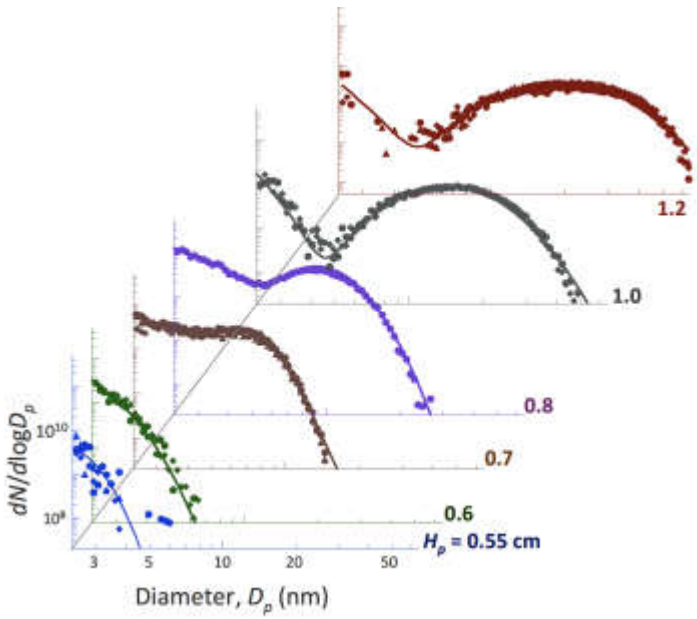


A typical DMA

Scanning Mobility Particle Size (SMPS)







Advantages

- Full size distribution down to about 2 nm

Disadvantages

- Ex situ
- Probe disturb the flame – can be remedied to an extent
- Mobility size versus real size

Outline

1. Why soot interests us?
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6. The processes of soot formation
    1. Overall process
    2. Precursor formation and growth
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    4. Size and mass growth
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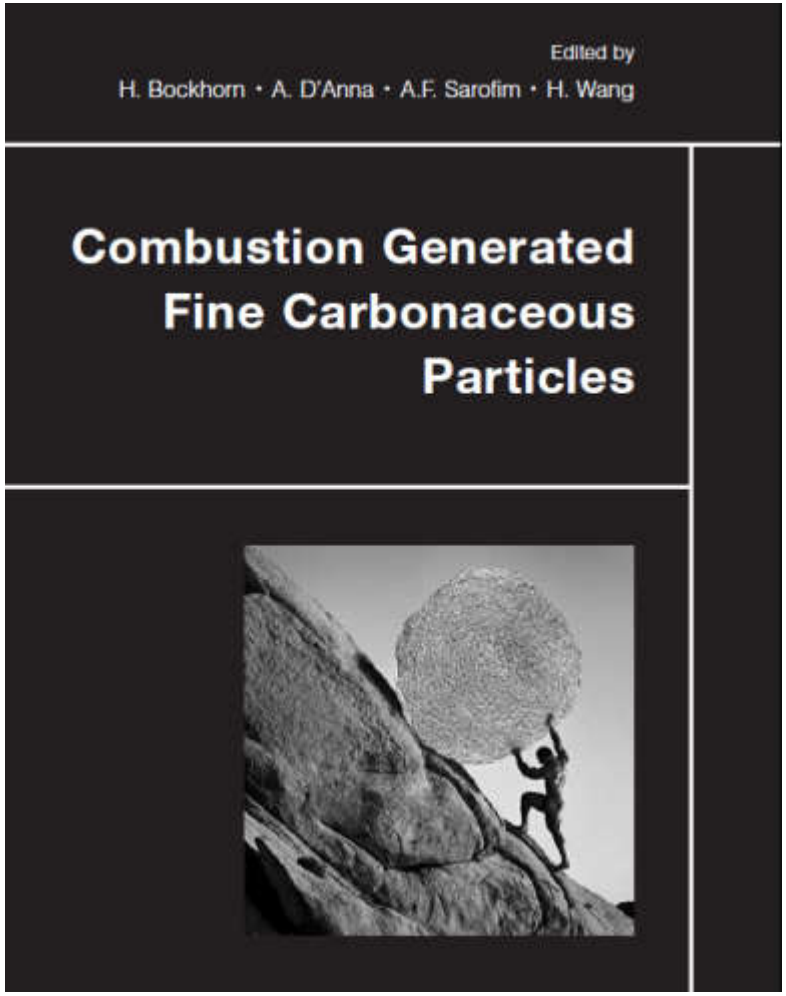
The Science of Soot Formation (and Its Difficulties)

Our View



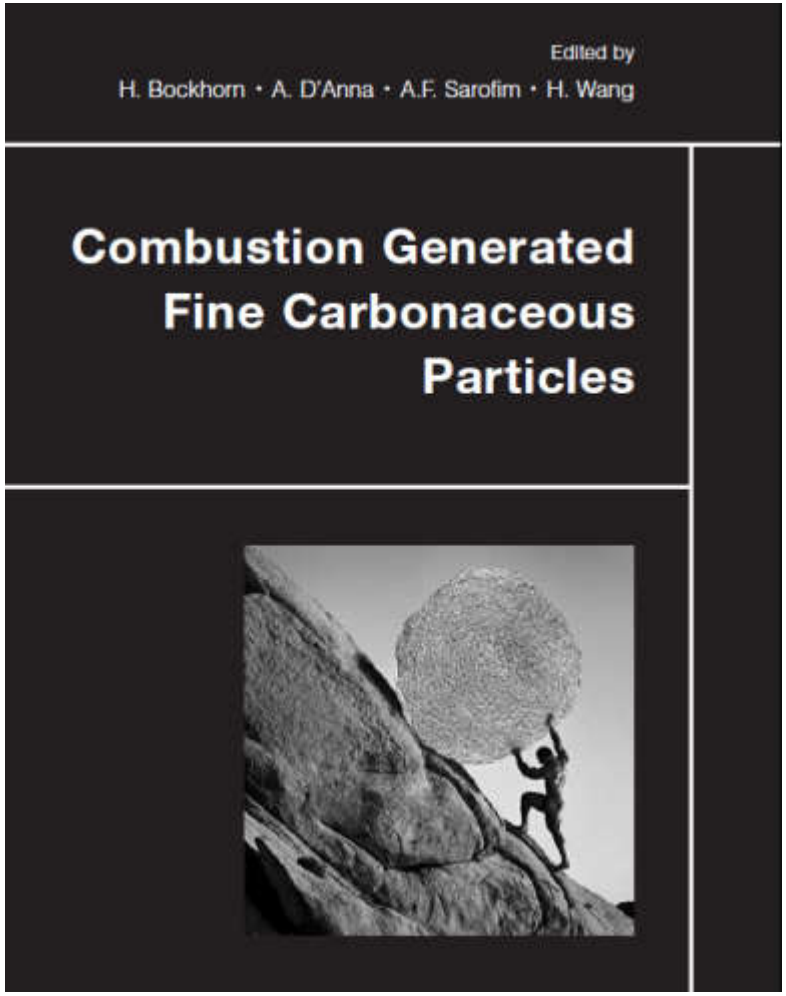
A. Ciajolo and A. Tregrossi
"Sysiphus rolling a soot particle up hill".

Nature's View

http://www.historyforkids.org/learn/science/fire.htm

The Science of Soot Formation (and Its Difficulties)

Our View

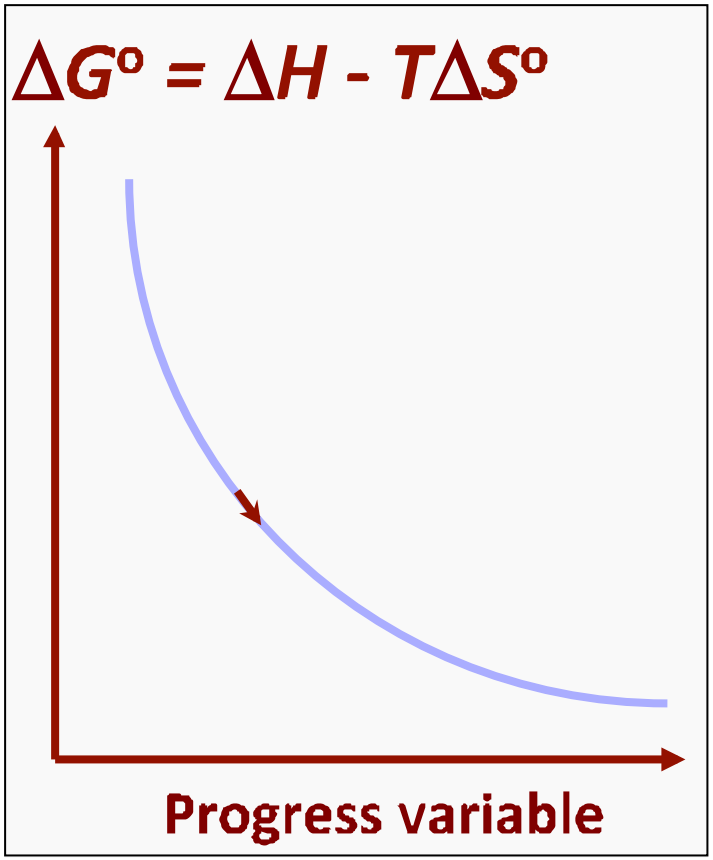


A. Ciajolo and A. Tregrossi
"Sysiphus rolling a soot particle up hill."

Nature's View

"Sysiphus stoping a soot particle falling off a potential energy cliff."

Why Does Condensed-Phase Matter Form in Flames?



Gas-to-Solid Transformation

- **Type 1: enthalpy driven (heat release)**

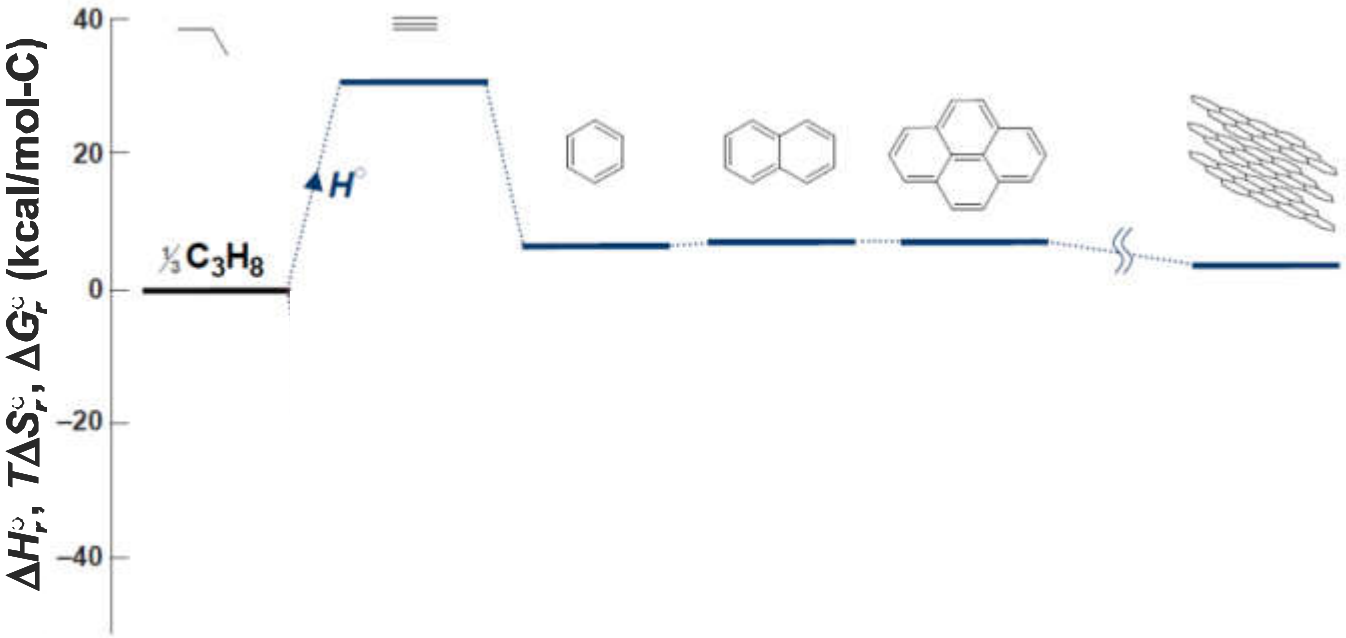
  metal oxides
  carbides, nitrides etc

- **Type 2: entropy driven**

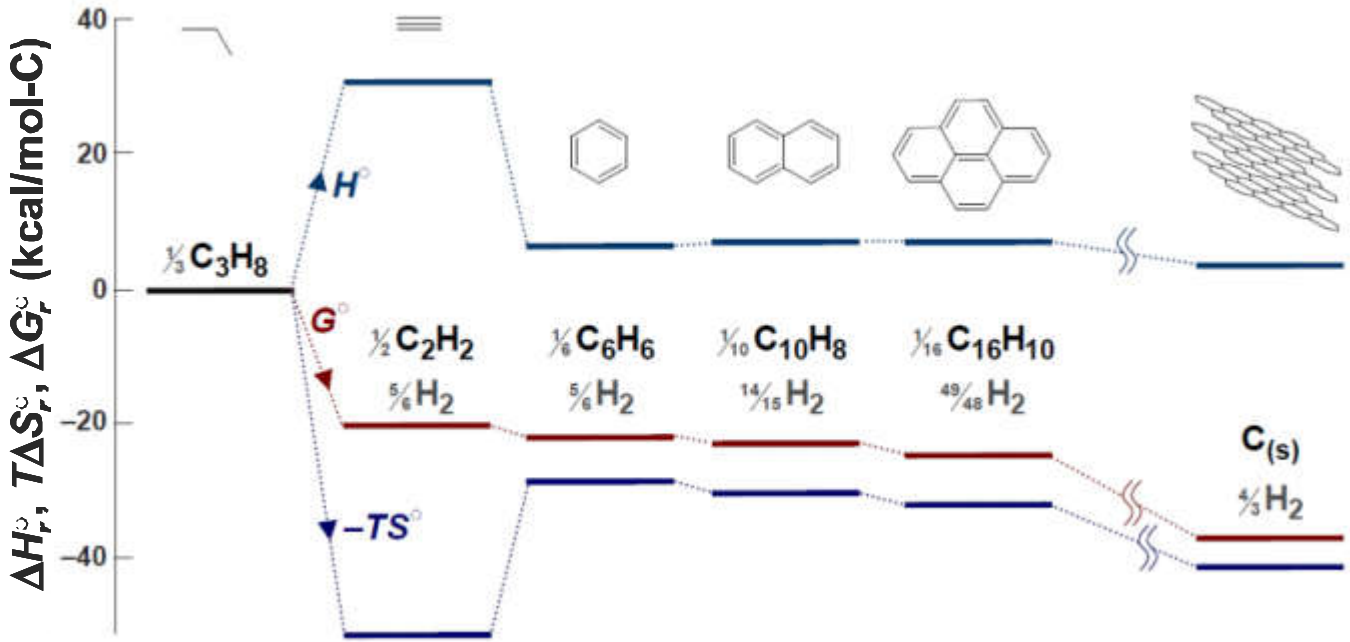
  soot

  $C_3H_8 \rightarrow$ solid carbon + $4H_2$
  ($\Delta H > 0$, but $\Delta S > 0$)

Driving Force – Soot Formation



Driving Force – Soot Formation



- Soot formation is entropy driven (H_2 goes free).
- Soot is an aerosol and its formation is kinetically controlled.

