ETH zürich

From nascent to mature soot light absorption during agglomeration and surface growth

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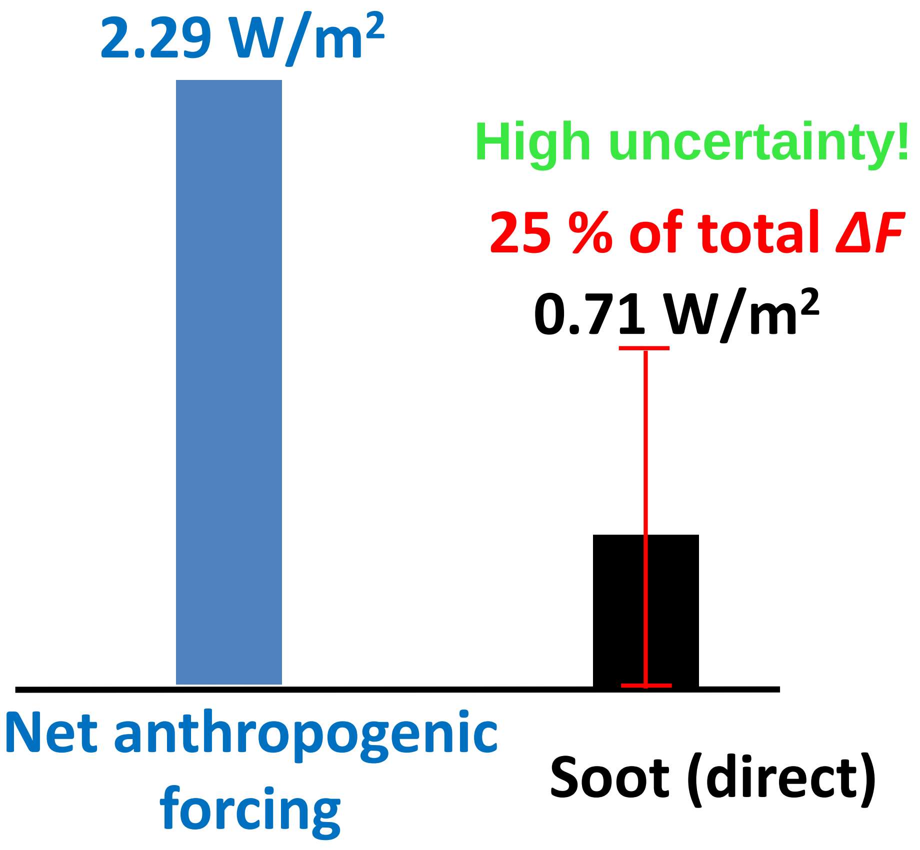
PTL
Particle Technology
Laboratory

Soot impact on global warming

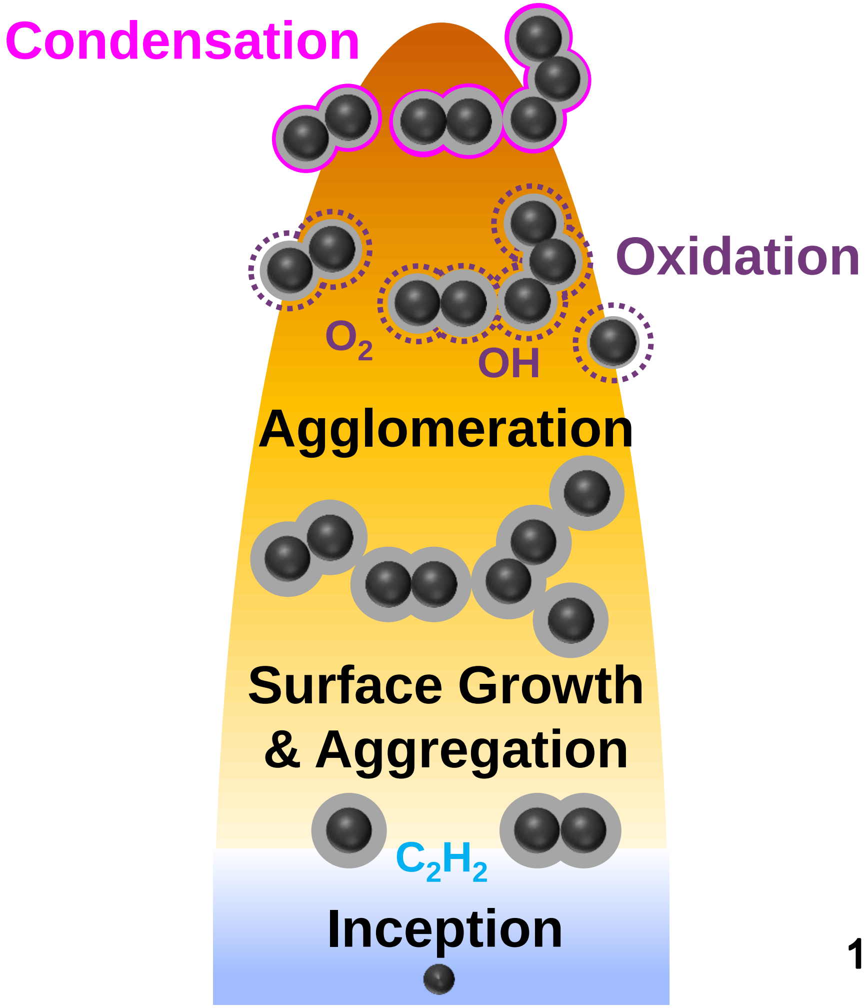
Radiative forcing, ΔF [1]:

Light absorbed by earth -
// reflected to space



Narrower *ΔF* accounting for:

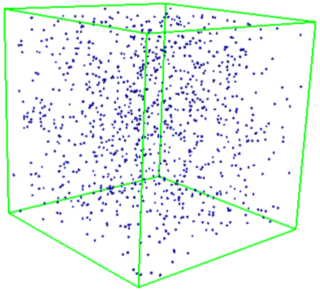
- **Evolving structure**
- **// composition**



[1] Bond, T. C.; Doherty, S. J.; Fahey, D., et al. J Geophys Res 2013, 118, 5380-5552.

Soot Dynamics by Discrete Element Modeling (DEM)

i) Initial configuration after inception has largely ended.



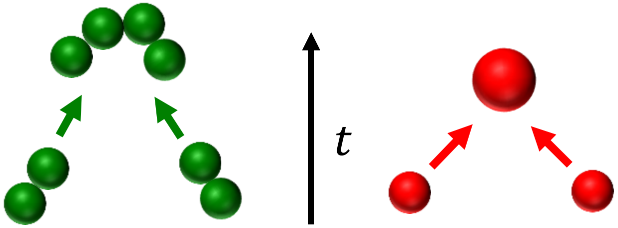
T = 1830 K

$d_{m,o}$ = 2 nm

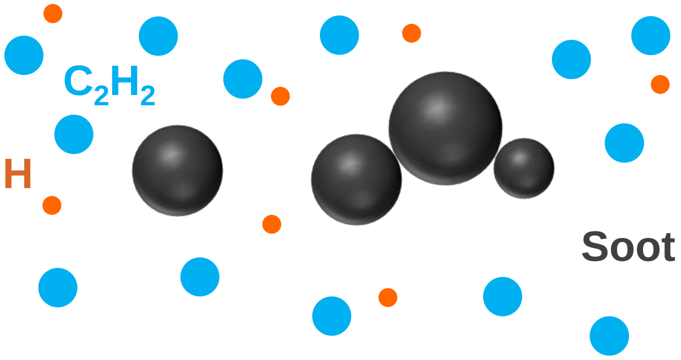
$N_{tot,o}$ = $4.5 \cdot 10^{16}$ m^{-3}

[1,2]

ii) Discrete Element Modeling (DEM) of **Particle Motion** and **Coagulation** [3]

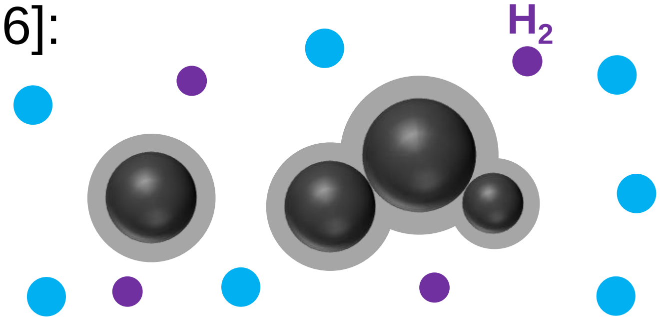


iii) **Surface Growth** (SG) by HACA mechanism [4-6]:



r_{HACA} [4]

β_{C2H2} [6]



Mass Balance for each C_2H_2 reaction:

$$\pi \frac{d_{p,new}^3}{6} \rho_{soot} = \pi \frac{d_{p,old}^3}{6} \rho_{soot} + m_{2c}$$

[1] Abid AD, Heinz N, Tolmachoff ED, Phares DJ, Campbell CS, Wang H. (2008) *Combust. Flame* **154**, 775.

[2] Camacho J, Liu C, Gu C, Lin H, Huang Z, Tang Q, You X, Saggese C, Li Y, Jung H, Deng L, Wlokas I, Wang H. (2015) *Combust. Flame* **162**, 3810.

