ETH zürich

Internal and Surface Soot Oxidation

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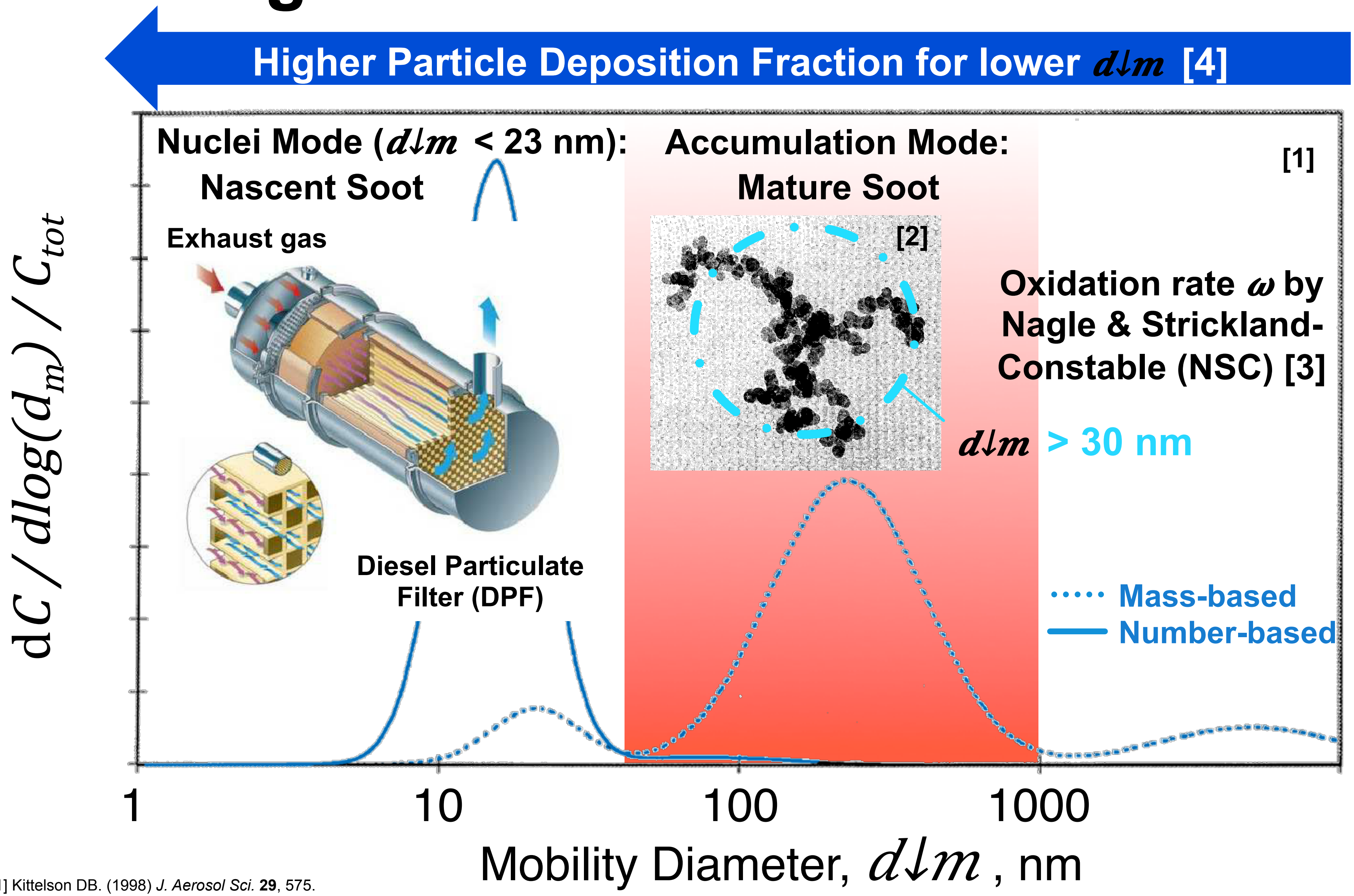
Particle Technology Laboratory, ETH Zürich, Switzerland