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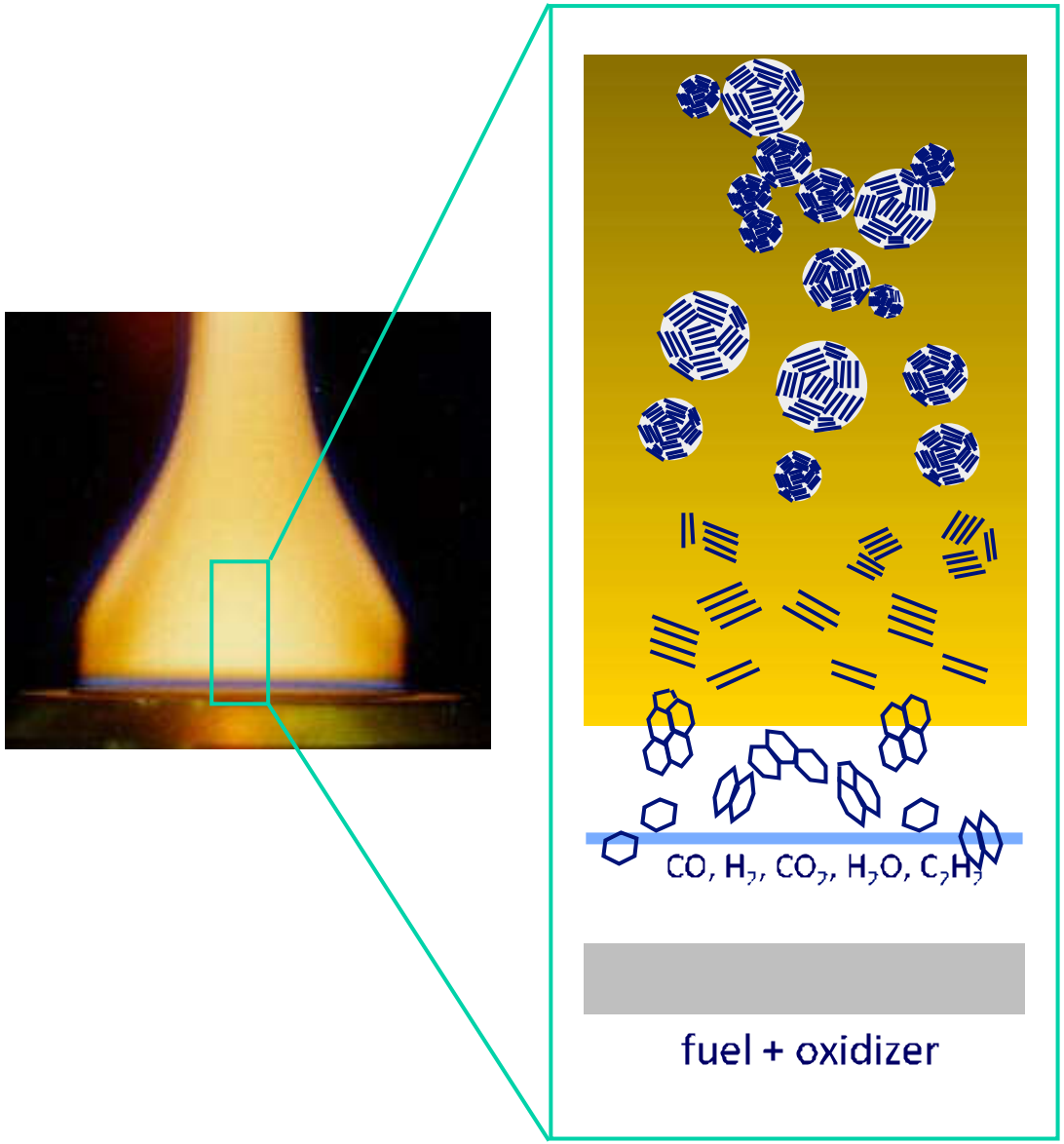
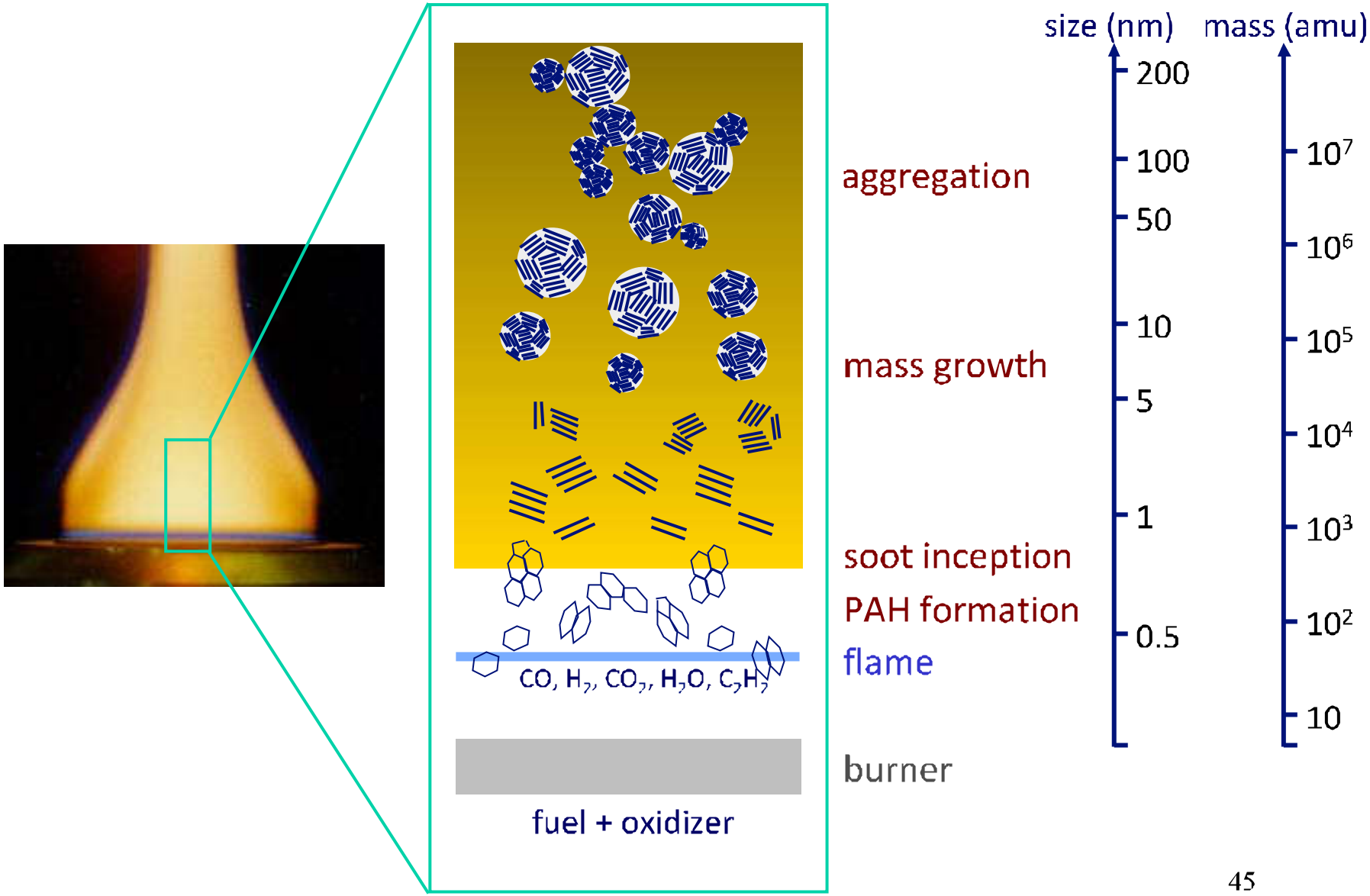
The Process of Soot Formation



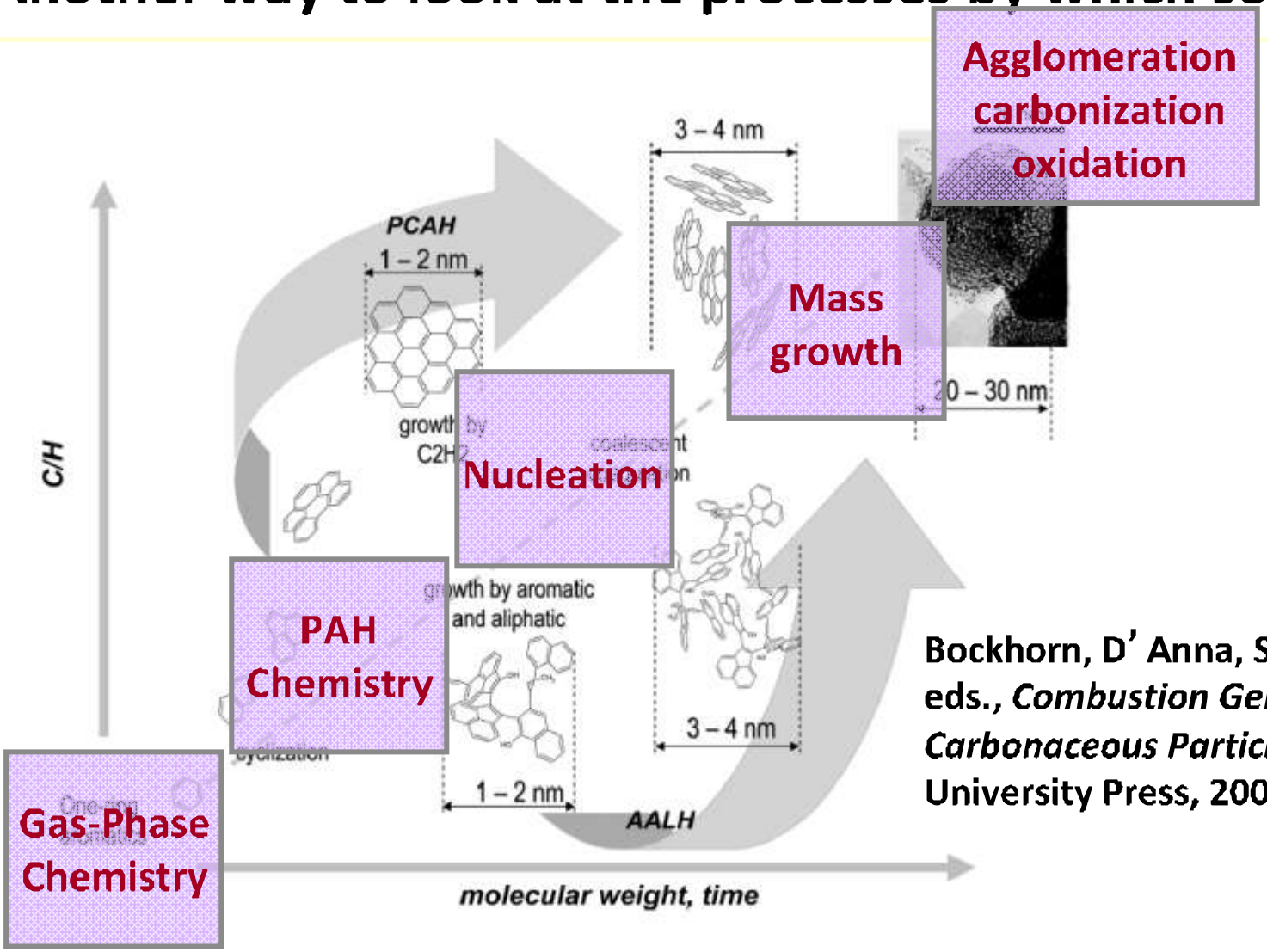
Calcote 1982

The Process of Soot Formation



Calcote 1982

Another way to look at the processes by which soot form.



Bockhorn, D' Anna, Sarofim, Wang, eds., *Combustion Generated Fine Carbonaceous Particles*, Karlsruhe University Press, 2009.

Courtesy of D' Anna

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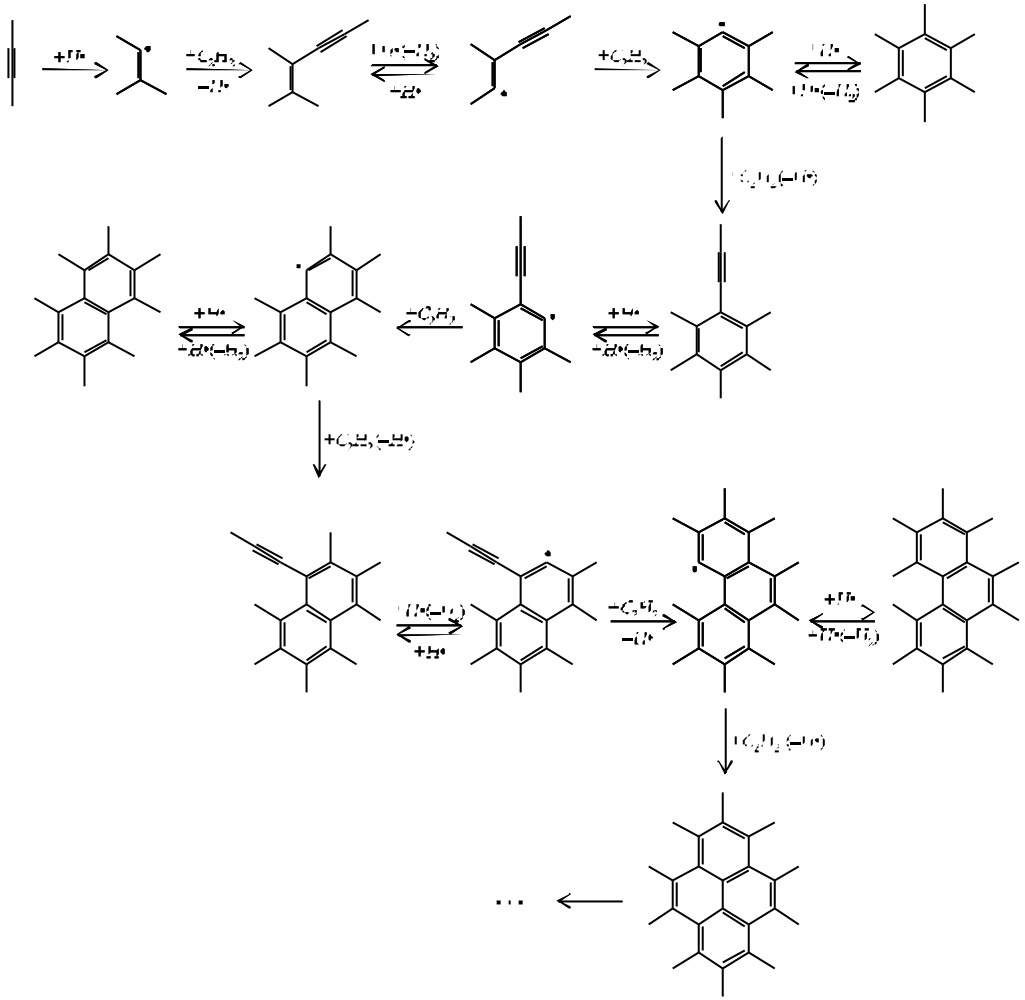
PAH Precursor Chemistry

The Hydrogen-Abstraction—Carbon Addition (HACA) Mechanism (Frenklach & Wang)

- Stein's stabilomers as soot building block
- Capture three important factors of molecular weight growth

	Flame chemistry	PAH formation
H atom	chain branching	activation
C_2H_2	dominant species	building block
High T	heat release	Arrhenius kinetics



PAH Precursor Chemistry

- **Earlier work aimed at developing consistent descriptions of PAH formation:**

thermodynamic

J Phys Chem 97 (1993) 3867.

transport

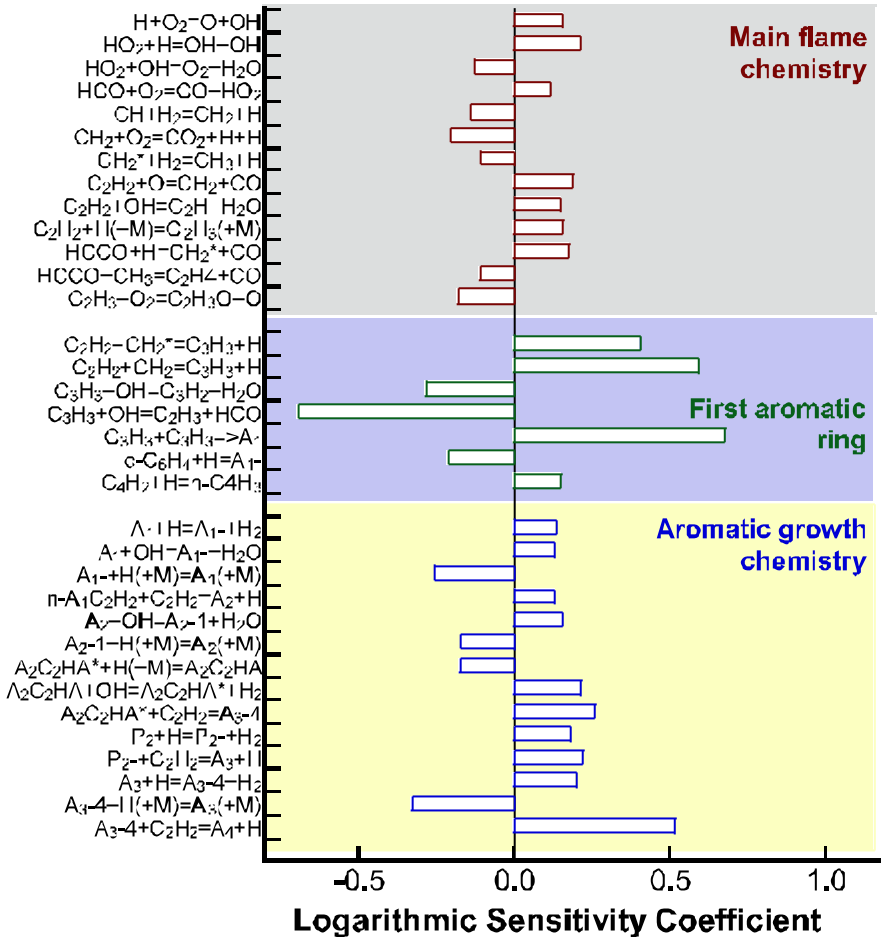
Combust Flame 96 (1994) 163.

chemical kinetic

J Phys Chem 98 (1994) 11465;
Combust Flame 110 (1997) 173;
Proc Combust Inst 23 (1990) 1559.