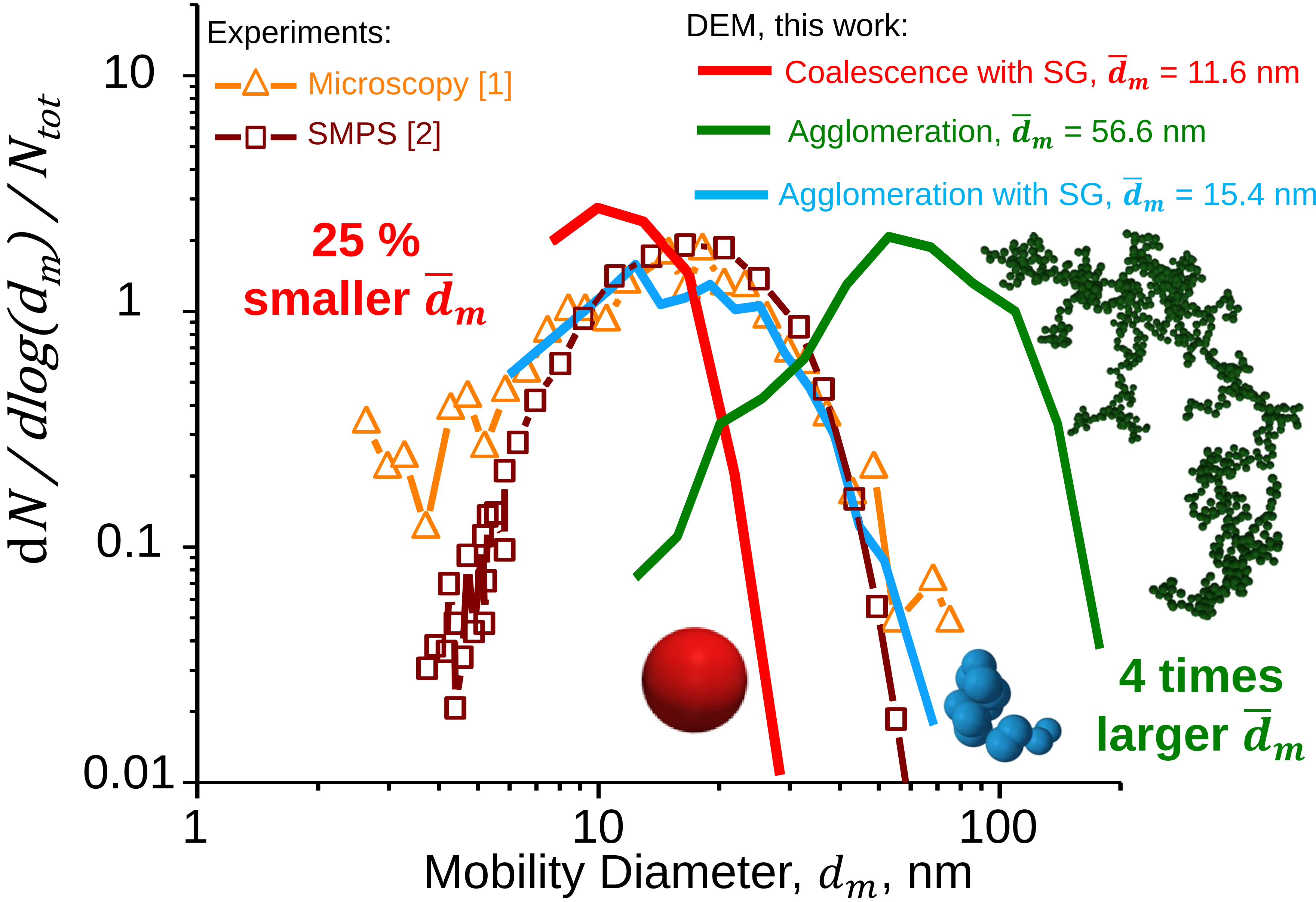
[3] Goudeli E, Eggersdorfer ML, Pratsinis SE. (2015) *Langmuir* **31**,1320.

[4] Appel J, Bockhorn H, Frenklach M. (2000) *Combust. Flame* **121**, 122.

[5] Saggese C, Ferrario S, Camacho J, Cuoci A, Frassoldati A, Ranzi E, Wang H, Faravelli T. Wang H. (2015) *Combust. Flame* **162**, 3356.

[6] Kelesidis GA, Goudeli E, Pratsinis SE. (2017) *Proc. Combust. Inst.* 36, 29.

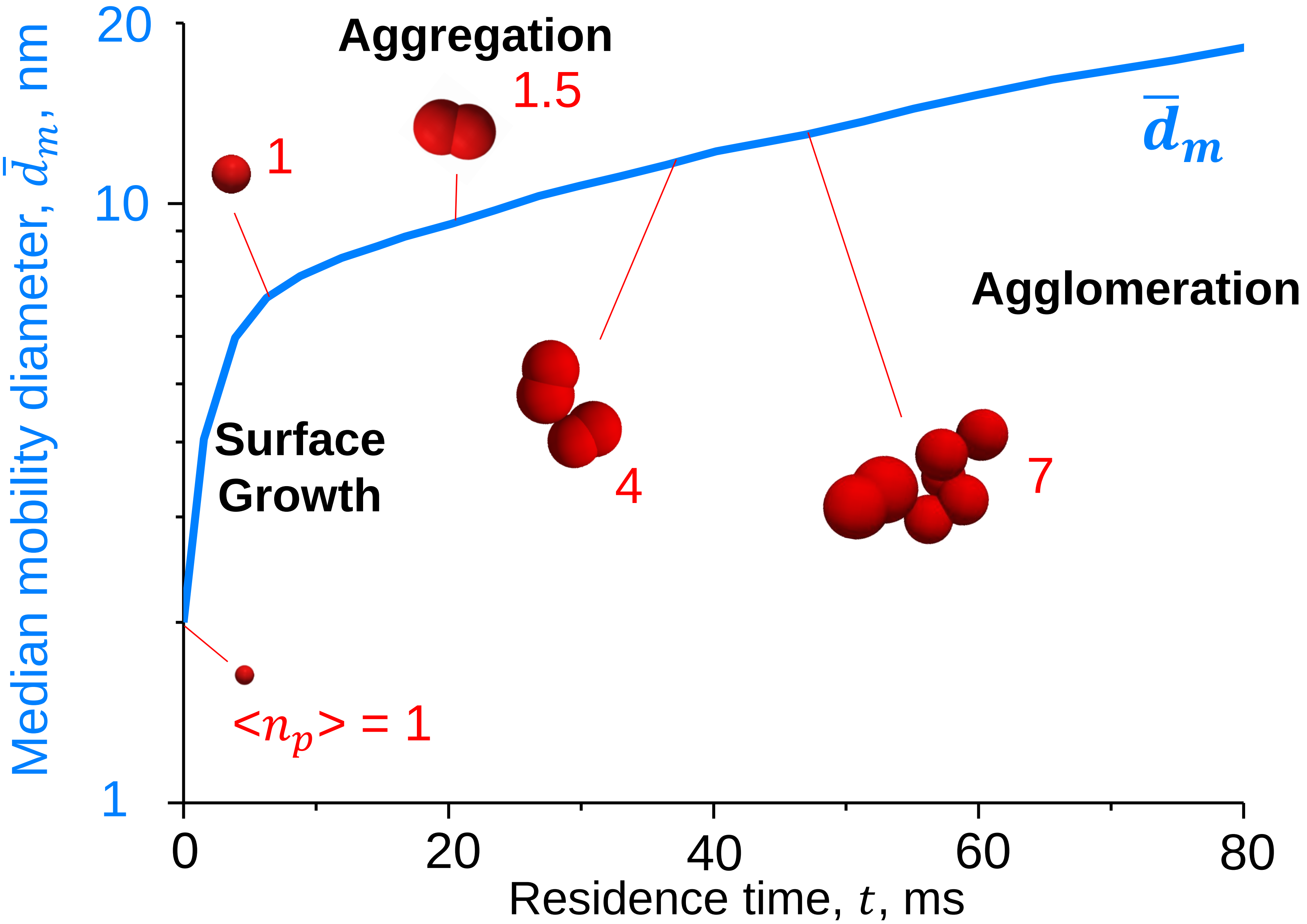
Soot Size Distribution, HAB = 1.2 cm



[1] Schenk M, Lieb S, Vieker H, Beyer A, Golzhauser A,Wang H, Kohse-Hoinghaus K. (2013) *PhysChemPhys* **14**, 3

[2] Camacho J, Liu C, Gu C, Lin H, Huang Z, Tang Q, You X, Saggese C, Li Y, Jung H, Deng L, Wlokas I, Wang H. (2015) *Combust. Flame* **162**, 3810.

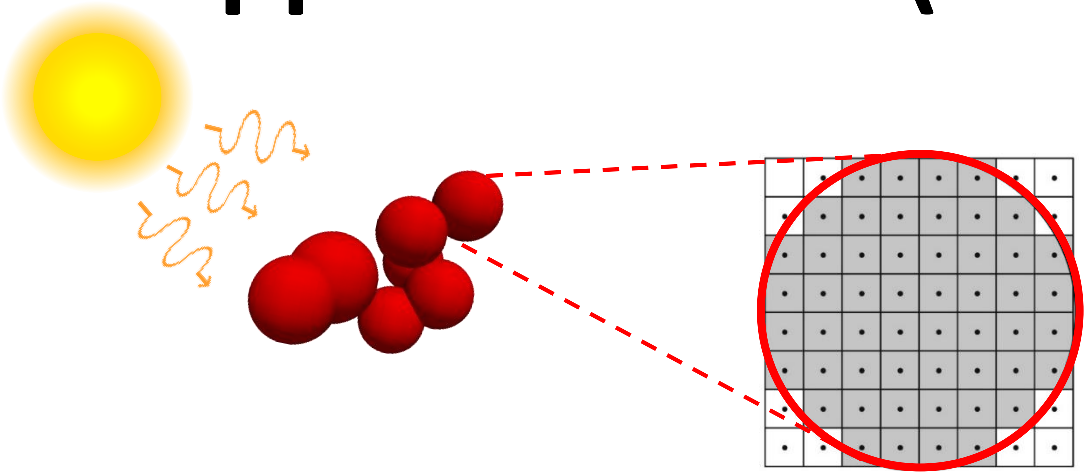
Soot Dynamics by DEM

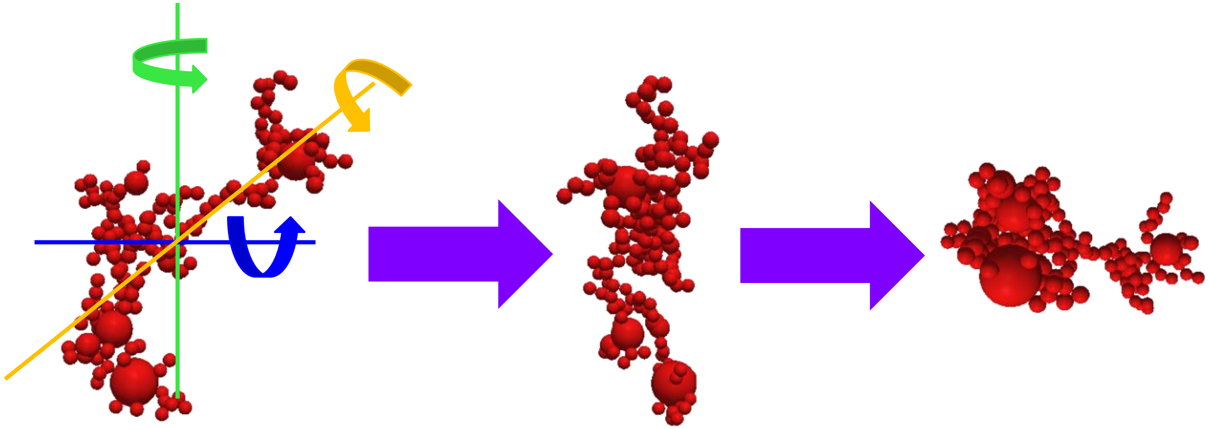


Discrete Dipole Approximation (DDA)

Input:

- Structure of DEM-derived agglomerate
- Refractive index, *RI*





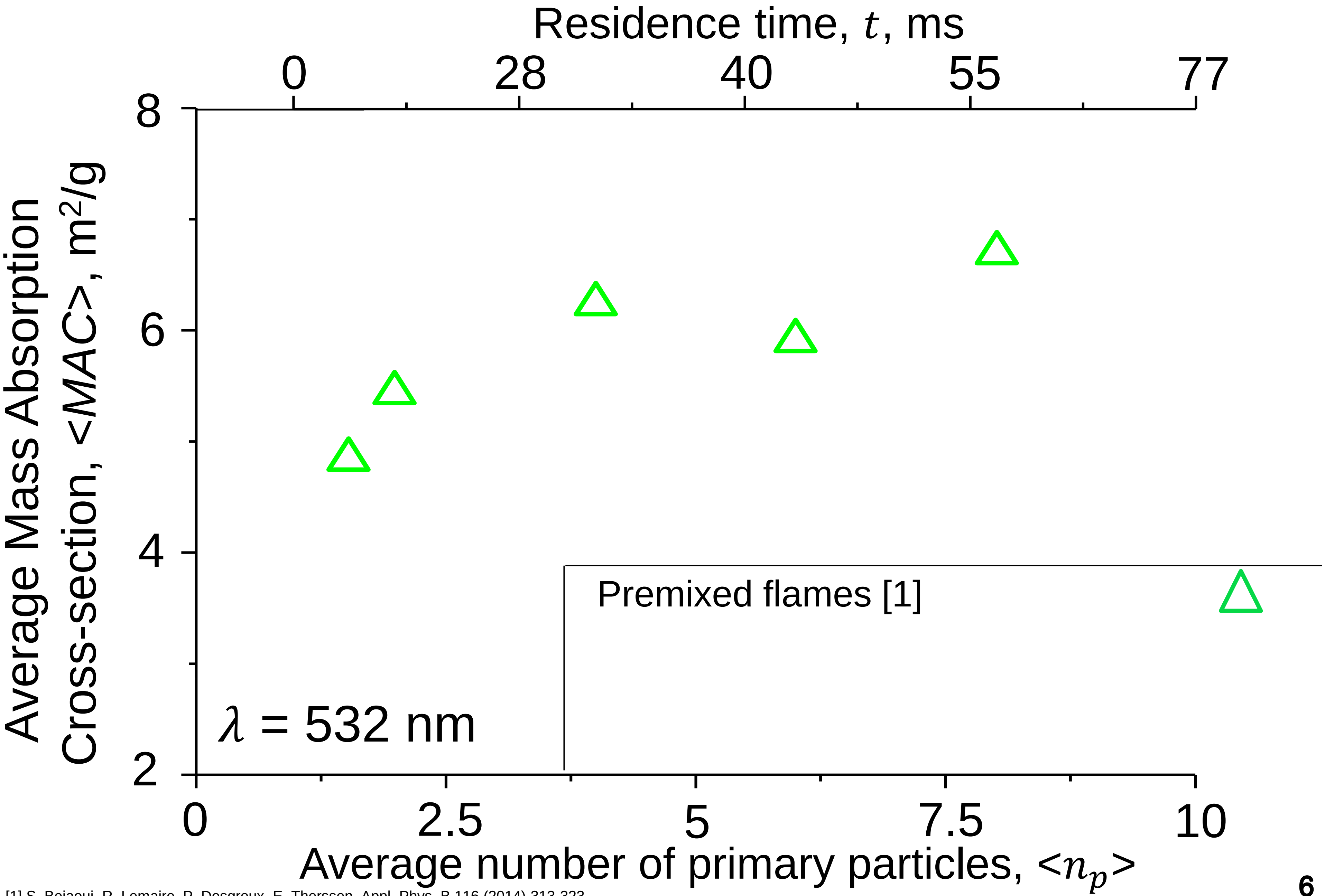
$$\underbrace{MAC}_{} = \frac{3Q_{abs}}{2d_v\rho}$$

Used to calculate radiative forcing!

Averaging of *MAC*:
- over 100 agglomerates per time step.
- over 343 orientations.

✓ Good statistics.
✓ Computational efficiency.

From nascent to mature soot *MAC*



[1] S. Bejaoui, R. Lemaire, P. Desgroux, E. Therssen, Appl. Phys. B 116 (2014) 313-323.