- **Lessons learned:**
  PAH formation is sensitive to a multitude of elementary reactions and local flame conditions.

Spectral sensitivity of pyrene concentration 90 Torr burner stabilized $C_2H_2/O_2/Ar$ flame (Bockhorn), *H* = 0.55 cm

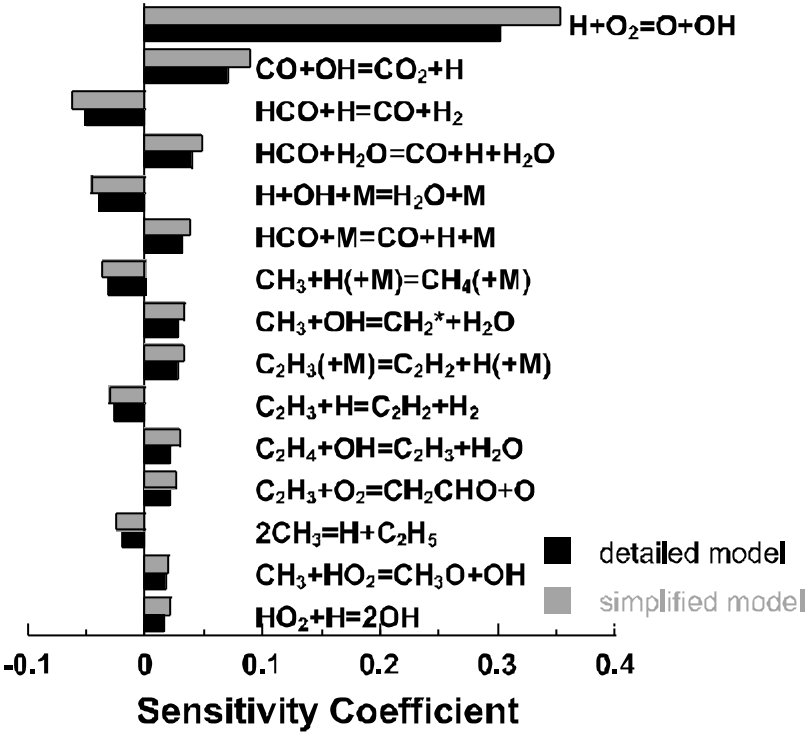


Wang & Frenklach, C&F (1997)

PAH Precursor Chemistry

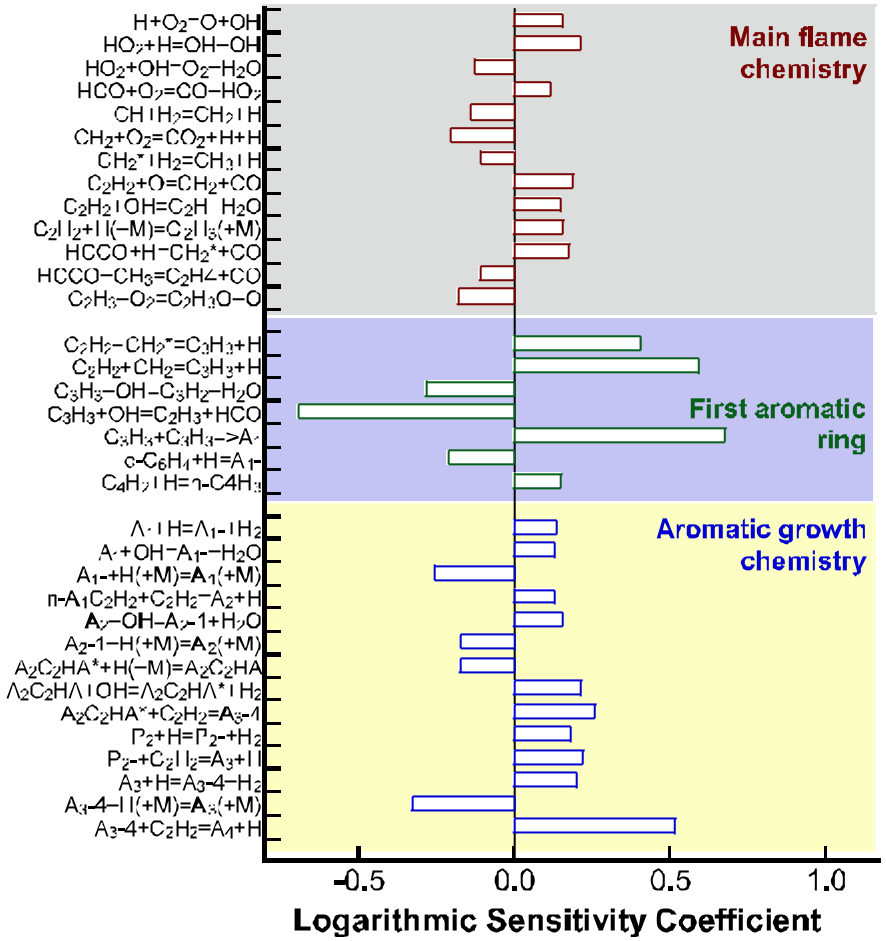
n-dodecane-air flame speed

$\phi = 1$, $T_0 = 403$ K



You et al. Proc. Combust. Inst. (2009)

Spectral sensitivity of pyrene concentration 90 Torr burner stabilized $C_2H_2/O_2/Ar$ flame (Bockhorn), $H = 0.55$ cm



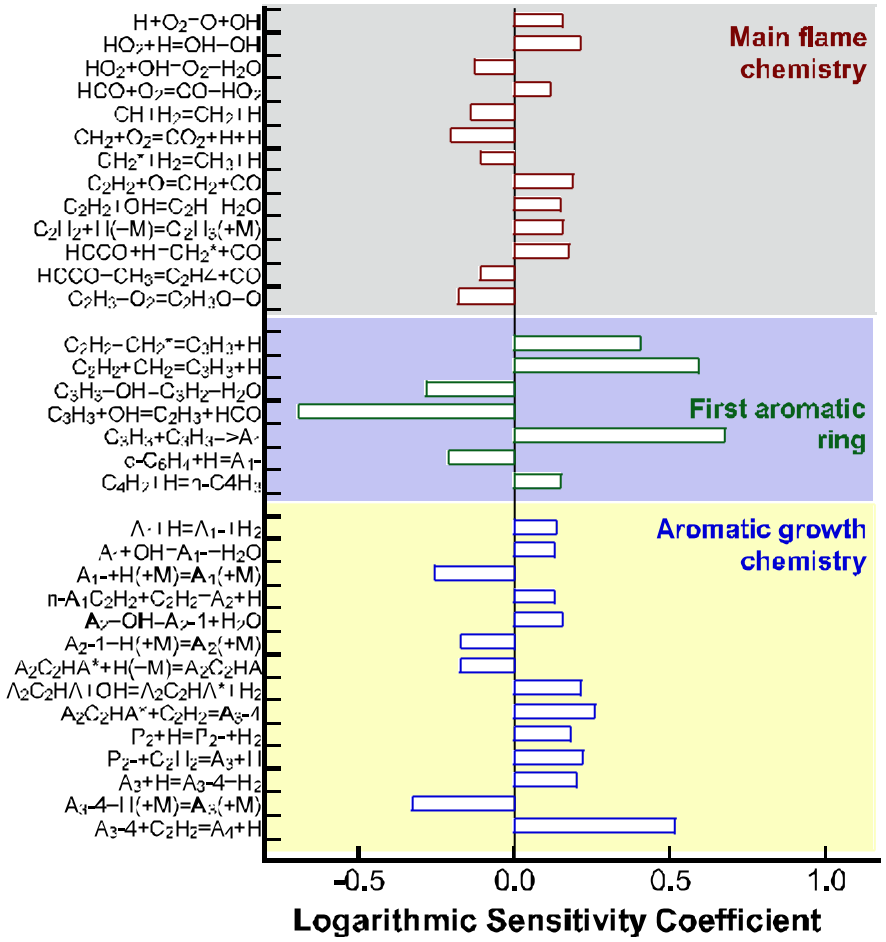
Wang & Frenklach, C&F (1997)

PAH Precursor Chemistry

Lessons learned:

- PAH formation is sensitive to a multitude of elementary reactions.
- Accurate prediction of PAH formation may require a precision in main flame chemistry currently unavailable.
- PAH formation can be highly sensitive to fuel structures.
- Possibly a large number of pathways to PAHs have yet been considered.

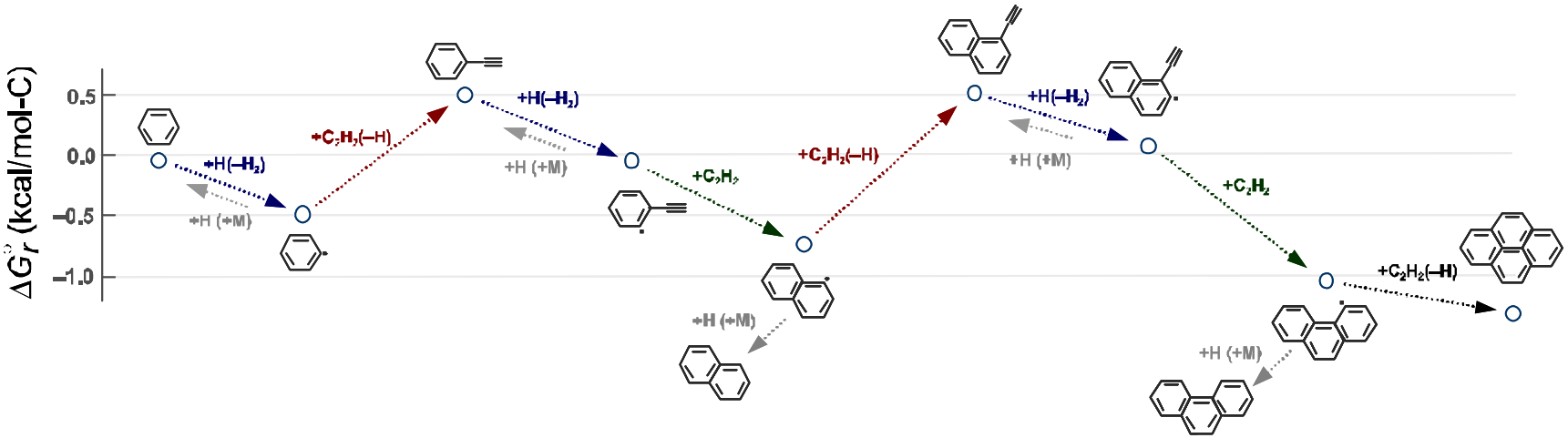
Spectral sensitivity of pyrene concentration 90 Torr burner stabilized $C_2H_2/O_2/Ar$ flame (Bockhorn), H = 0.55 cm



Wang & Frenklach, C&F (1997)

PAH Precursor Chemistry

Thermodynamic Origin of PAH Formation/Growth Beyond HACA



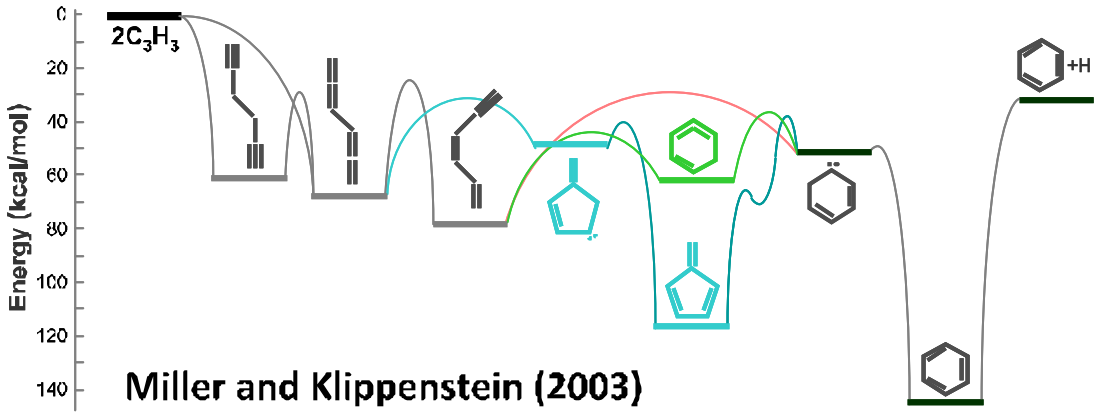
C_2H_2	5	5	4	4	3	2	2	1	0
H	1	0	1	0	0	1	0	0	1
H_2	0	1	1	2	2	2	3	3	3

- **While HACA captures the thermokinetic requirements for PAH formation, its reversibility opens it to competitions from other pathways – the many pathway problem – especially for real, multicomponent fuels.**

PAH Precursor Chemistry (5)

Known Pathways beyond HACA

- Propargyl combination (Fahr & Stein 1990)



Rate coefficient calculation require high-quality PES (e.g., CASPT2), RRKM/ Master equation modeling, flexible, variational transition state theory

- Sequential dehydrogenation from cycloparaffins (Westmoreland 2007)
- Phenyl addition/cyclolization pathway (Koshi 2010)
- Fulvenallene + acetylene (Bozzelli 2009)
- Cyclopentadienyl + acetylene (Carvallotti et al. 2007)
- Cyclopentadienyl + cyclopentadienyl (Colket 1994; Mebel 2009)

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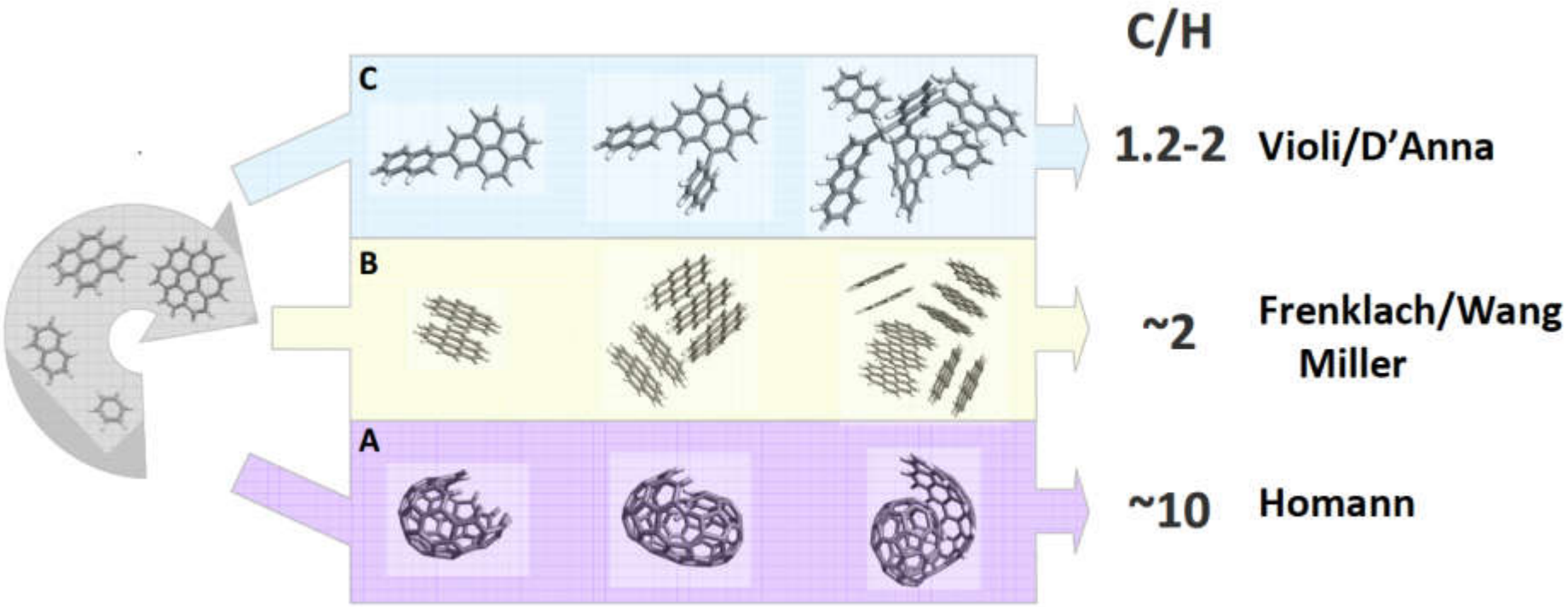
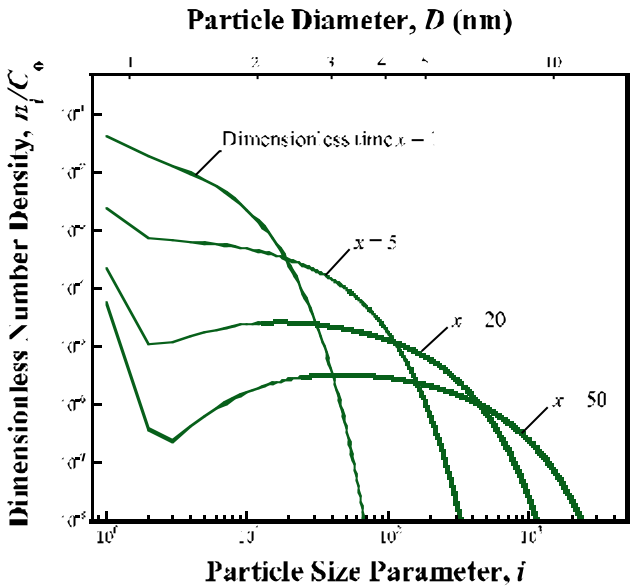
Soot Nucleation

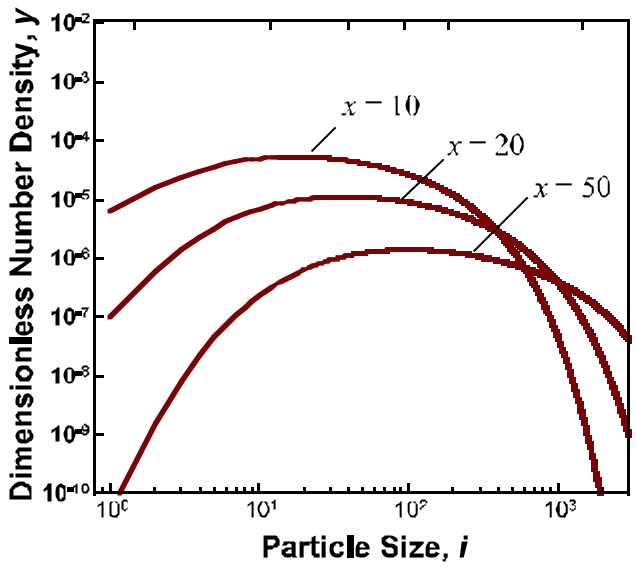


Soot Nucleation

- **Second-order nucleation kinetics – dimerization of soot precursors – leads to Persistent *bimodality*.**



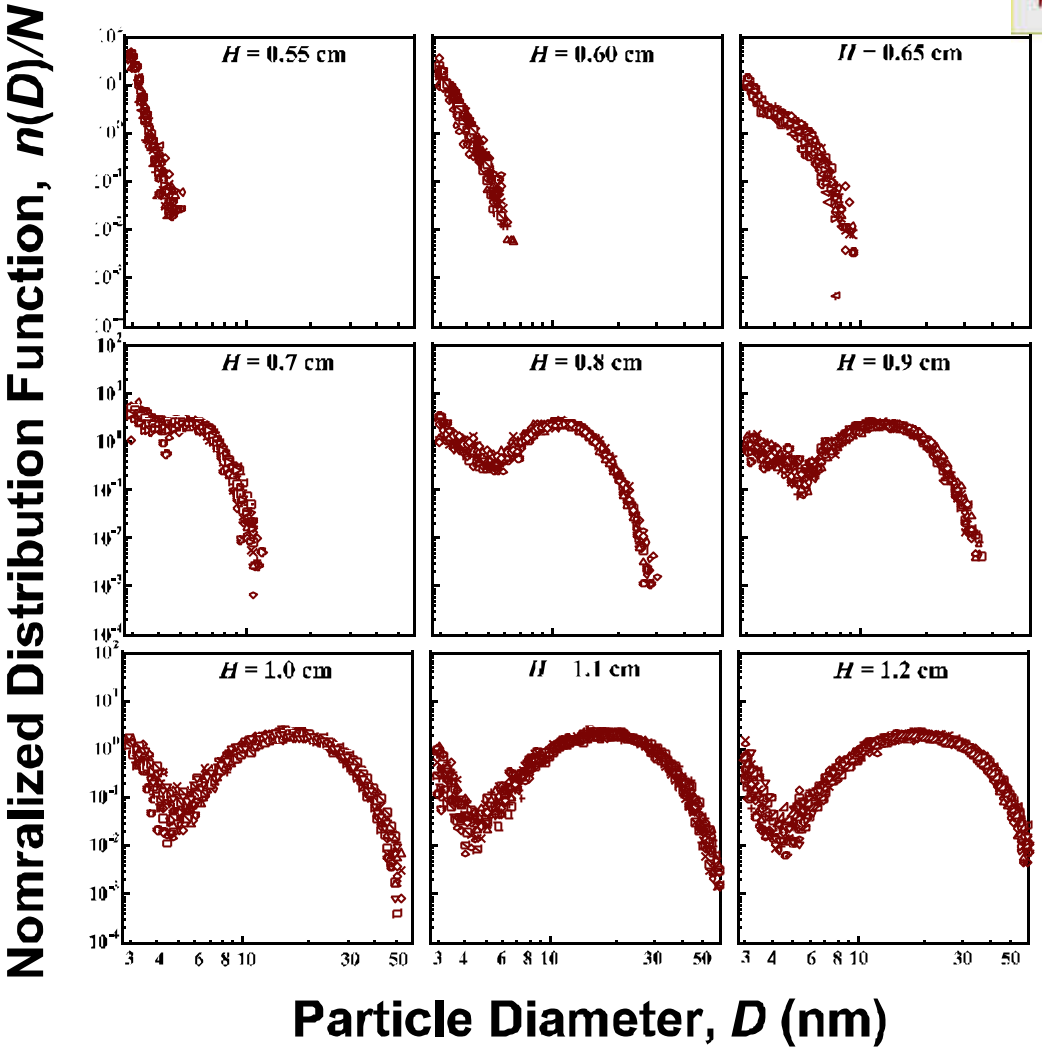
- **First-order nucleation kinetics gives PSDFs that are persistently unimodal.**

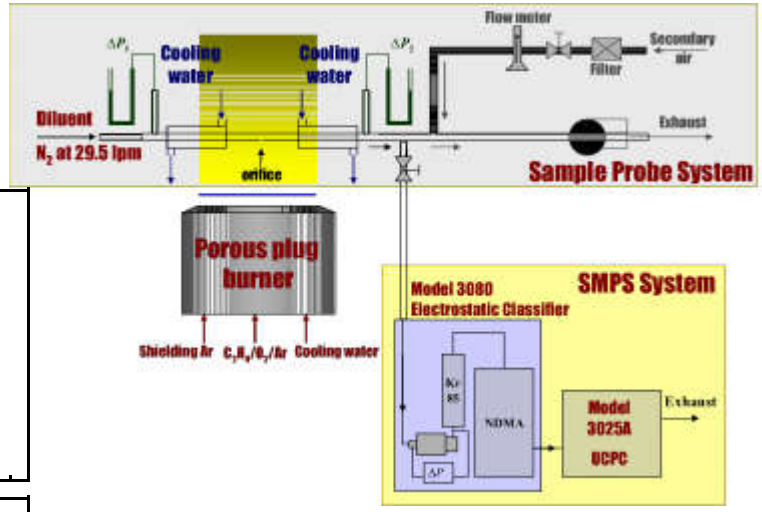


Zhao et al. (2003)

Soot Nucleation

Measured PSDFs are indeed bimodal

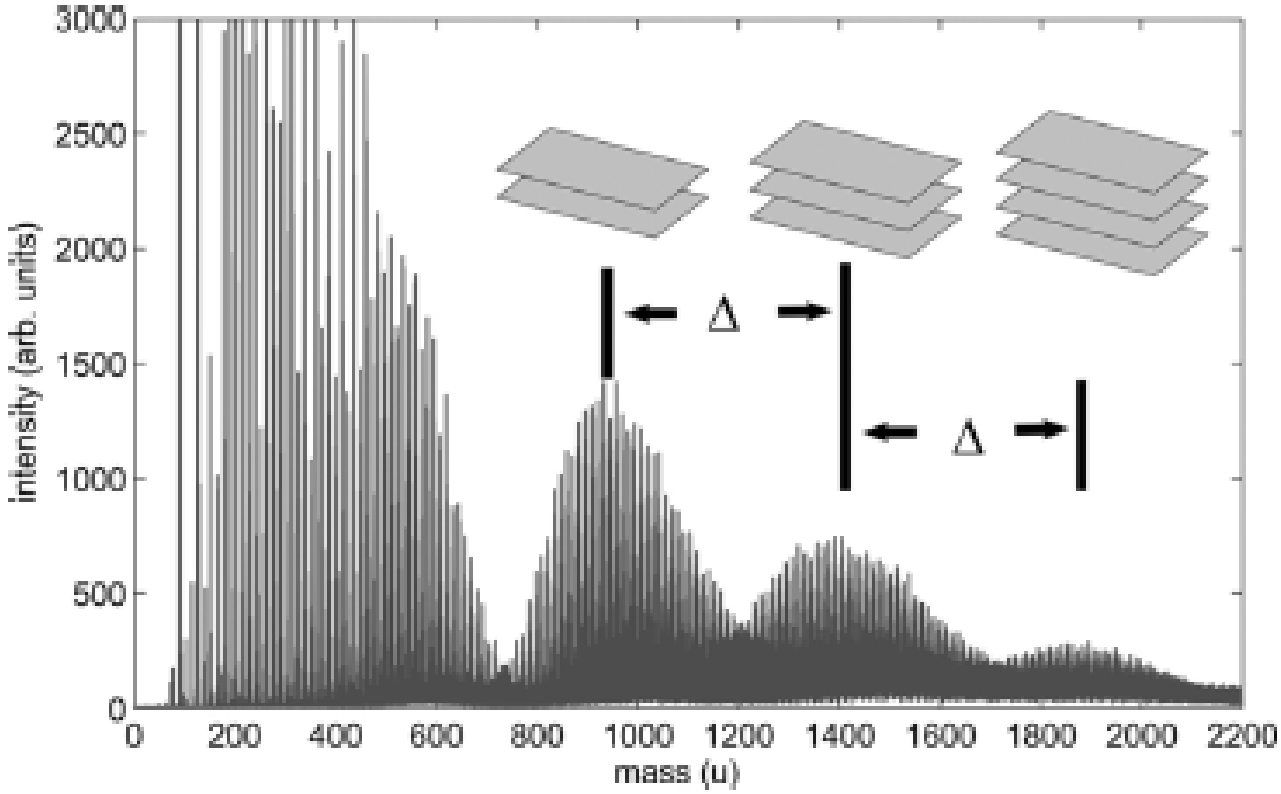




Zhao et al. 2003

Soot Nucleation

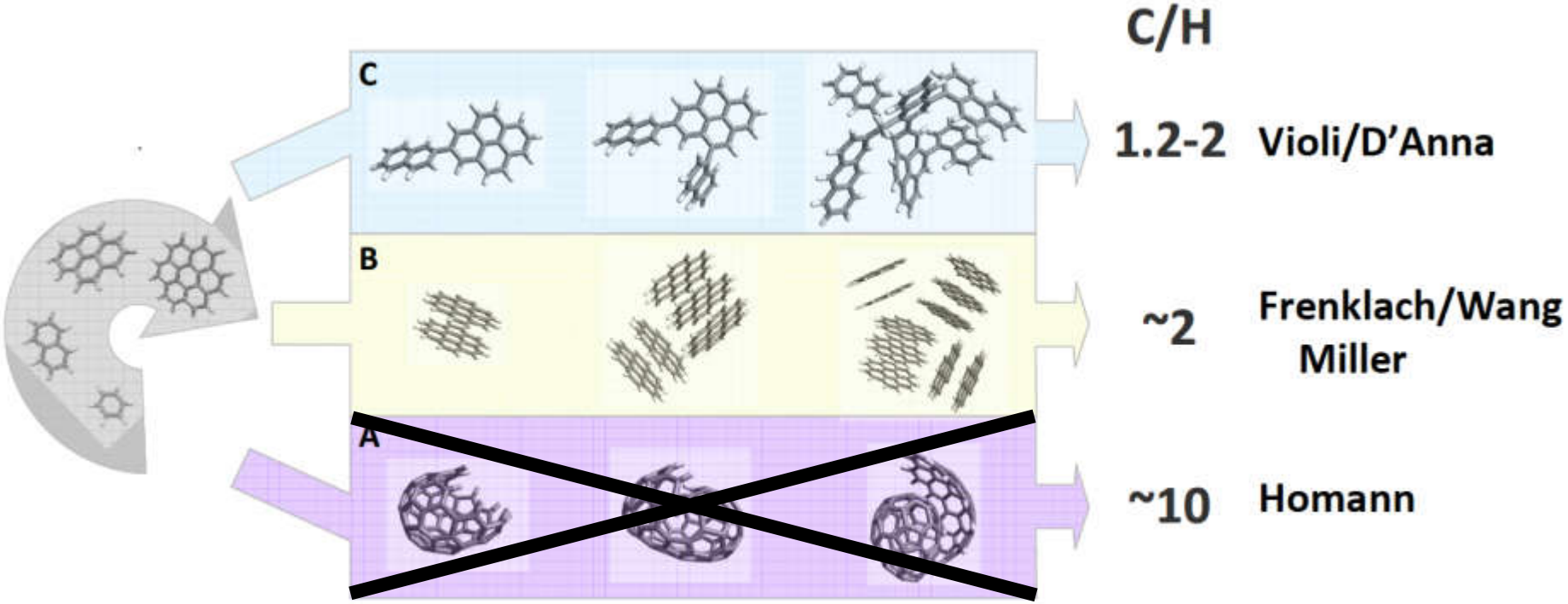
Mass spectrum of fragments from photoionization of "infant" soot show periodicity



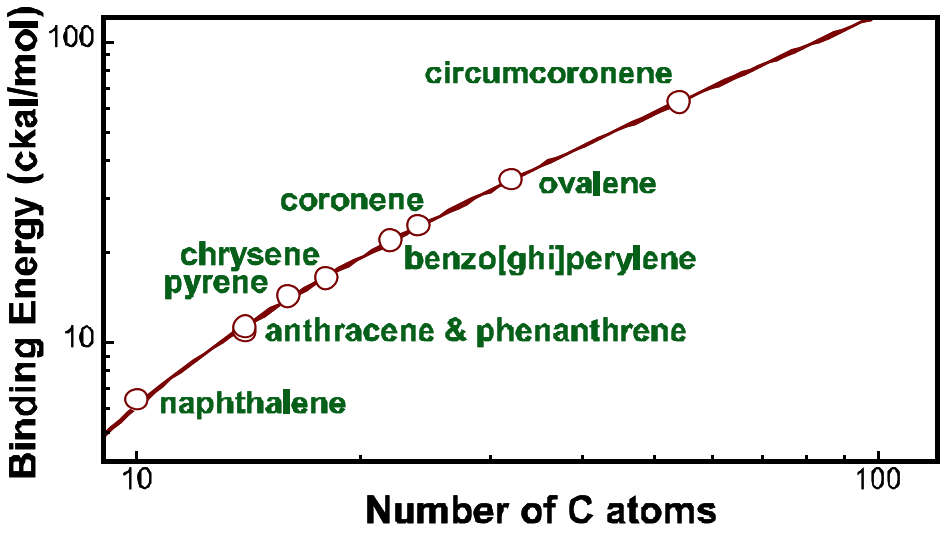
100-Torr acetylene-oxygen flame (ϕ = 3.25)

Courtesy of Grotheer

Soot Nucleation (1)