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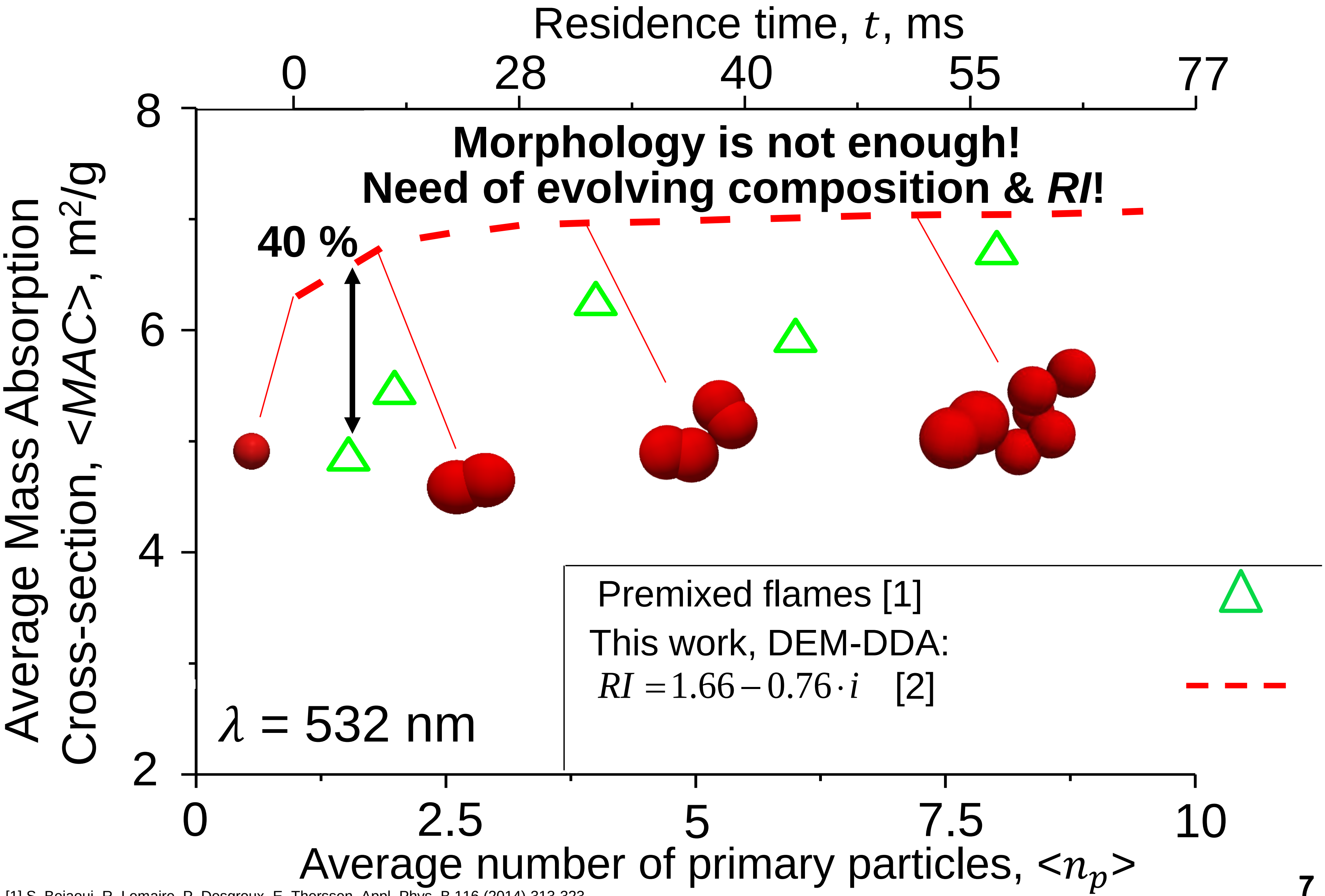
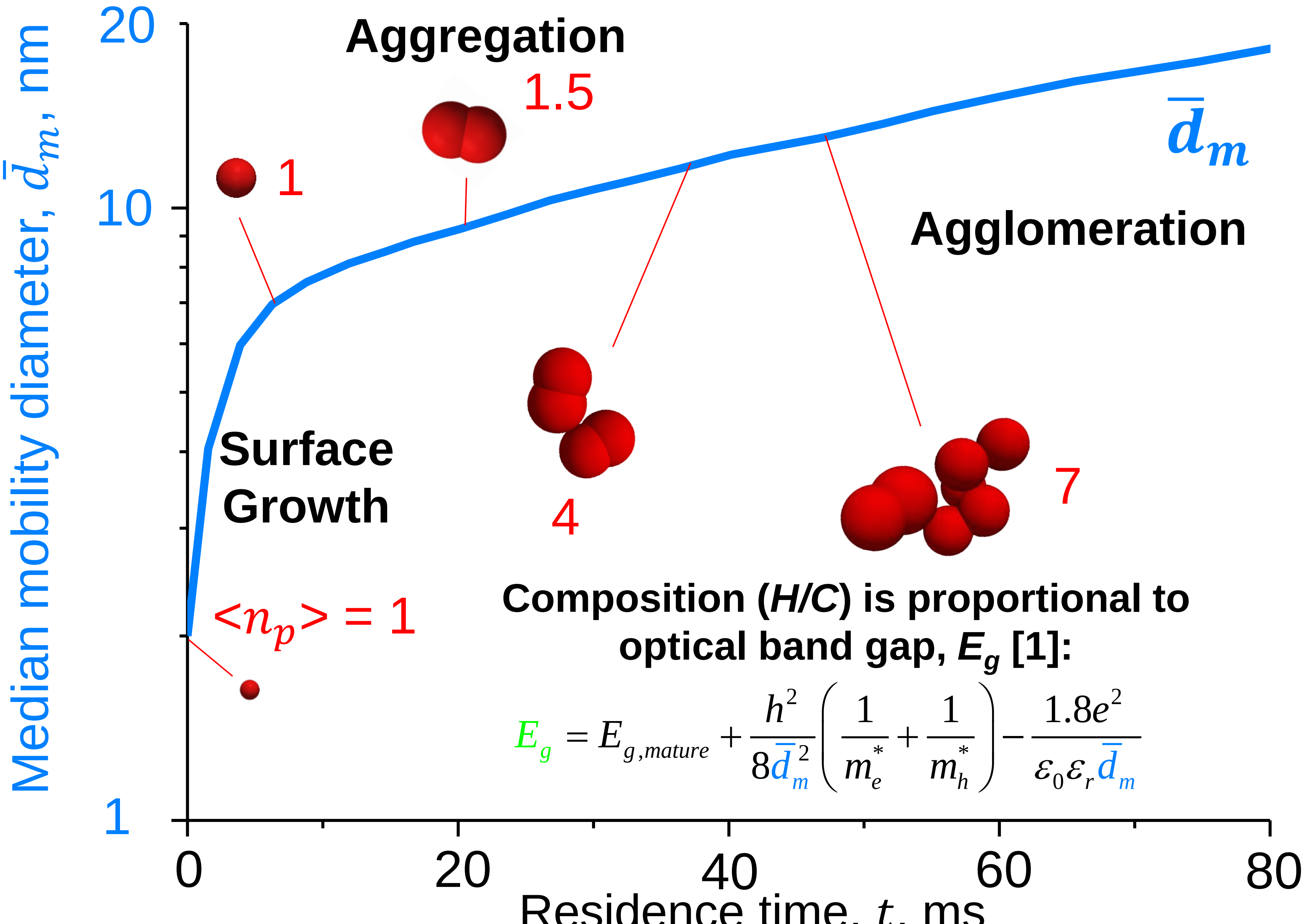


Morphology is not enough!
Need of evolving composition & *RI*!

[1] S. Bejaoui, R. Lemaire, P. Desgroux, E. Therssen, Appl. Phys. B 116 (2014) 313-323.
[2] J. Yon, A. Bescond, F. Liu, J. Quant. Spectrosc. Radiat. Transf. 162 (2015) 197-206.

Evolution of soot composition



Composition (*H/C*) is proportional to optical band gap, E_g [1]:

$$E_g = E_{g,mature} + \frac{h^2}{8\bar{d}_m^{\,2}}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{\varepsilon_0 \varepsilon_r \bar{d}_m}$$

[1] A.V. Singh, C. Liu, K. Wan, H. Wang, 10th U.S. National Combustion Meeting: Environmental Aspects of Combustion (2017) 1-6.

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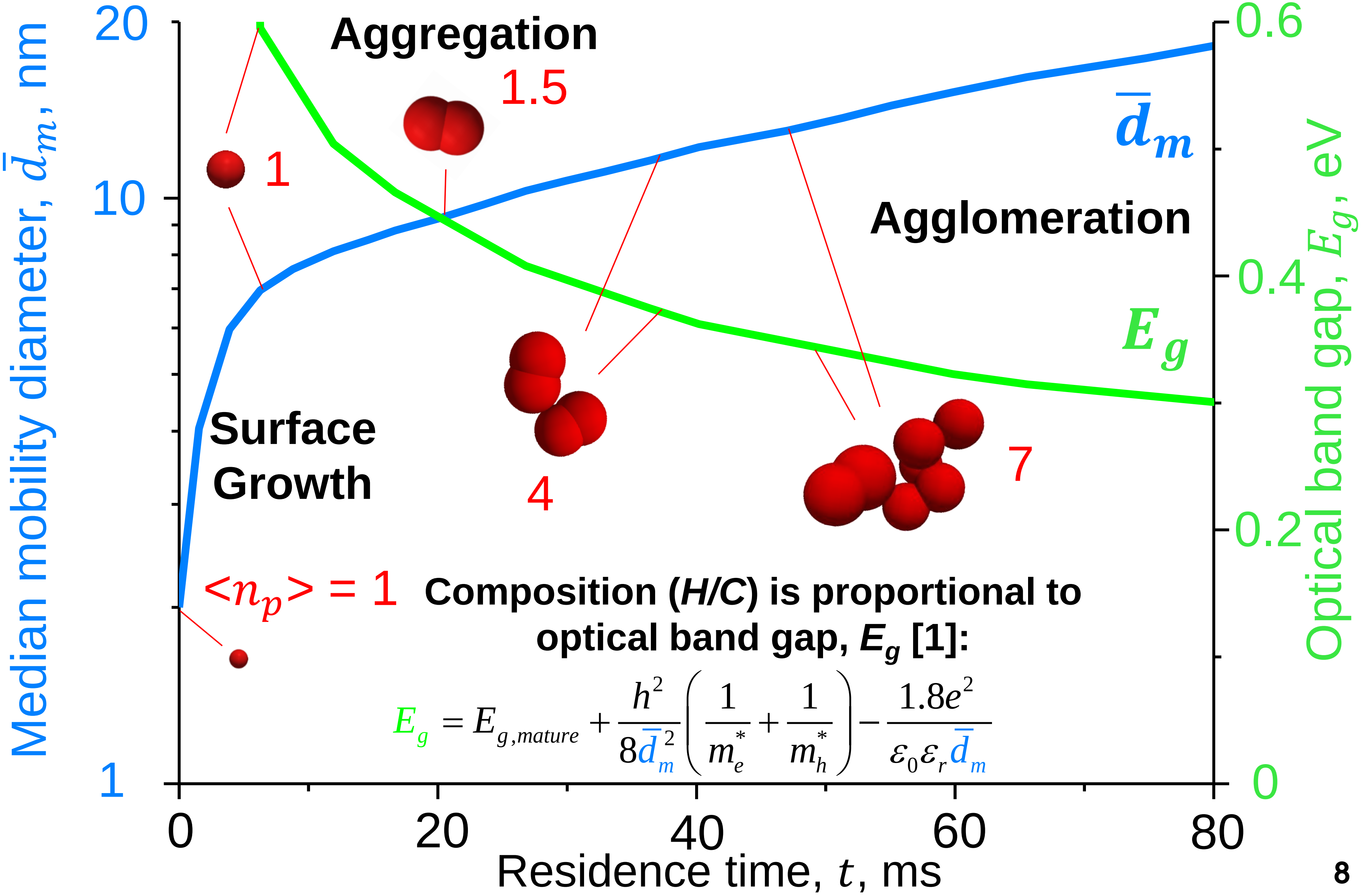