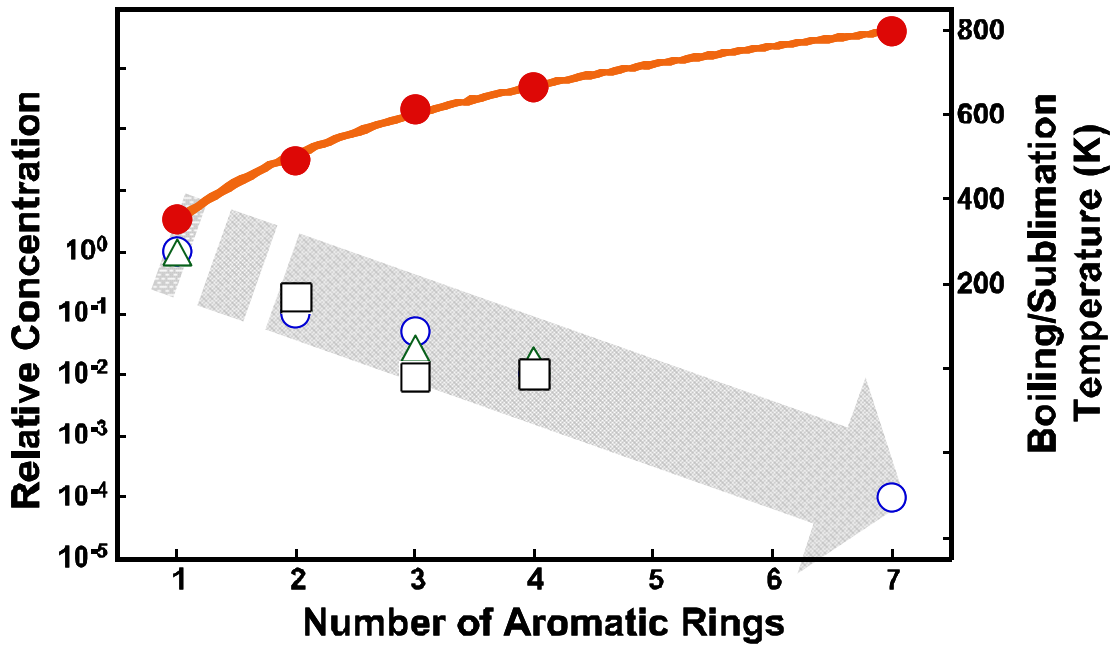


Soot Nucleation (6)



Herdman and Miller (2008)

Binding energy of coronene = 25 kcal/mol



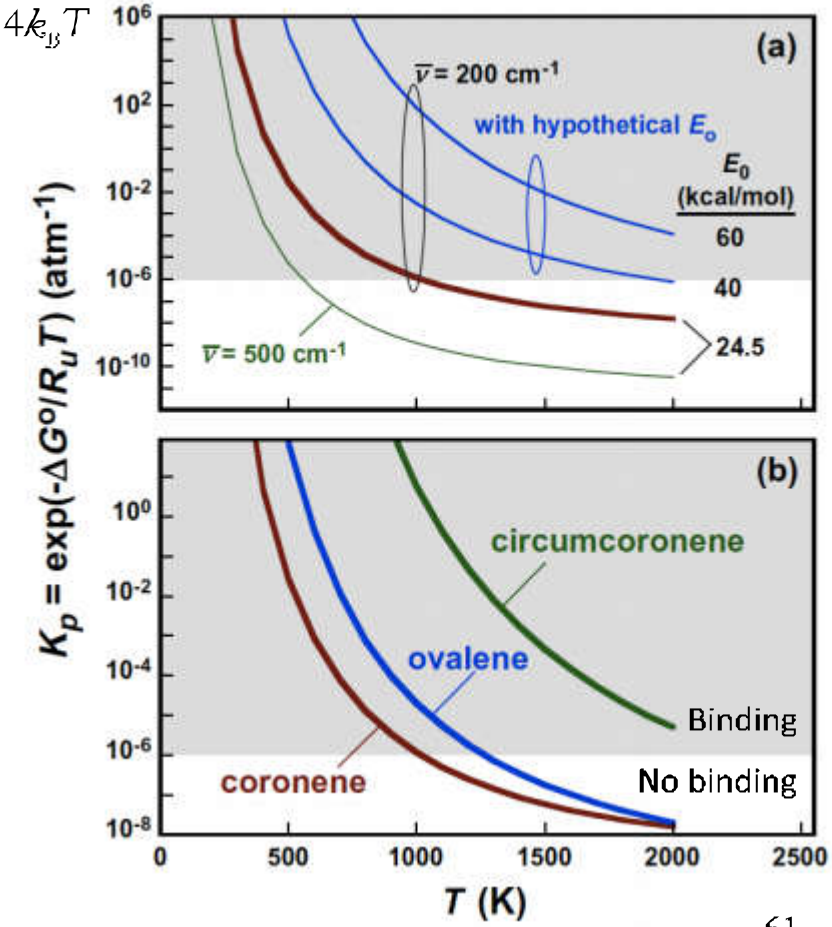
Soot Nucleation

Is 25.4 kcal/mol enough to bind a pair of coronene together?

2 coronene → (coronene)$_2$

$$\Delta H^0 \cong -E_0 + \sum_{i=1}^{6}\left\{1+\frac{1}{\exp\left[h\nu_i/(k_B T)\right]-1}\right\}h\nu_i - 4k_B T$$

$$\frac{\Delta S^0}{R_u} \cong \ln\left[\left(\frac{2\bar{B}}{m}\right)^{3/2}\frac{h^3 p^0}{\pi^2 (e k_B T)^4}\frac{\sigma_1^2}{\sigma_2}\right] + \sum_{i=1}^{6}\left[\frac{h\nu_i/k_B T}{e^{h\nu_i/k_B T}-1} - \ln\left(1-e^{-h\nu_i/k_B T}\right)\right]$$



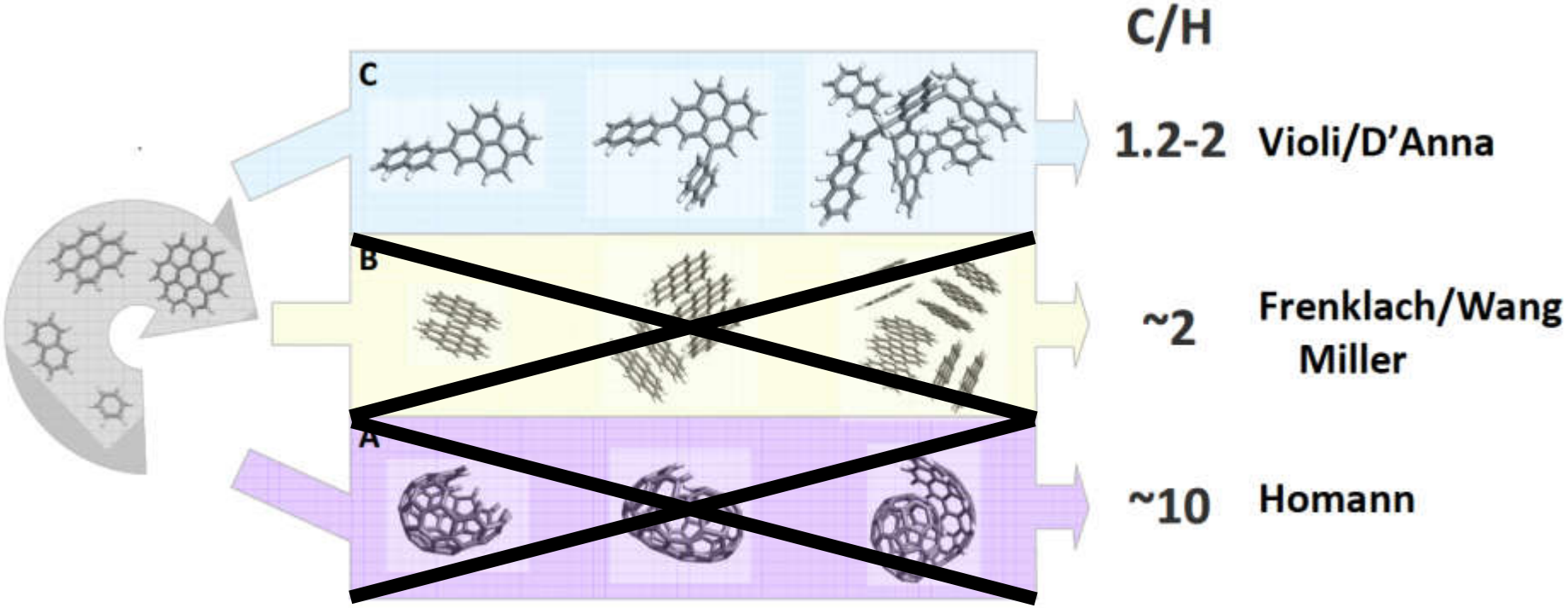
Assumptions:

- ν_i = 200 cm^{-1}
- B (cm^{-1}) = 1510 x $MW^{-2.12}$
- σ_2 = 1

Ovalene E_0 = 35 kcal/mol

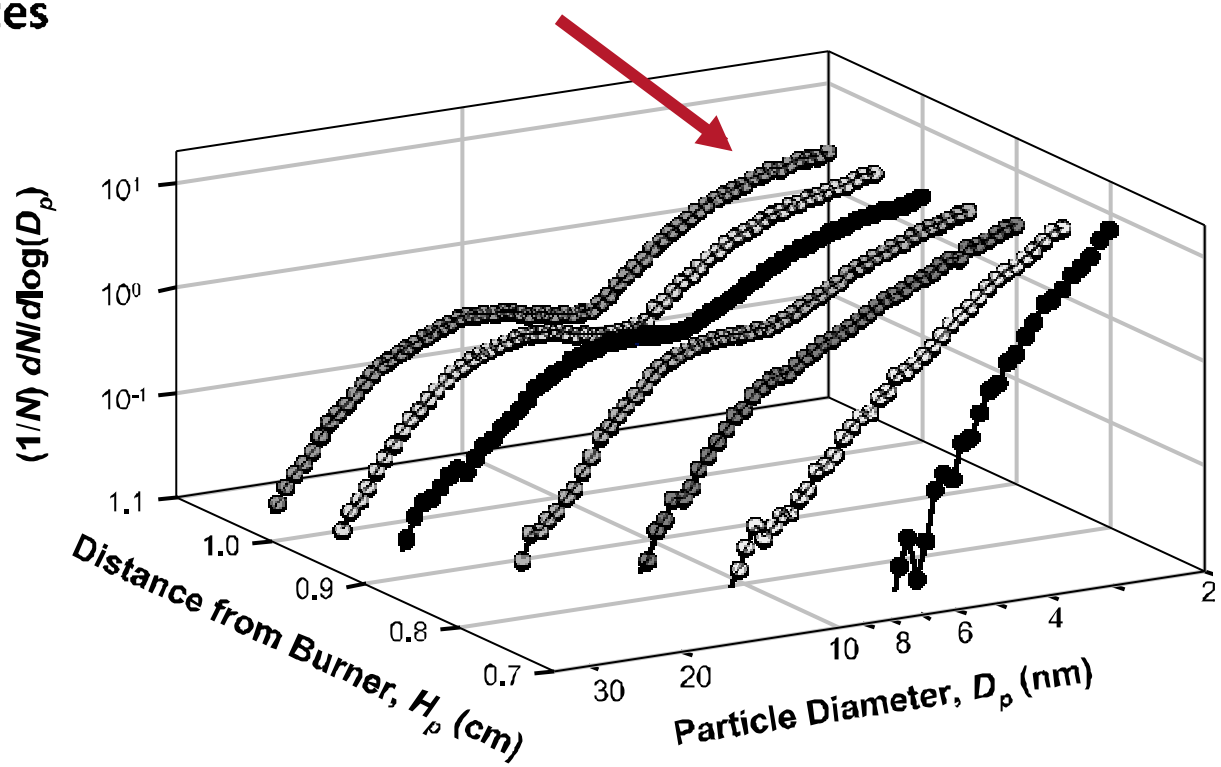
Circumcoronene E_0 = 63 kcal/mol

Soot Nucleation (1)



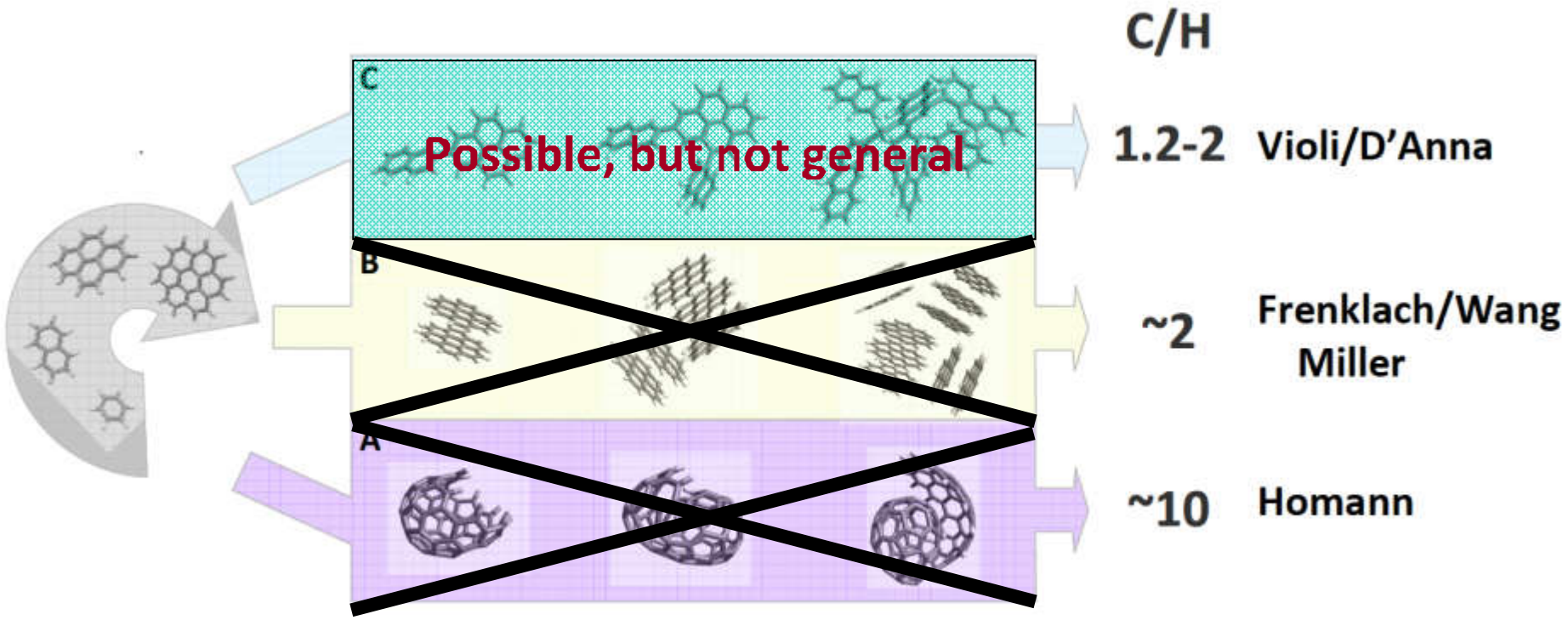
Soot Nucleation

- $T < 1500$ K, $x_H < 10^{-5}$
- Temperature is too low to explain persistent nucleation if mechanism C dominates



Abid et al. (2009)