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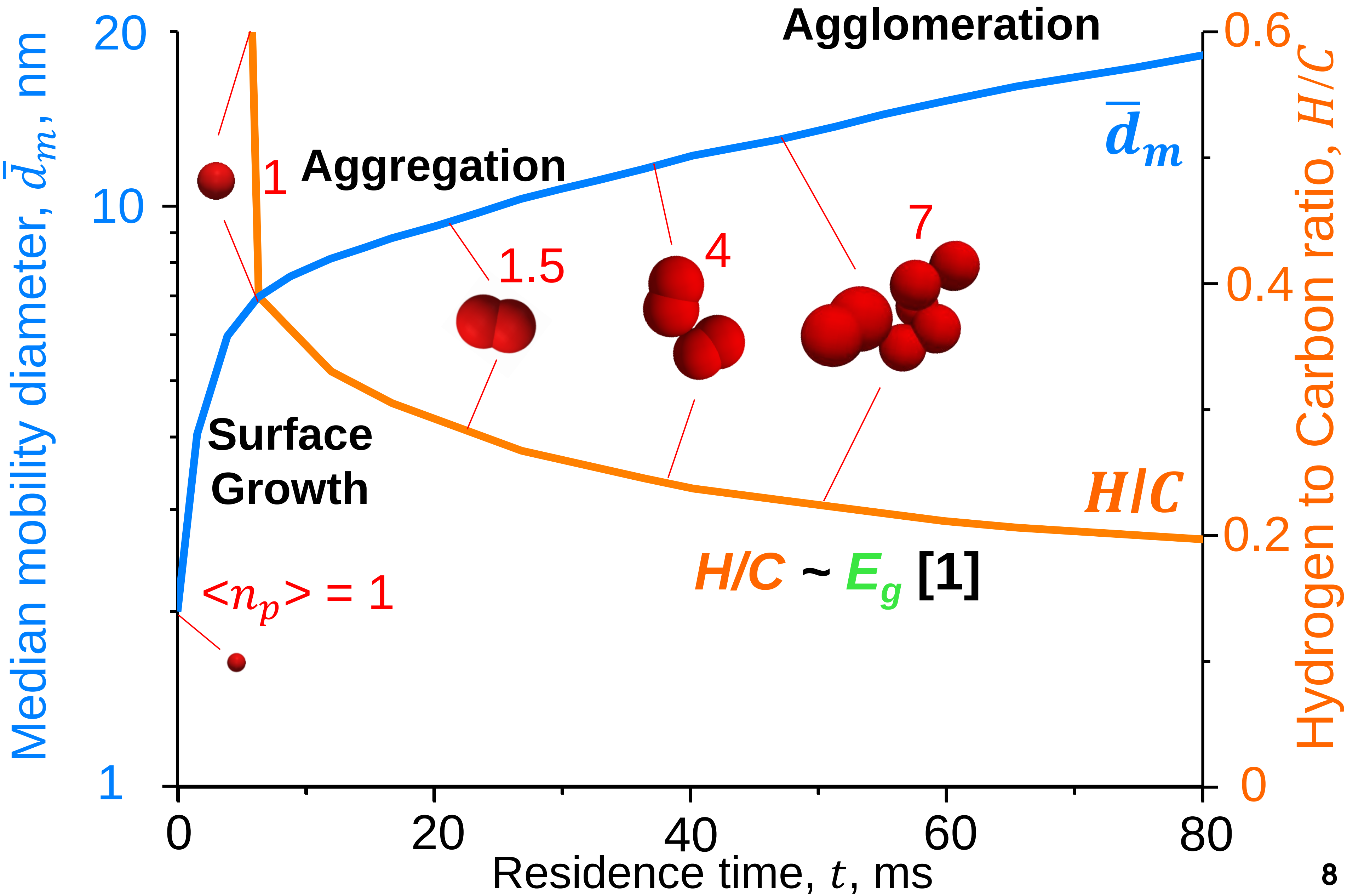
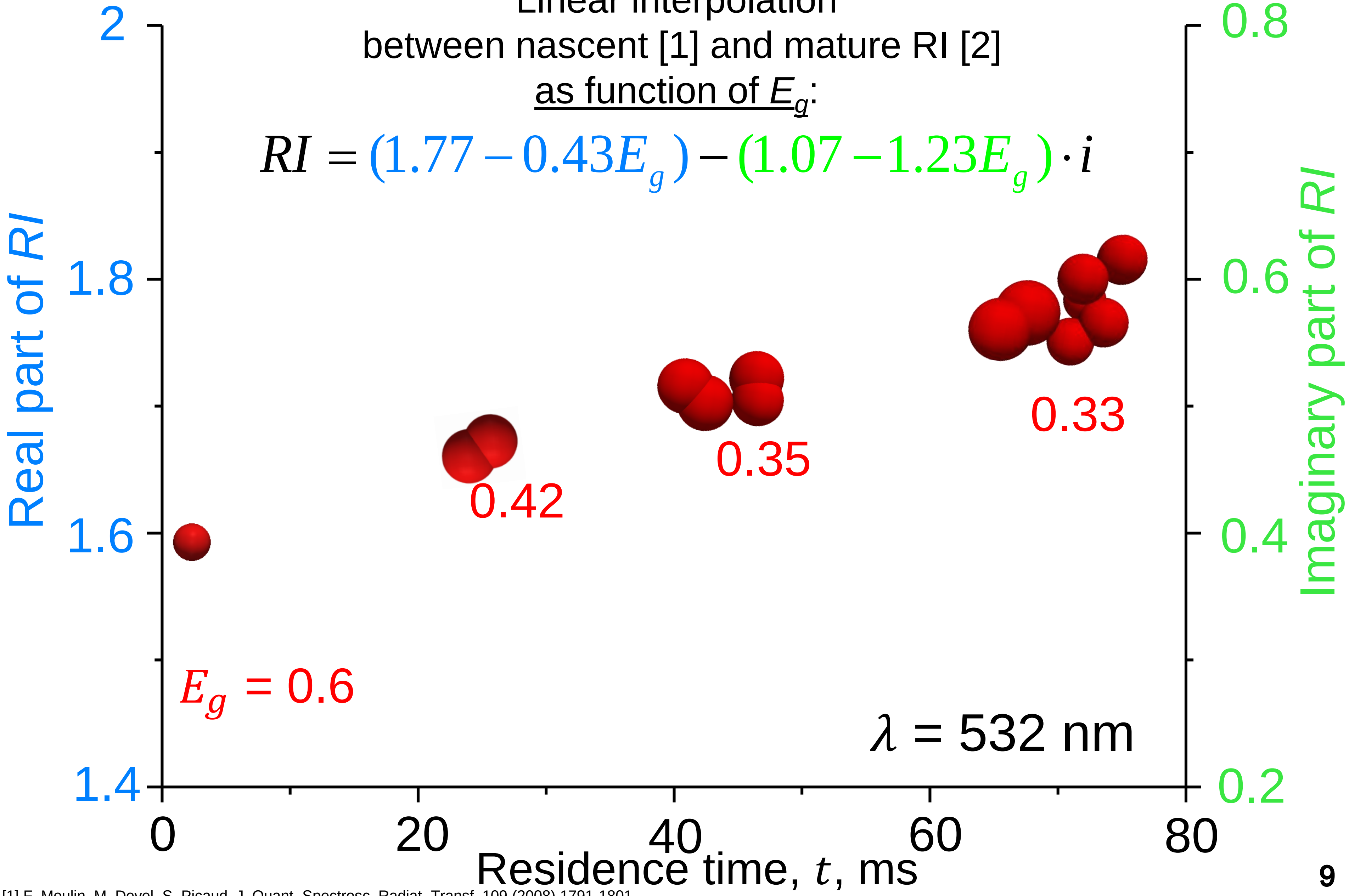


[1] Minutolo, P.; Gambi, G.; D'Alessio, A. Proc. Combust. Inst. 1996, 26, 951-957

Evolution of refractive index, *RI*

Linear interpolation
between nascent [1] and mature RI [2]
as function of E_g:

$$RI = (1.77 - 0.43E_g) - (1.07 - 1.23E_g)\cdot i$$



[1] F. Moulin, M. Devel, S. Picaud, J. Quant. Spectrosc. Radiat. Transf. 109 (2008) 1791-1801.
[2] Yon, J.; Bescond, A.; Liu, F. J Quant Spectrosc Radiat Transfer 2015, 162, 197-206.

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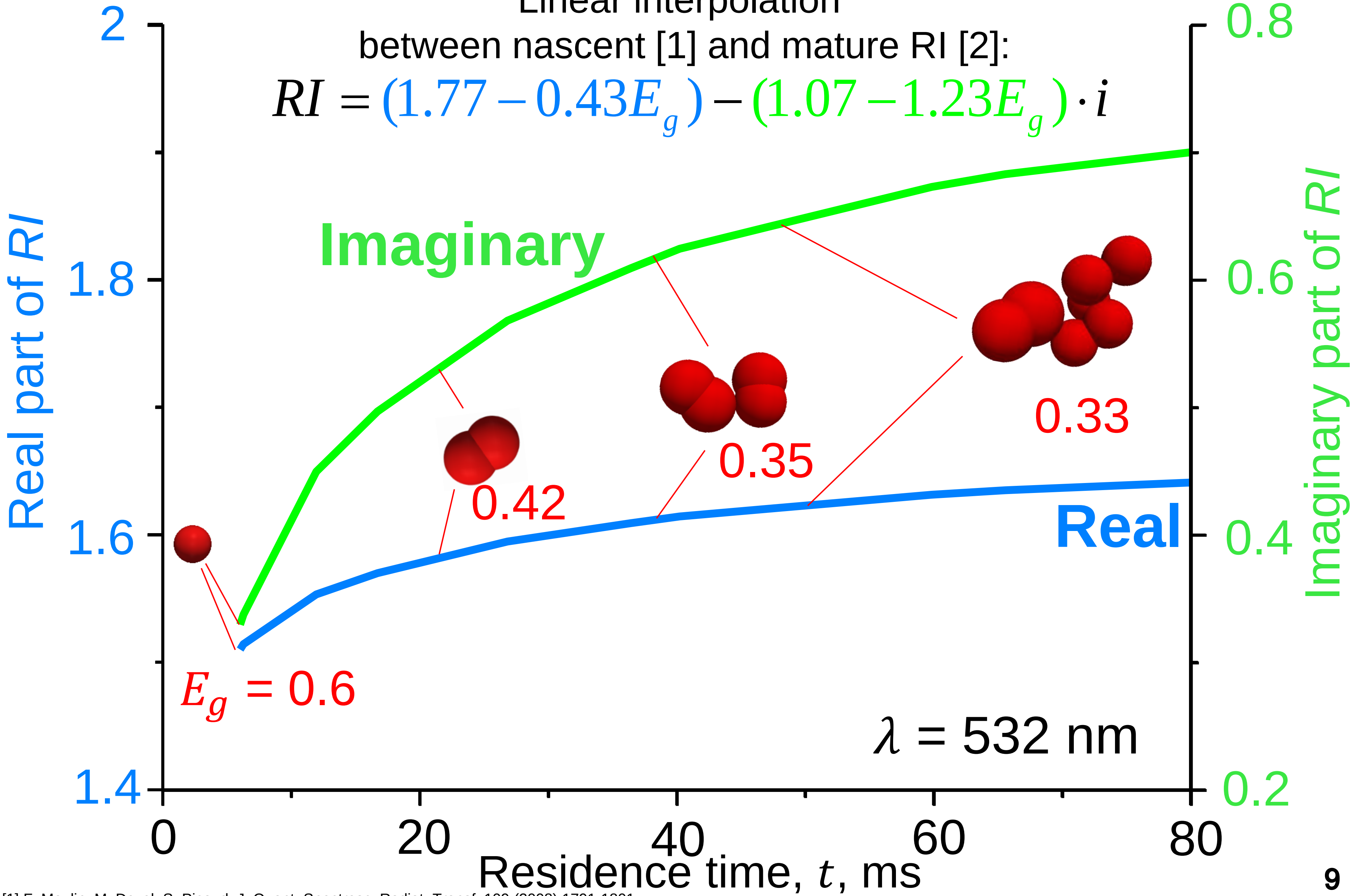

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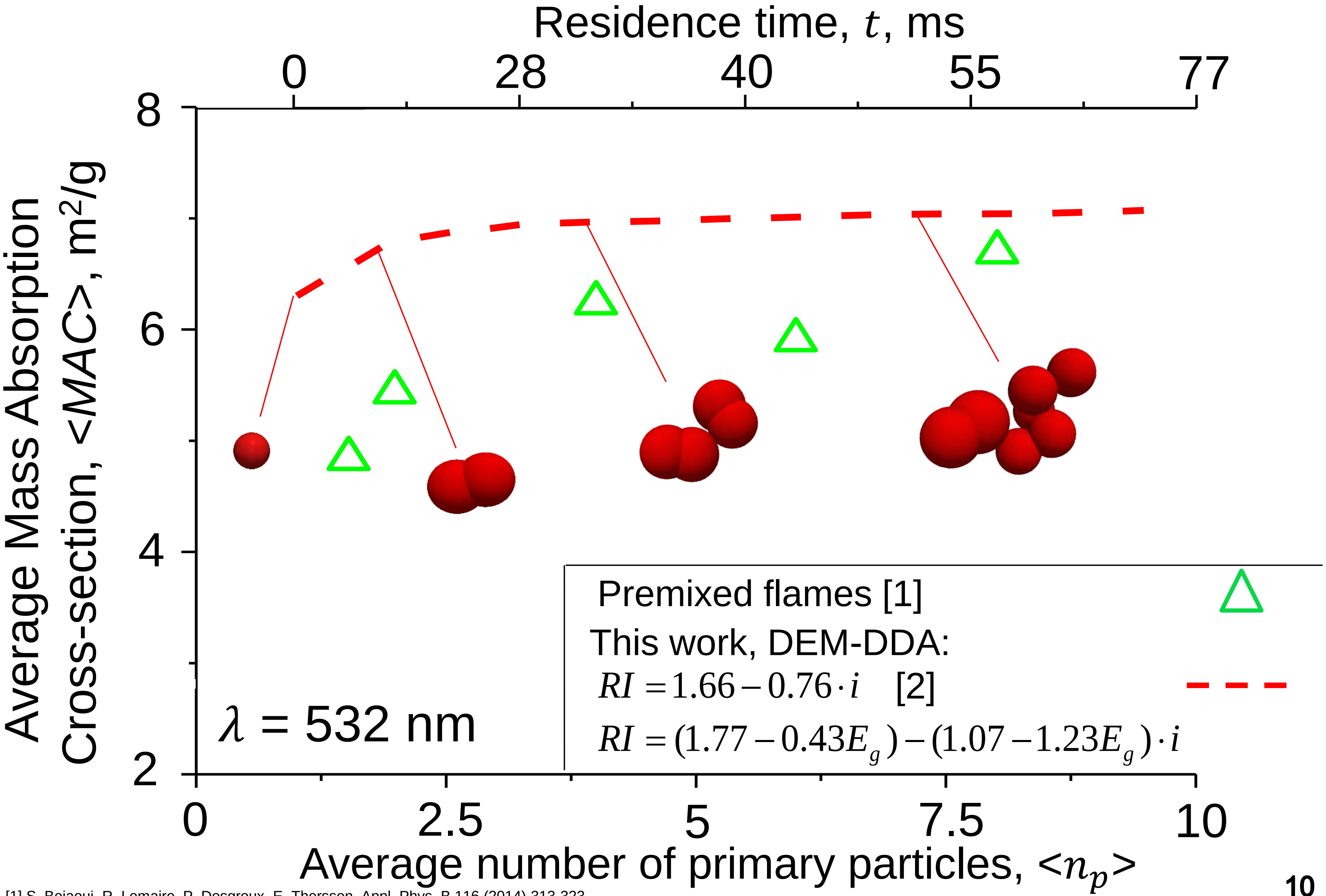
From nascent to mature soot *MAC*