Soot Nucleation



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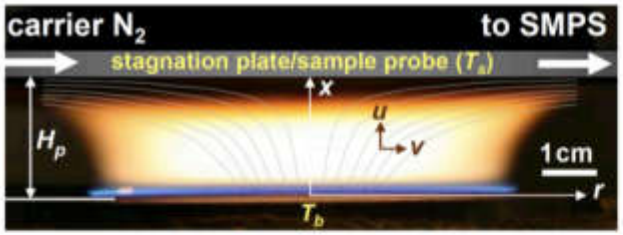
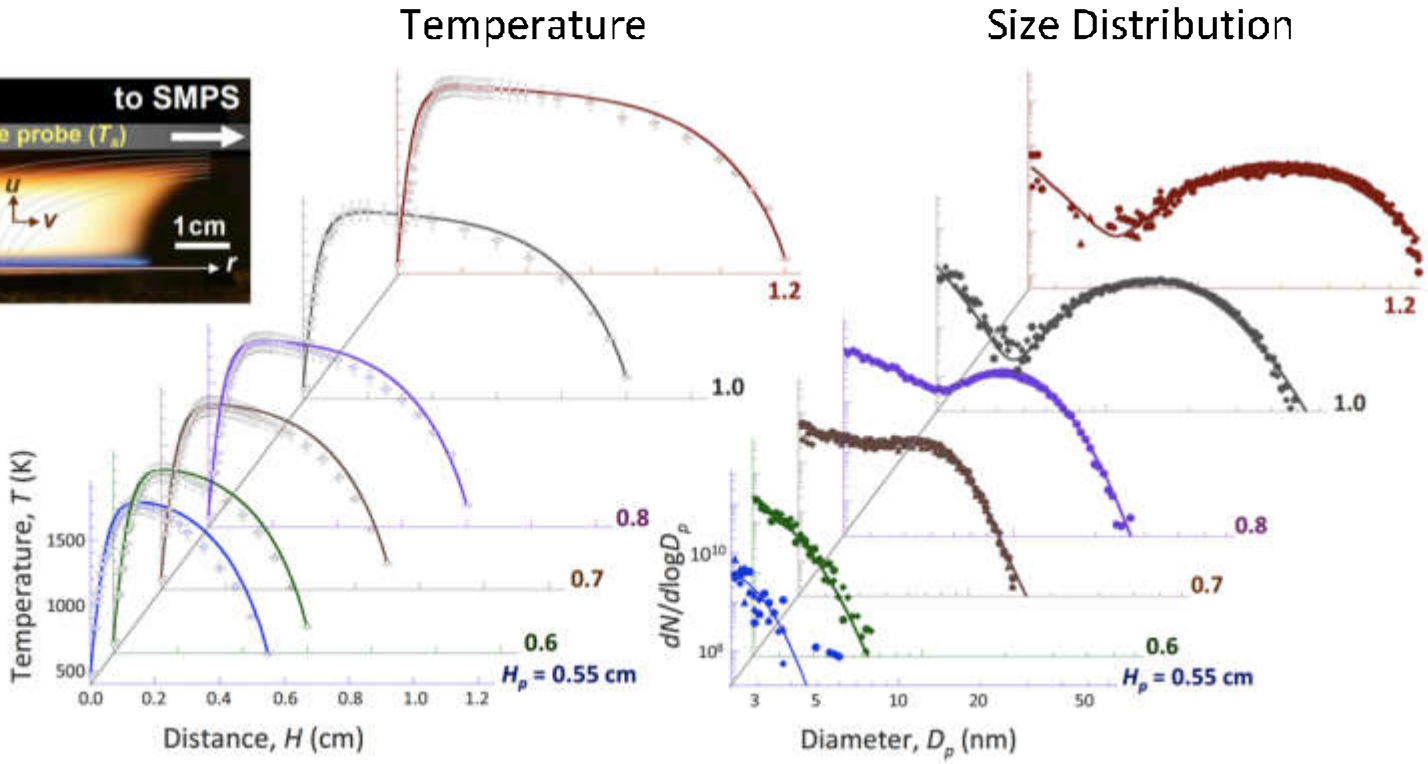
Recent Highlights (4)

Burner-stabilized stagnation flame approach and mobility sizing

$C_2H_4/O_2/Ar$ flame (ϕ = 2.1)



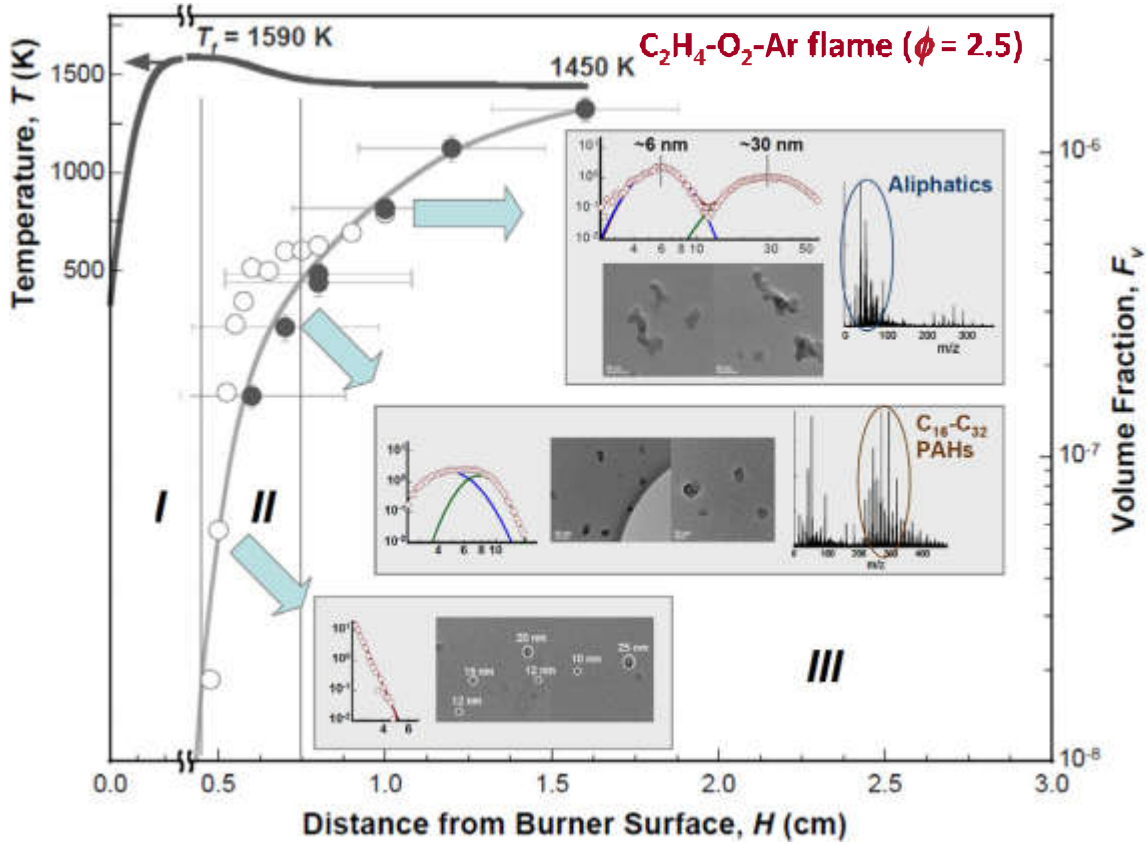


Abid et al. (2009)

"Infant" Soot – Growth, Composition and Morphology

"Infant" soot is entirely unlike mature soot.

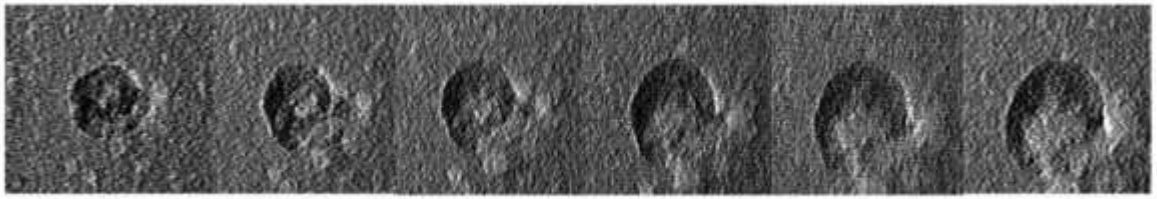
- They grow very rapidly – the growth rate determines the final amount of soot in a flame.
- Comparison of mobility and TEM measurements shows nascent soot is liquid-like rather than carbonized or rigid.
- Small angle neutron scattering and thermocouple densitometry suggest that nascent soot has C/H ~ 1 and $\rho < 1.5$ g/cc.
- Photoionization aerosol mass spectrometry indicates that nascent soot is rich in aliphatics (in addition aromatics).



Wang et al. 2003; Oktem et al. 2005, Zhao et al. 2007

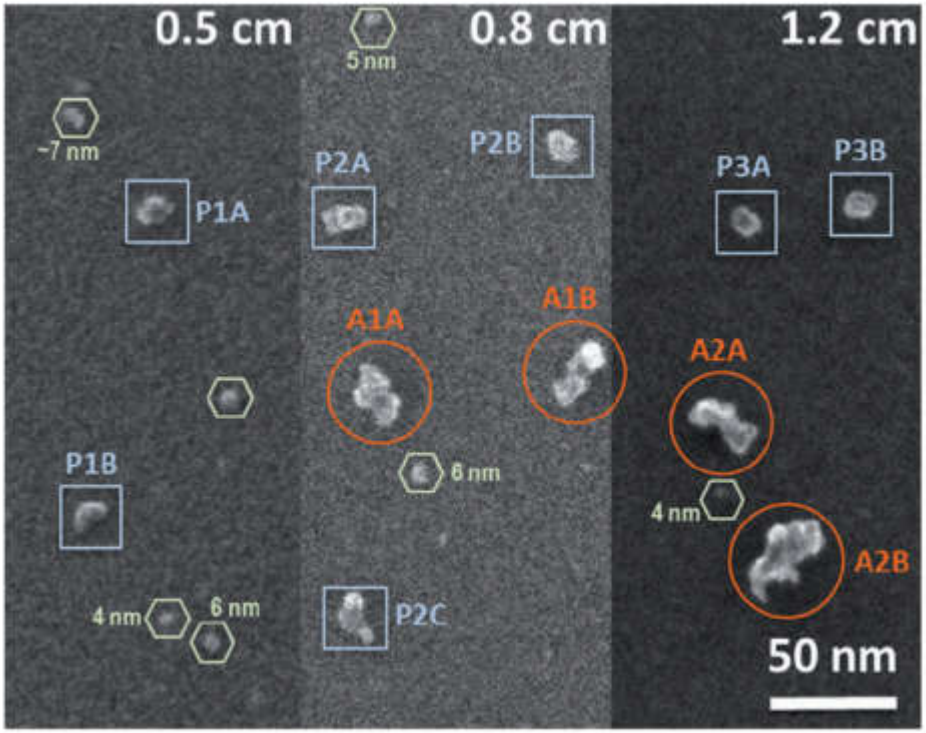
“Infant” Soot is quite different from mature soot

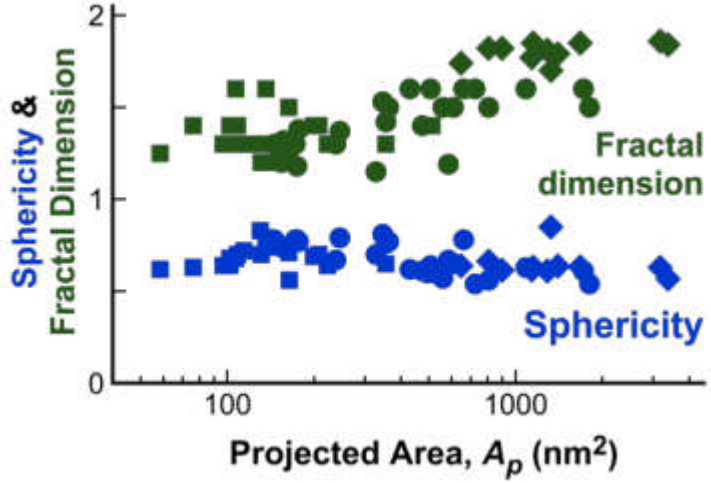
TEM tends to damage nascent soot samples



t = 5 min *t* = 10 min *t* = 15 min *t* = 20 min *t* = 25 min *t* = 30 min

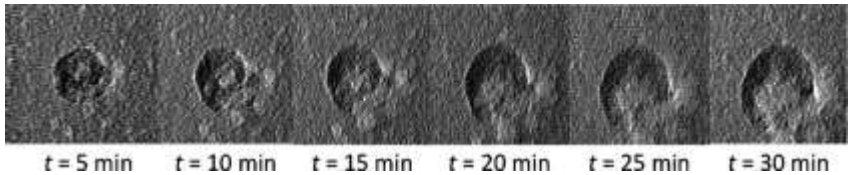
Helium ion microscopy (HIM) shows irregular, inhomogeneous “primary” soot structures



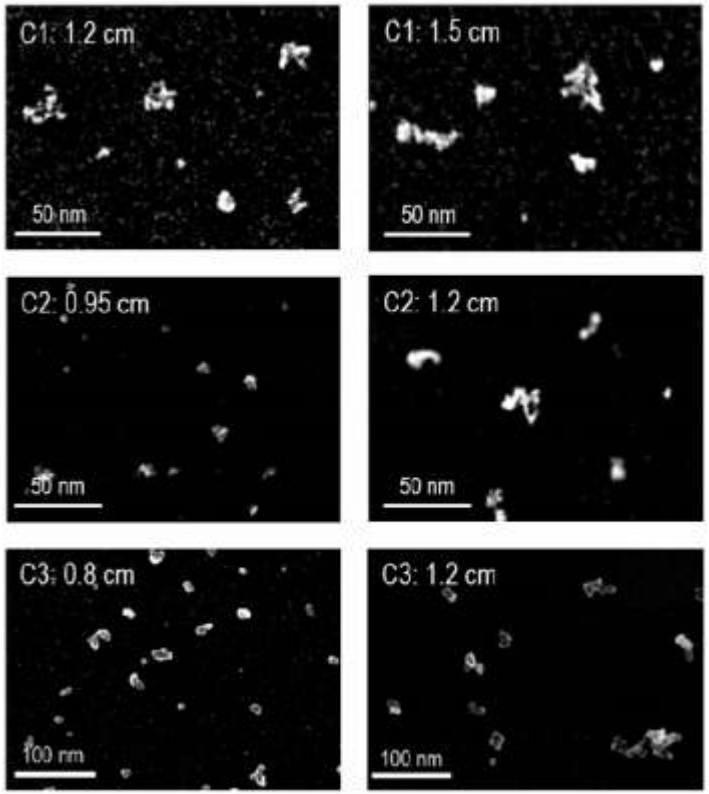


Schenk et al. (2013, 2014)

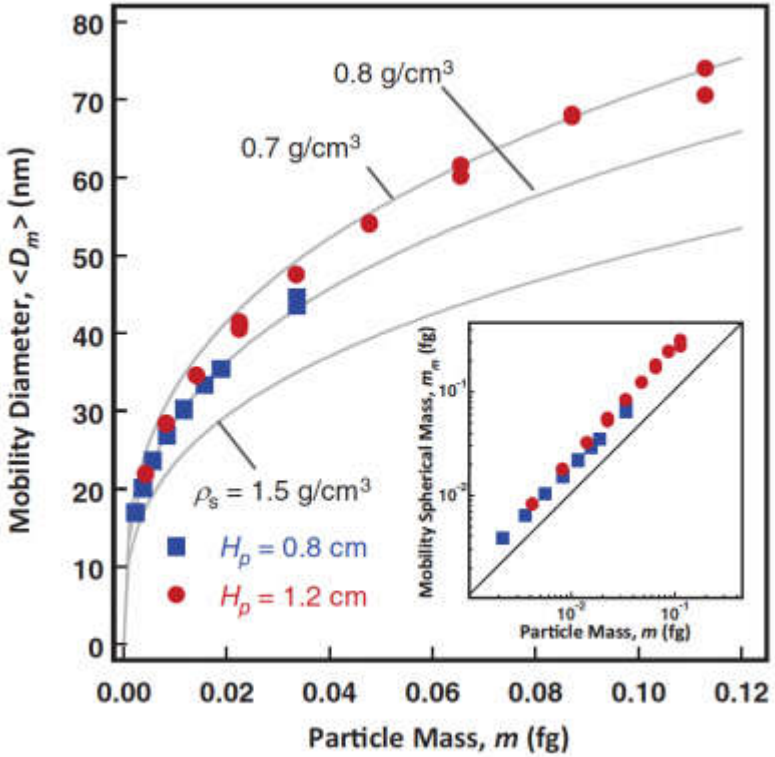
“Infant” Soot is quite different from mature soot



Damage by electron beam in a low-res TEM (Schenk et al. 2013)