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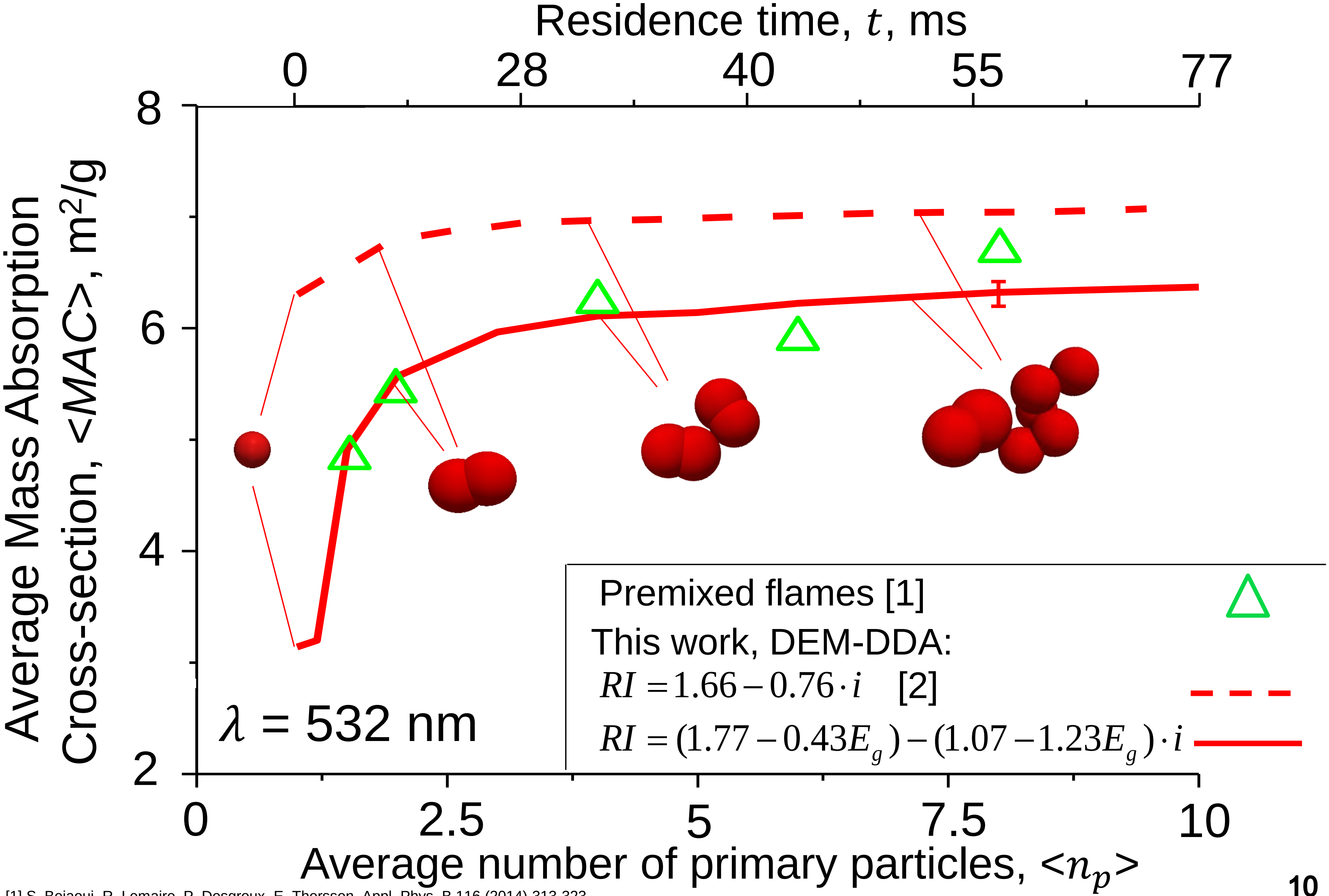

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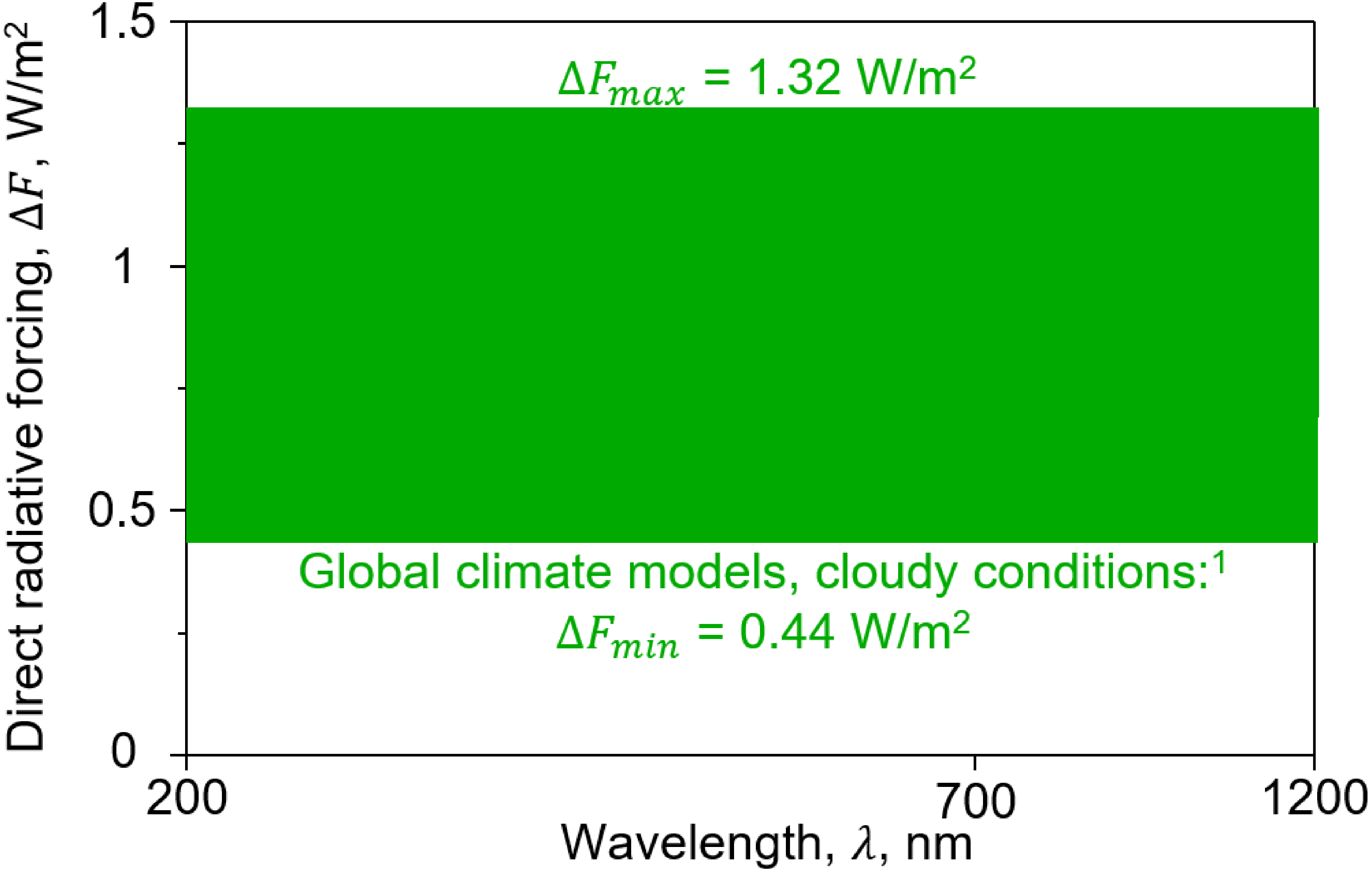
Narrowing soot global warming estimations



[1] Bond, T. C.; Doherty, S. J.; Fahey, D., et al. J Geophys Res 2013, 118, 5380-5552.

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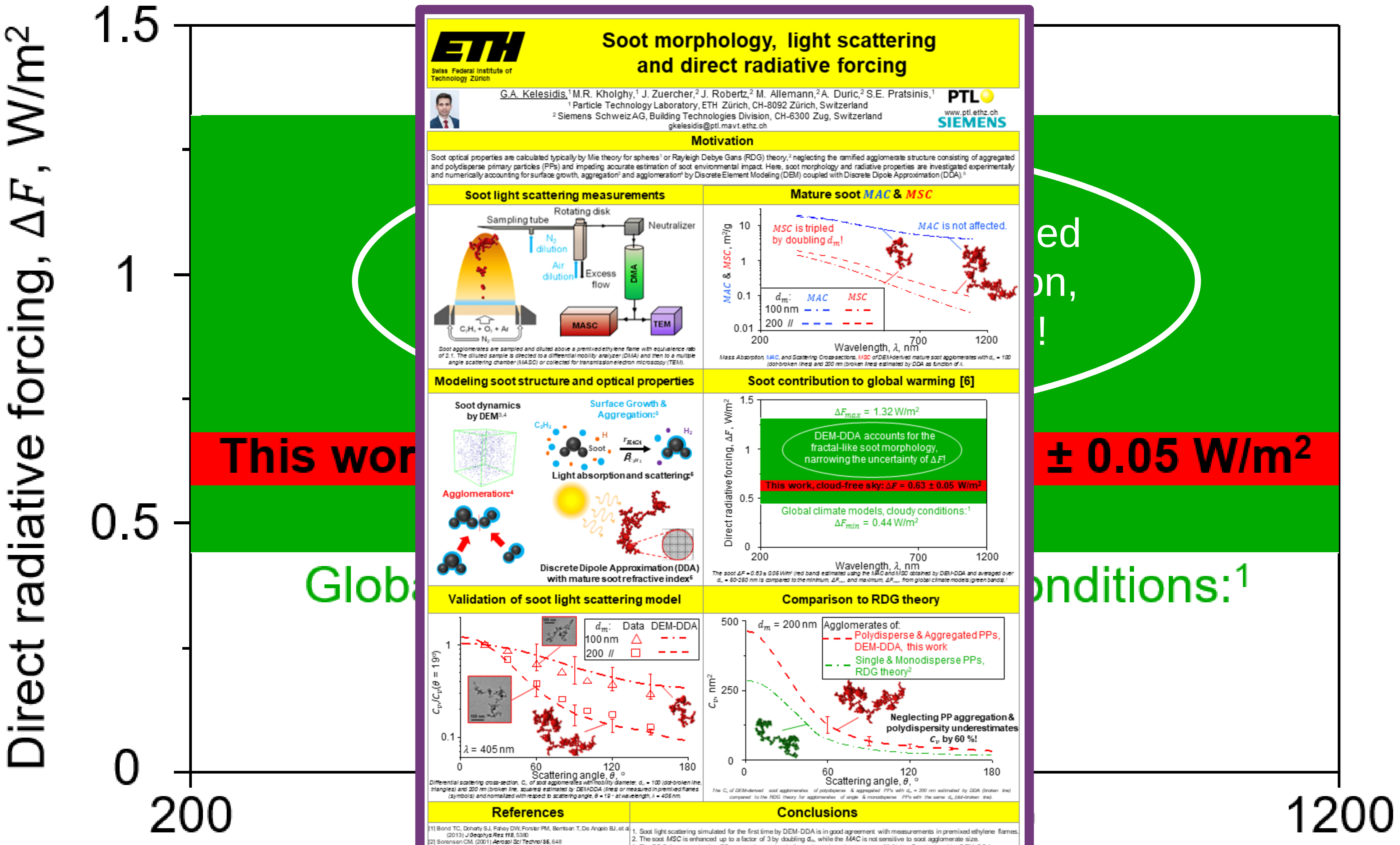

Soot morphology, light scattering and direct radiative forcing

Swiss Federal Institute of Technology Zürich

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SIEMENS

Motivation

Soot optical properties are calculated typically by Mie theory for spheres[1] or Rayleigh Debye Gans (RDG) theory,[2] neglecting the ramified agglomerate structure consisting of aggregated and polydisperse primary particles (PPs) and impeding accurate estimation of soot environmental impact. Here, soot morphology and radiative properties are investigated experimentally and numerically accounting for surface growth, aggregation[3] and agglomeration[4] by Discrete Element Modeling (DEM) coupled with Discrete Dipole Approximation (DDA).[5]

Soot light scattering measurements

Soot agglomerates are sampled and diluted above a premixed ethylene flame with equivalence ratio of 2.1. The diluted sample is directed to a differential mobility analyzer (DMA) and then to a multiple angle scattering chamber (MASC) or collected for transmission electron microscopy (TEM).

Mature soot *MAC* & *MSC*

Mass Absorption, *MAC*, and Scattering Cross-sections, *MSC* of DEM-derived mature soot agglomerates with d_m = 100 (dot-broken lines) and 200 nm (broken lines) estimated by DDA as function of λ.

Modeling soot structure and optical properties

Soot contribution to global warming [6]

The soot ΔF = 0.63 ± 0.05 W/m² (red band) estimated using the MAC and MSC obtained by DEM-DDA and averaged over d_m = 60-250 nm is compared to the minimum, ΔF_{min}, and maximum, ΔF_{max}, from global climate models (green bands).[1]

Validation of soot light scattering model

Differential scattering cross-section, C_v, of soot agglomerates with mobility diameter, d_m = 100 (dot-broken line, triangles) and 200 nm (broken line, squares) estimated by DEM-DDA (lines) or measured in premixed flames (symbols) and normalized with respect to scattering angle, θ = 19 ° at wavelength, λ = 405 nm.

Comparison to RDG theory

The C_v of DEM-derived soot agglomerates of polydisperse & aggregated PPs with d_m = 200 nm estimated by DDA (broken line) compared to the RDG theory for agglomerates of single & monodisperse PPs with the same d_m (dot-broken line).

References

[1] Bond TC, Doherty SJ, Fahey DW, Forster PM, Berntsen T, De Angelo BJ, et al. (2013) *J Geophys Res* **118**, 5380
[2] Sorensen CM. (2001) *Aerosol Sci Technol* **35**, 648
[3] Kelesidis GA, Goudeli E, Pratsinis SE. (2017) *Proc Combust Inst* **36**, 29
[4] Kelesidis GA, Goudeli E, Pratsinis SE. (2017) *Carbon* **121**, 527
[5] Yon J, Bescond A, Liu F. GA. (2015) *J Quant Radiat Transfer* **162**, 197
[6] Chylek P, Wong J. (1995) *Geophys Res Lett* **22**, 929

Conclusions

1. Soot light scattering simulated for the first time by DEM-DDA is in good agreement with measurements in premixed ethylene flames.
2. The soot *MSC* is enhanced up to a factor of 3 by doubling d_m, while the *MAC* is not sensitive to soot agglomerate size.
3. The RDG theory neglecting PP aggregation and polydispersity underestimates up to 60 % the C_v calculated by DEM-DDA.
4. The average *ΔF* = 0.63 ± 0.05 W/m² estimated here for a cloud-free sky is in between the global climate model predictions using the Mie/ RDG theories for cloudy conditions. This indicates that *ΔF* might be overpredicted by these models that need to account for soot structure and polydispersity.

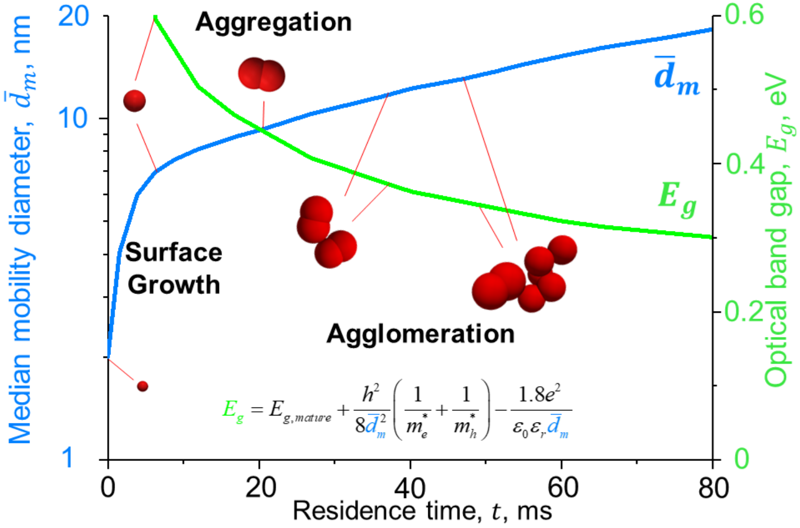
More during the Poster session!

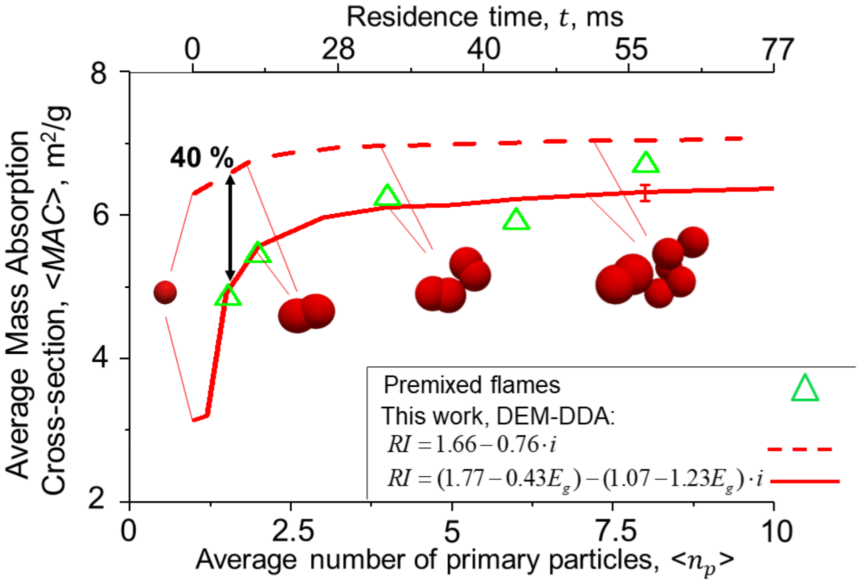
(Today, 15:40)

[1] Bond, T. C.; Doherty, S. J.; Fahey, D., et al. J Geophys Res 2013, 118, 5380-5552.

Conclusions

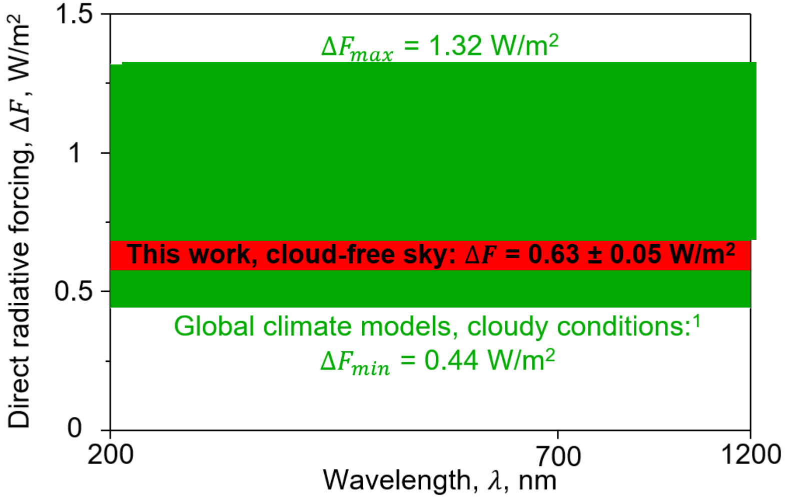
- Soot E_g decreases exponentially with d_m during flame synthesis.





- **Both morphology AND composition needed for *MAC*!**

$$\boxed{RI = (1.77 - 0.43E_g) - (1.07 - 1.23E_g) \cdot i}$$



- **Accounting for soot morphology and composition may narrow *ΔF!***

Thank you for your attention!