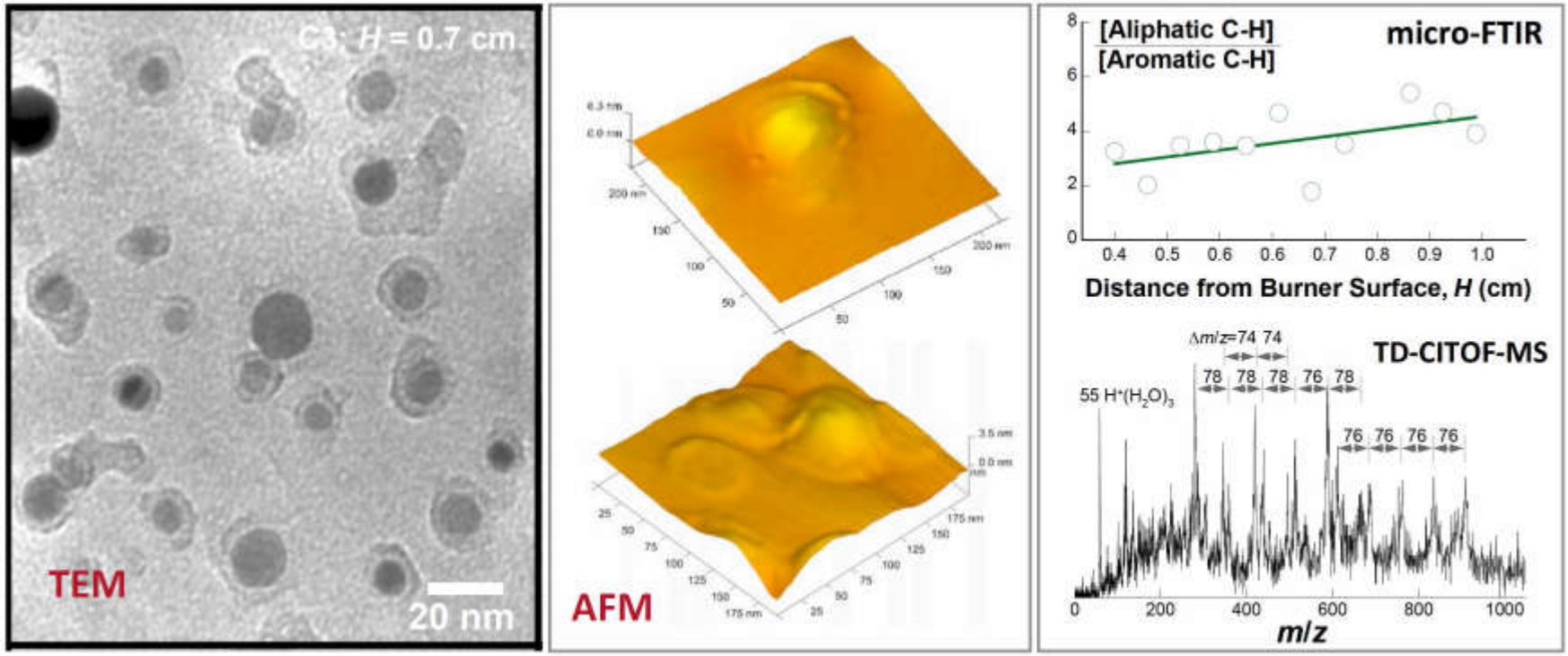
Structural inhomogeneity as shown by Helium Ion Microscopy (HIM) – Schenk et al. (2015)



Mobility diameter/mass relationship shows substantially smaller mass densities than previously understood (Camacho & Jung et al. (2015)

"Infant" Soot is quite different from mature soot

C_2H_4-O_2-Ar flame (ϕ = 2.07, T_f = 1736±50 K)

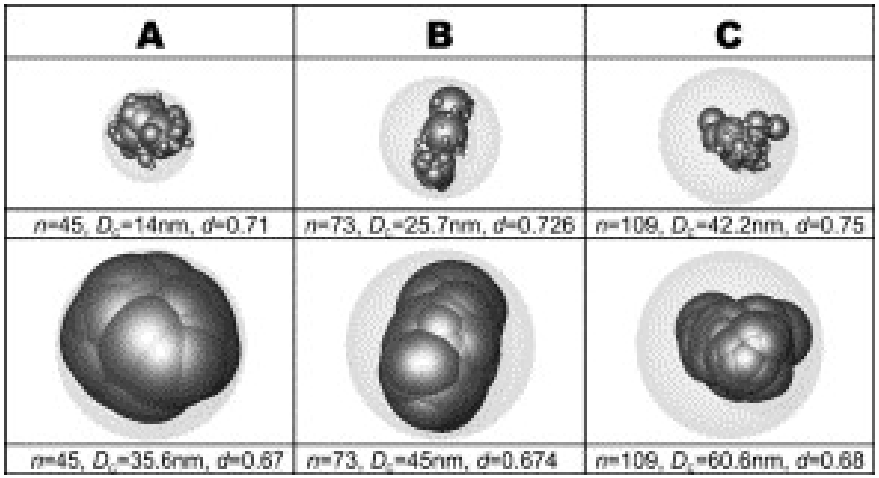


- "Sunny-side up" morphology (TEM & AFM) suggests an aromatic core-aliphatic shell structure.
- Micro-FTIR measurements again show aliphatic dominance
- Thermal desorption/chemical ionization (extreme soft) show broad mass spectrum, suggesting that nascent soot is alkylated.

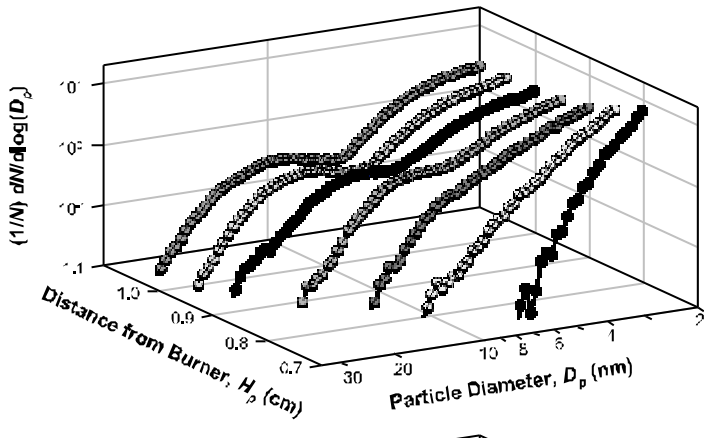
Abid et al. 2008; Cain et al. 2010

Recent Highlights (2)

- **Kinetic Monte Carlo simulation explains the origin of sphericity (or nonsphericity) of nascent soot particles**

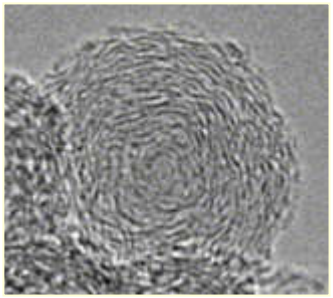


Balthasar, Frenklach (2005)



Abid et al. (2009)
C_2H_4-O_2-Ar flame f = 2.1

Eventually



Mass and Size Growth

- **The mass of soot is gained thru surface reaction**

The HACA Mechanism

$$S_i\text{–H} + \text{H}\bullet \leftrightarrow S_i\bullet + \text{H}_2 \quad (1)$$
$$S_i\bullet + \text{H}\bullet \rightarrow S_i\text{–H} \quad (2)$$
$$S_i\bullet + C_2H_2 \rightarrow S_{i+2}\text{–H} + \text{H}\bullet \quad (3)$$

$$\omega_s\left(\frac{\text{mol C-atom}}{\text{cm}^3\text{s}}\right) \approx 2k_3 \frac{k_{1f}}{k_{1b}} \frac{[\text{H}\bullet]}{[\text{H}_2]}[S_i\text{-H}][C_2H_2]$$

- The mass growth rate is proportional to H atom concentration

- **Particle size grows by particle-particle coagulation**
  - The Smolokowski equation

$$\frac{dN_1}{dt} = -N_1 \sum_{j=1}^{\infty} \beta_{1,j} N_j$$
$$\frac{dN_i}{dt} = \frac{1}{2}\sum_{j=1}^{i-1} \beta_{j,i-j} N_j N_{i-j} - n_i \sum_{j=1}^{\infty} \beta_{i,j} N_j \quad (i = 2, \cdots \infty)$$

where N_i is the number concentration of particle of size i and the collision kernel in the free molecule regime

The collision kernel

$$\beta_{i,j} = \sqrt{\frac{8\pi k_B T}{\mu_{i,j}}}\sigma_{i,j}^2$$
$$= \left(\frac{3m_1}{4\pi\rho}\right)^{2/3} \sqrt{\frac{8\pi k_B T}{m_1}}\left(\frac{1}{i}+\frac{1}{j}\right)^{1/2}\left(i^{1/3}+j^{1/3}\right)^2$$

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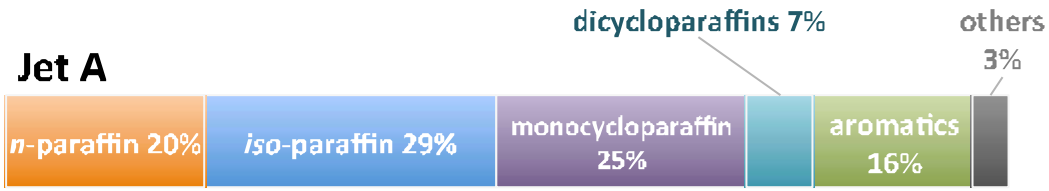
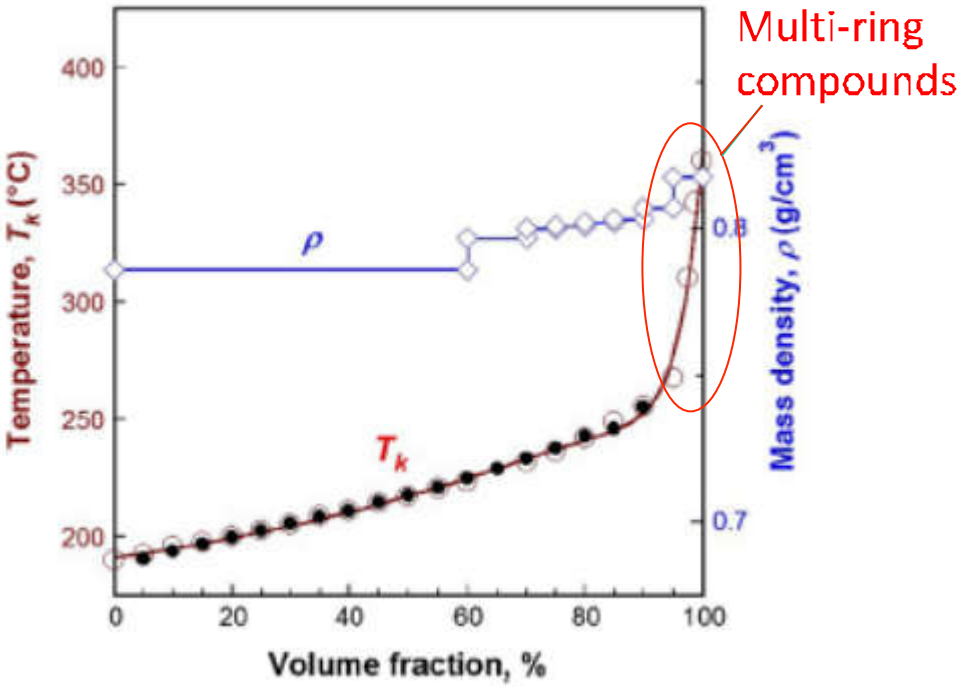
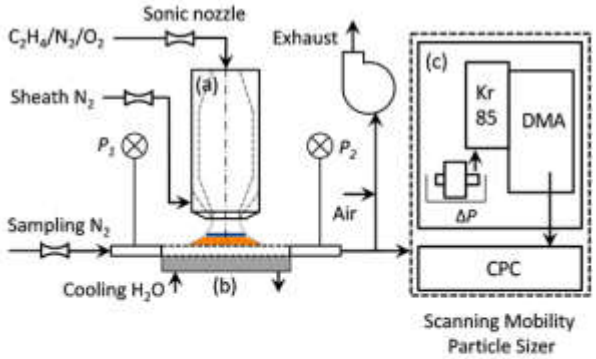
Soot Formation in (Real) Distillate Fuels

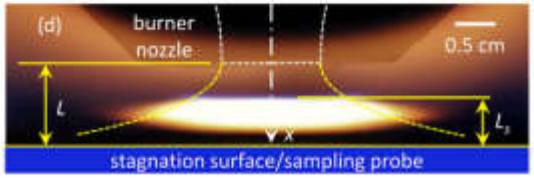
Real fuels are often multicomponent in composition

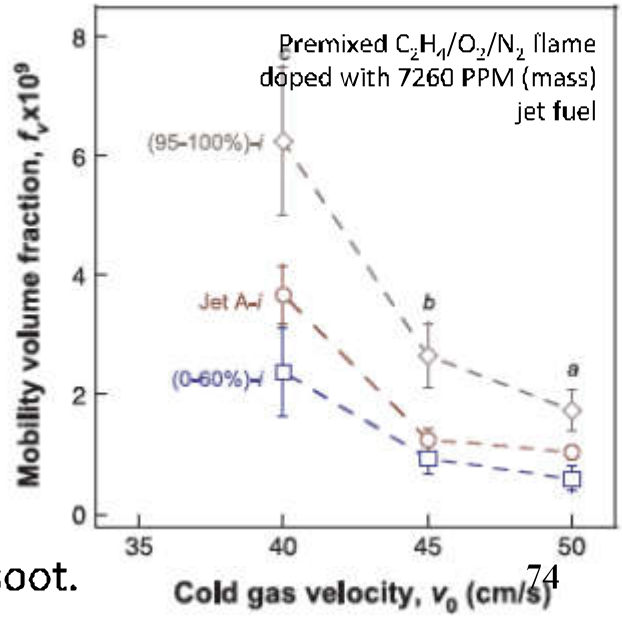




Saggese et al. *Fuel* (2019)







The tail-end components nucleate more soot.

Soot Formation in (Real) Distillate Fuels

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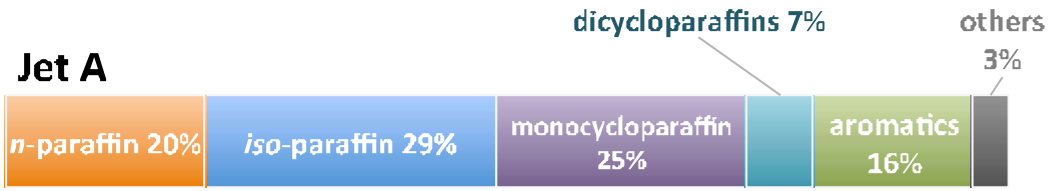
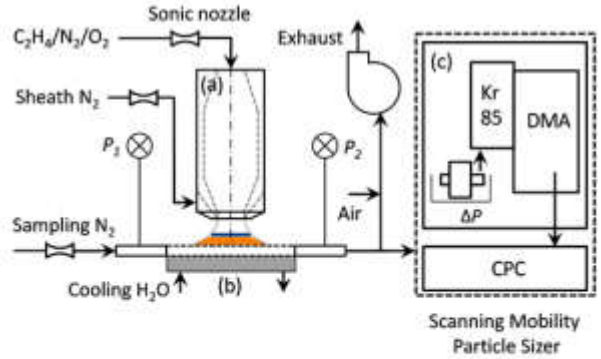
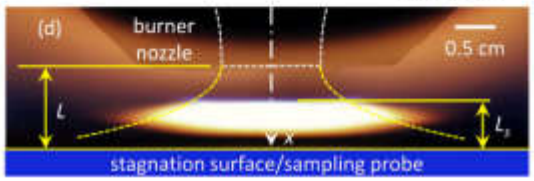
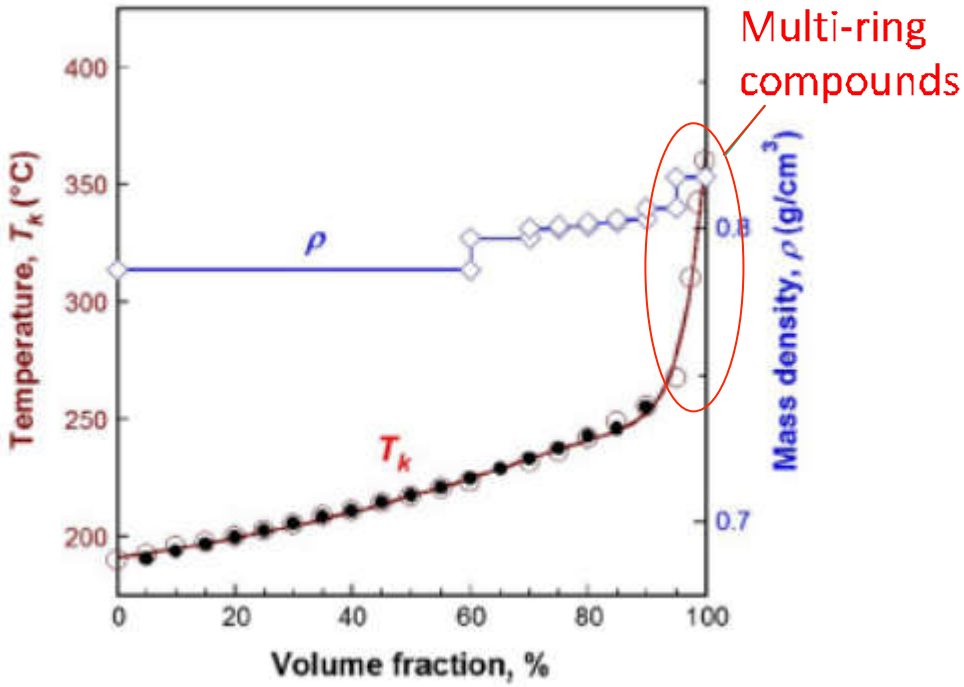
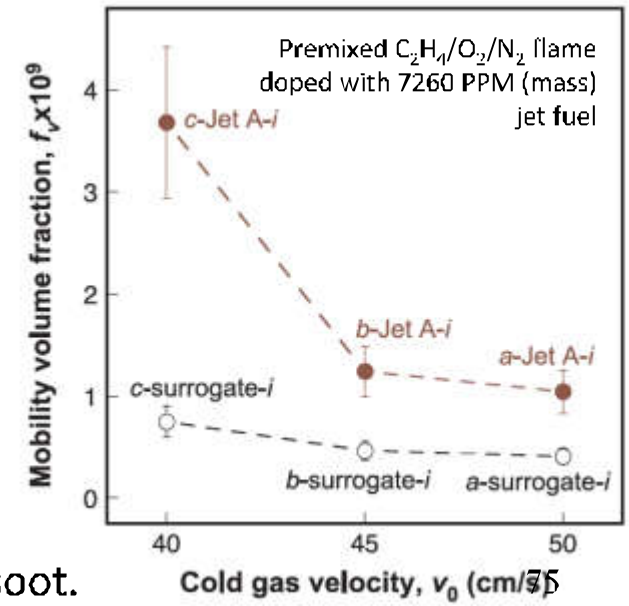








Saggese et al. *Fuel* (2019)



The tail-end components nucleate more soot.

For this reason, a surrogate modeling approach would not work

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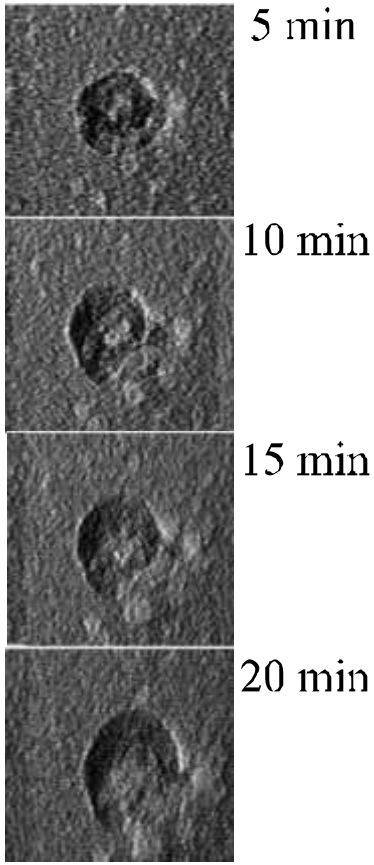
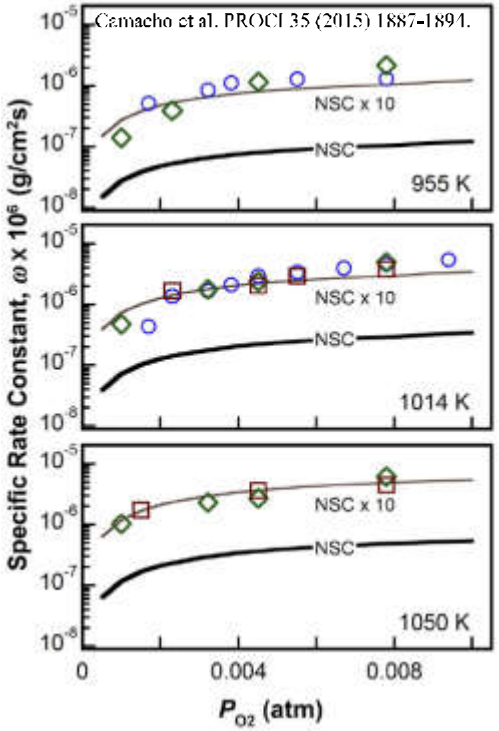
What is infant soot made of?

- Easily damaged by e-beam

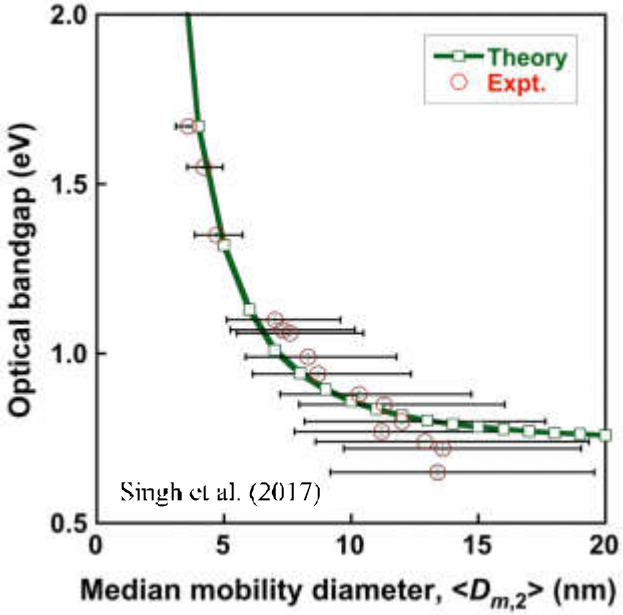


Schenk et al. *ChemPhysChem* 14 (2013) 3248-3254.

- Oxidized faster than mature soot

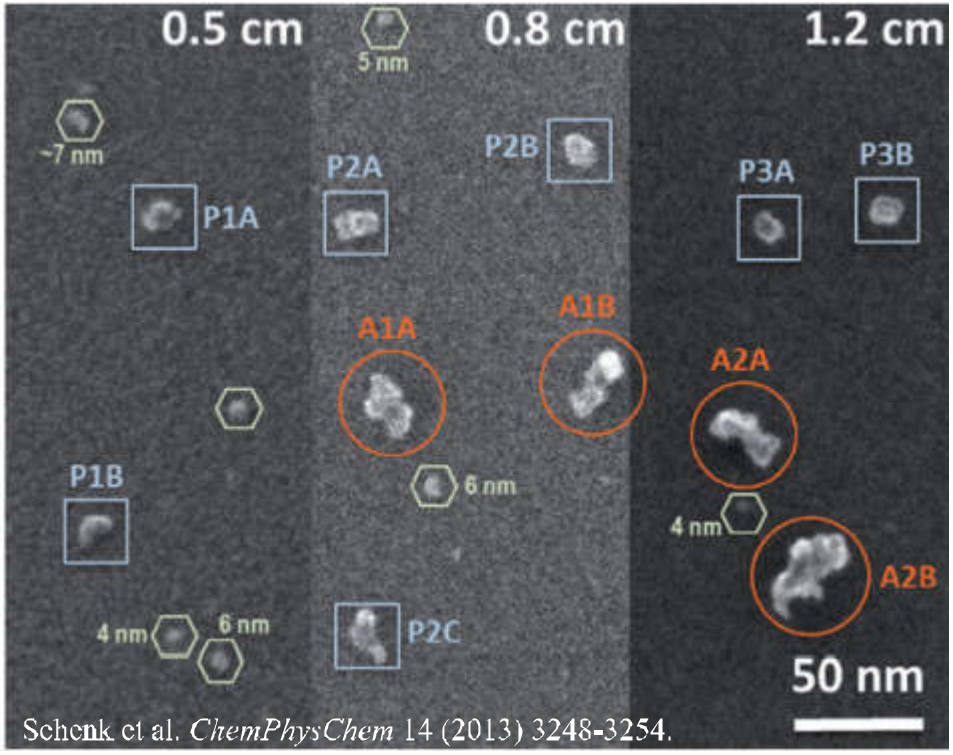


- Behaves like quantum dots (not a broadband absorbing material)



What is infant soot made of?

- Does not appear to be a homogeneous, well defined material
- Neither spherical, nor homogeneous even at a size of a few nanometers.



- **Implication**: Added diagnostic challenges

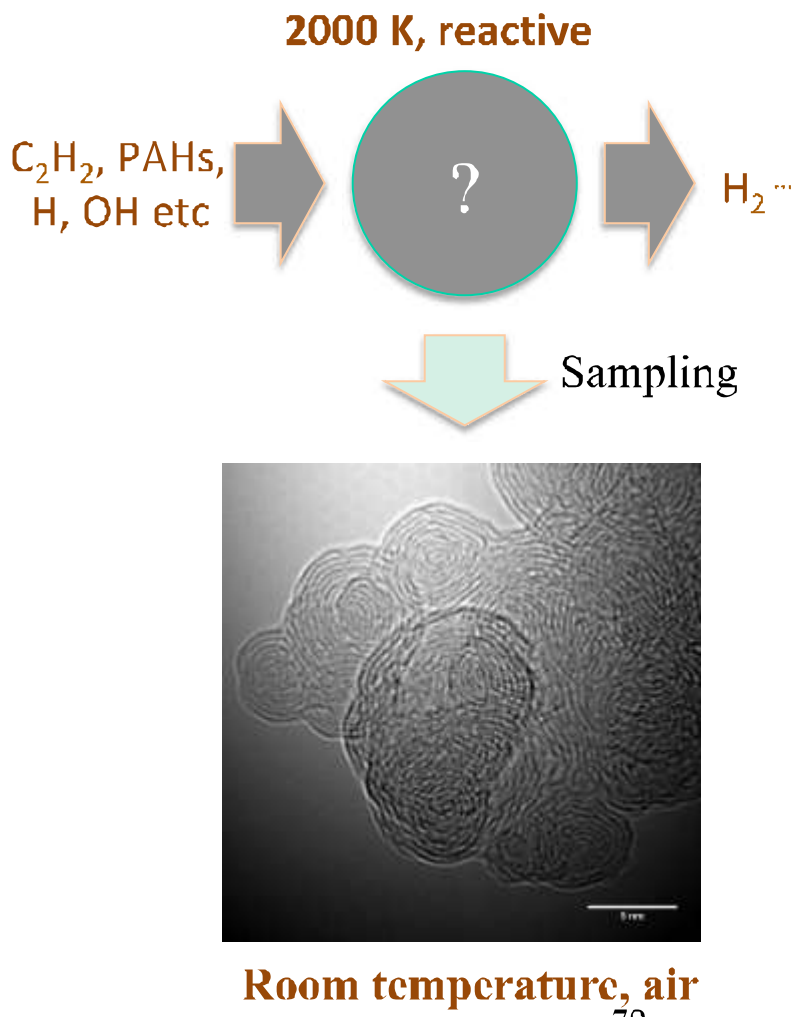
Schenk et al. *PROCI* 34 (2015) 1879-1886.

Are properties of soot identical before and after we extract it a flame?

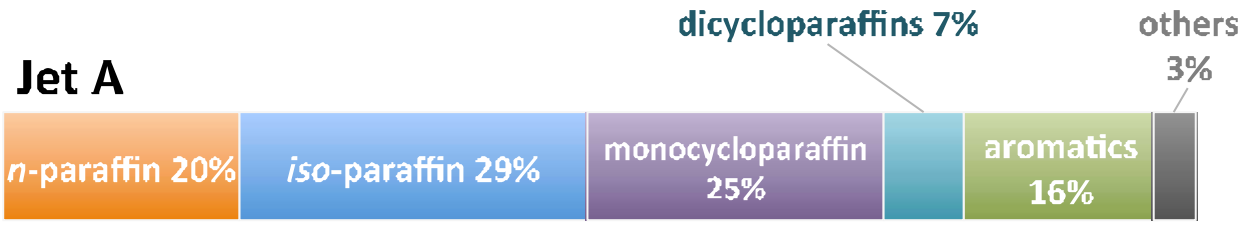
- Physical and chemical properties of in-flame soot is the result of competitions of several processes
  - e.g., growth vs. dehydrogenation

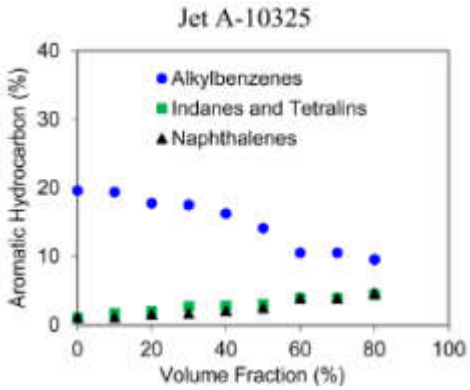
- No reason to expect that the physical and chemical properties of particles are "frozen" during sampling

- **Implication**: limited diagnostic options; need more advanced in-situ technique.

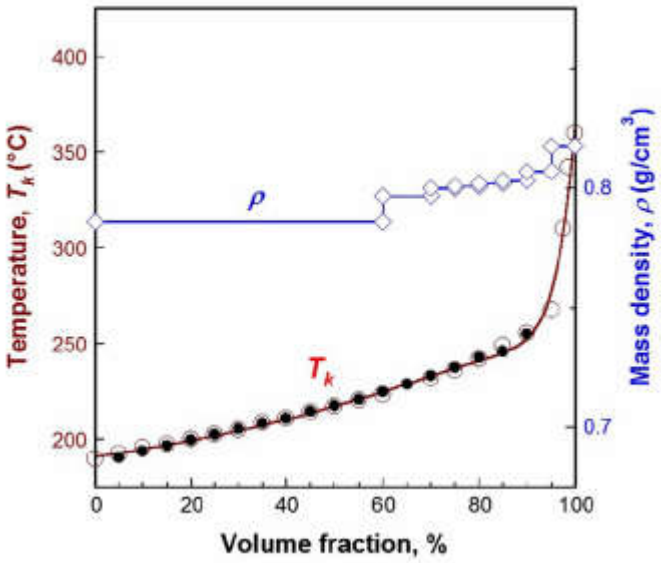


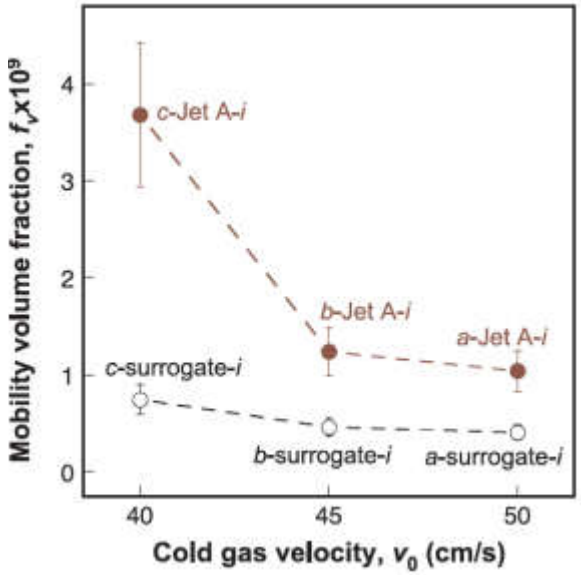
Are the pathways to soot identical between neat and real (distillate) fuels?





Bruno & coworkers *Energy Fuel*. (2016).





- Jet fuels contain multi-ring compounds, which are predominantly in the tail end of the distillation curve.
- The large compounds naturally existing in the fuel jump-start the soot nucleation and growth process.
- How much PAH reactions are actually involved if the fuel already contains some large aromatics? Would a surrogate modeling approach work?

Concluding Remarks

- Since Michael Faradays' first description of soot in a candle flame, much progress has been made in our understooding about soot formation in flames
- Yet, every time we scratch the surface, a new layer of complexity emerges

"It's soot, Mom. You told us to play in the fresh air."

- The sensitivity of soot formation to local thermodynamic conditions makes it a daunting task to make predictions at the fundamental level.
- As we continue to play with it, we must be constantly reminded about the real (societal) problem we try tosolve.