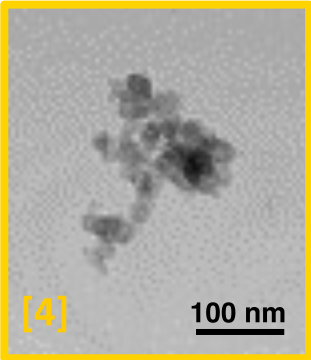
PTL
Particle Technology Laboratory

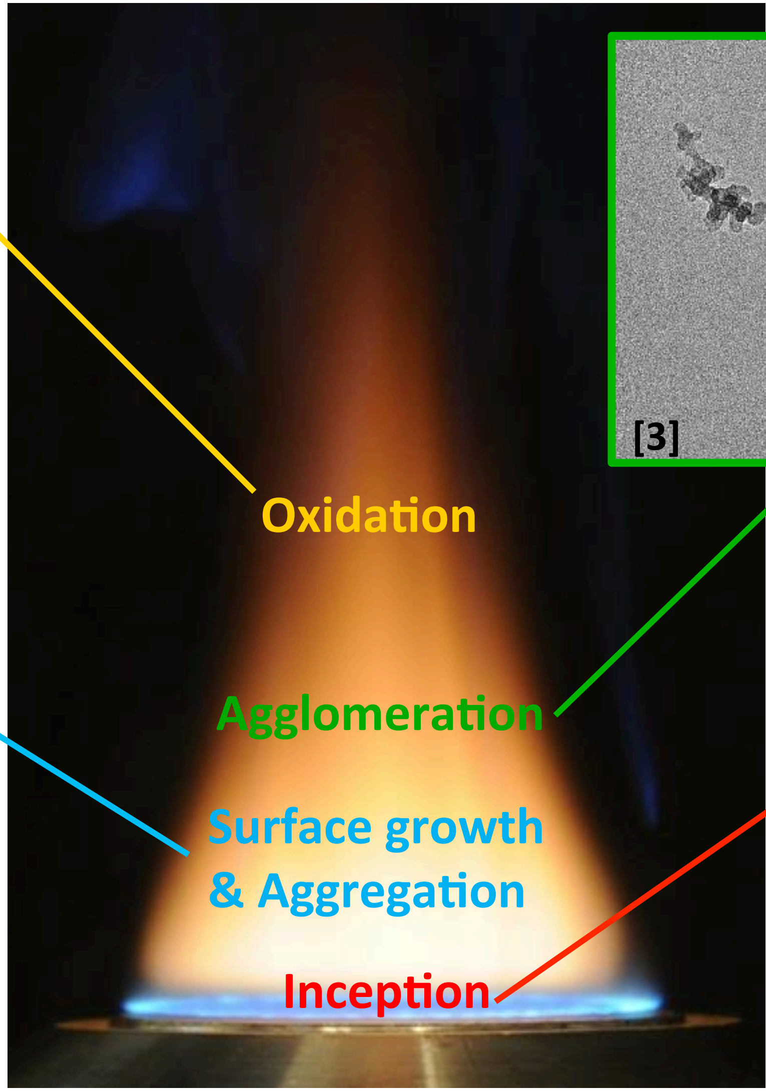
Engine exhaust after-treatment



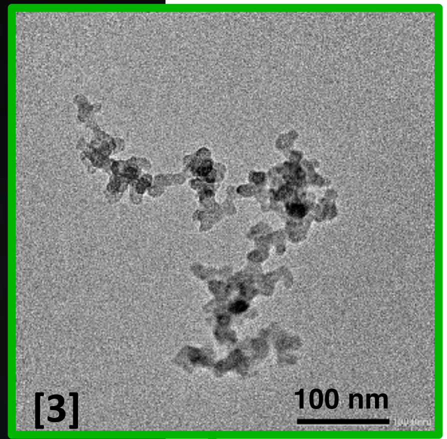
[1] Kittelson DB. (1998) *J. Aerosol Sci.* **29**, 575.
[2] Koylu UO, Faeth GM, Farias TL, Carvalho MG. (2007) *Combust. Flame* **100**, 621.
[3] Nagle J, Strickland-Constable RF. (1961) *Proceedings of the Fifth Conference on Carbon*, **1**, 154.
[4] Rissler J, Swietlicki E, Bengtsson A, Boman C, Pagels J, Sandström T, Blomberg A, Löndahl J. (2012) *J. Aerosol Sci.* **48,** 18.
[5] Giechaskiel B, Manfredi U, Martini G. (2014) *Int. J. Fuels Lubr.* **7**, 950.

Soot formation dynamics





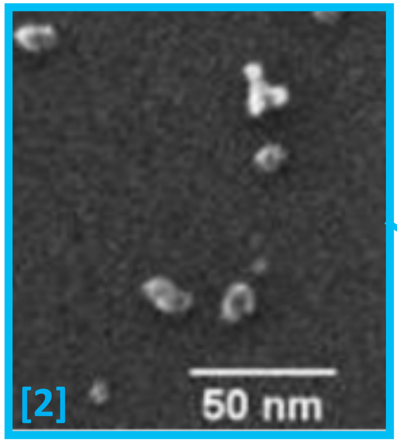
Ethylene Combustion



Mature soot:

d↓m > 30 nm

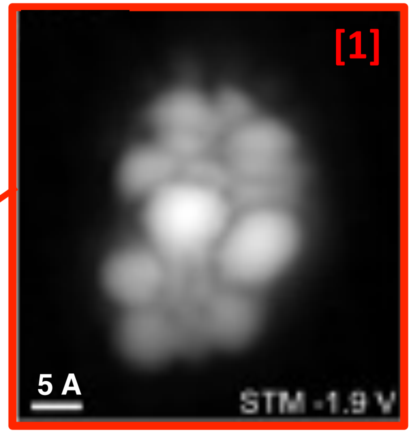
Accumulation mode



Nascent soot:

3 nm < d↓m < 30 nm

Nucleation mode

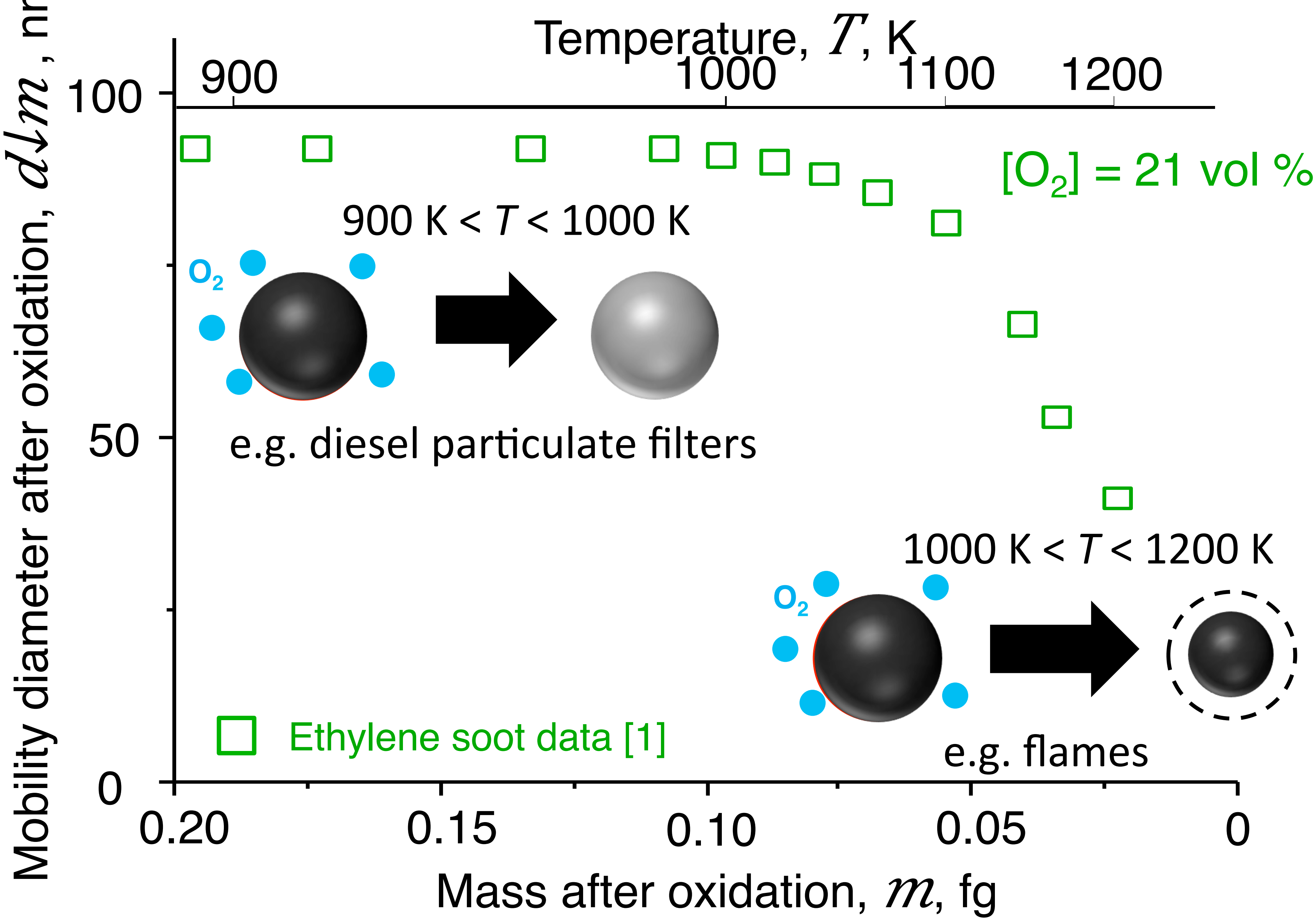


Incipient soot:

d↓m < 3 nm

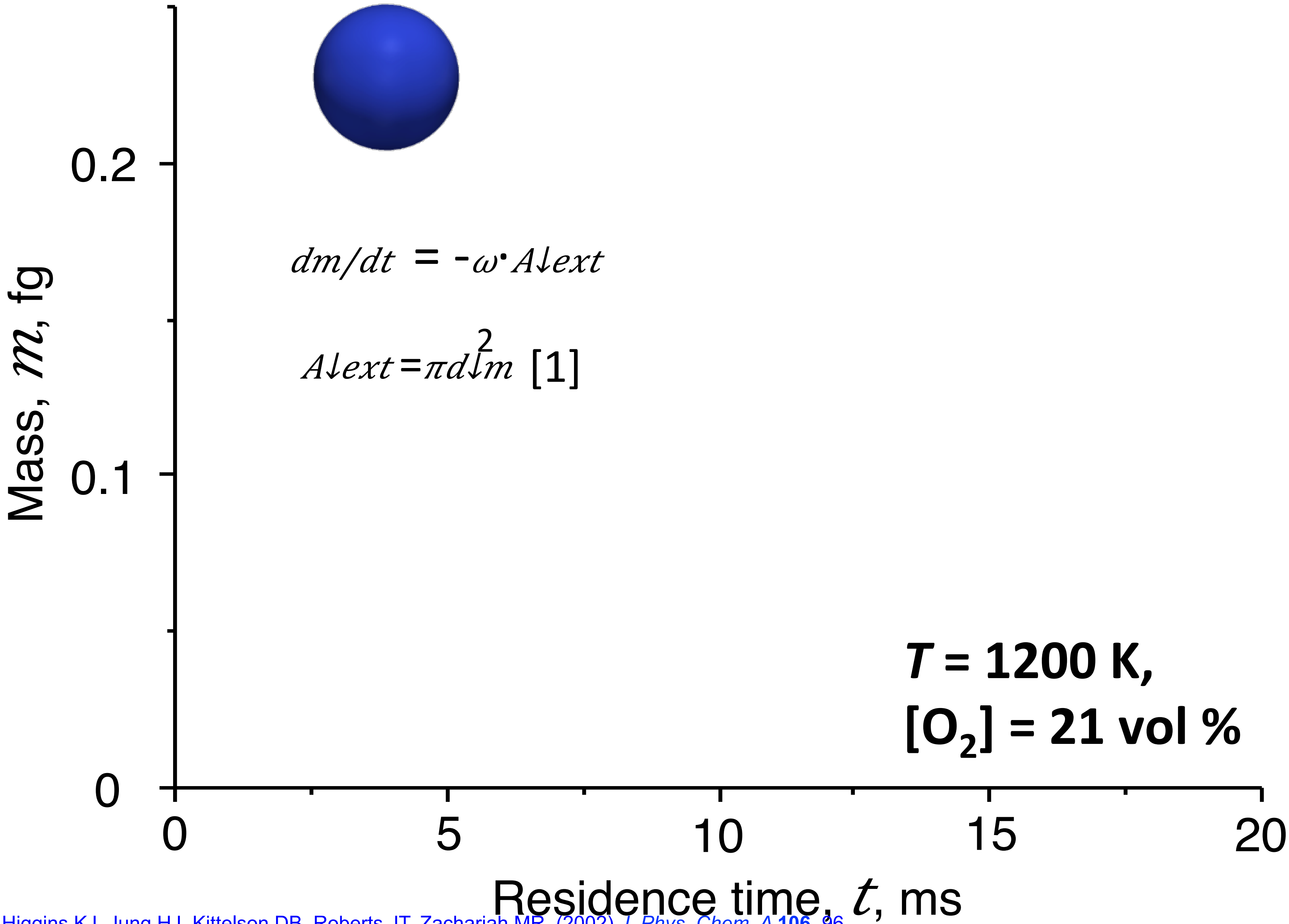
[1] Schultz F, Commodo M, Kaiser K, De Falco G, Minutolo P, Meyer G, D'Anna A, Gross L. (2019) *Proc. Combust. Inst.* **37**, 885.
[2] Schenk M, Lieb S, Vieker H, Beyer A, Golzhauser A, Wang H, Kohse-Hoinghaus K. (2013) *ChemPhysChem* **14**, 3248.
[3] Kelesidis GA, Kholghy MR, Zurcher J, Robertz J, Allemann M, Duric A, Pratsinis SE. (2019) *Powder Technol.* in press.
[4] Jung HJ, Kittelson DB, Zachariah MR. (2004) *Combust. Flame* **136**, 445.

Internal & Surface Oxidation



[1] Ma X, Zangmeister CD, Zachariah MR. (2013) *J. Phys. Chem. C* **117**, 10723.

Soot oxidation dynamics

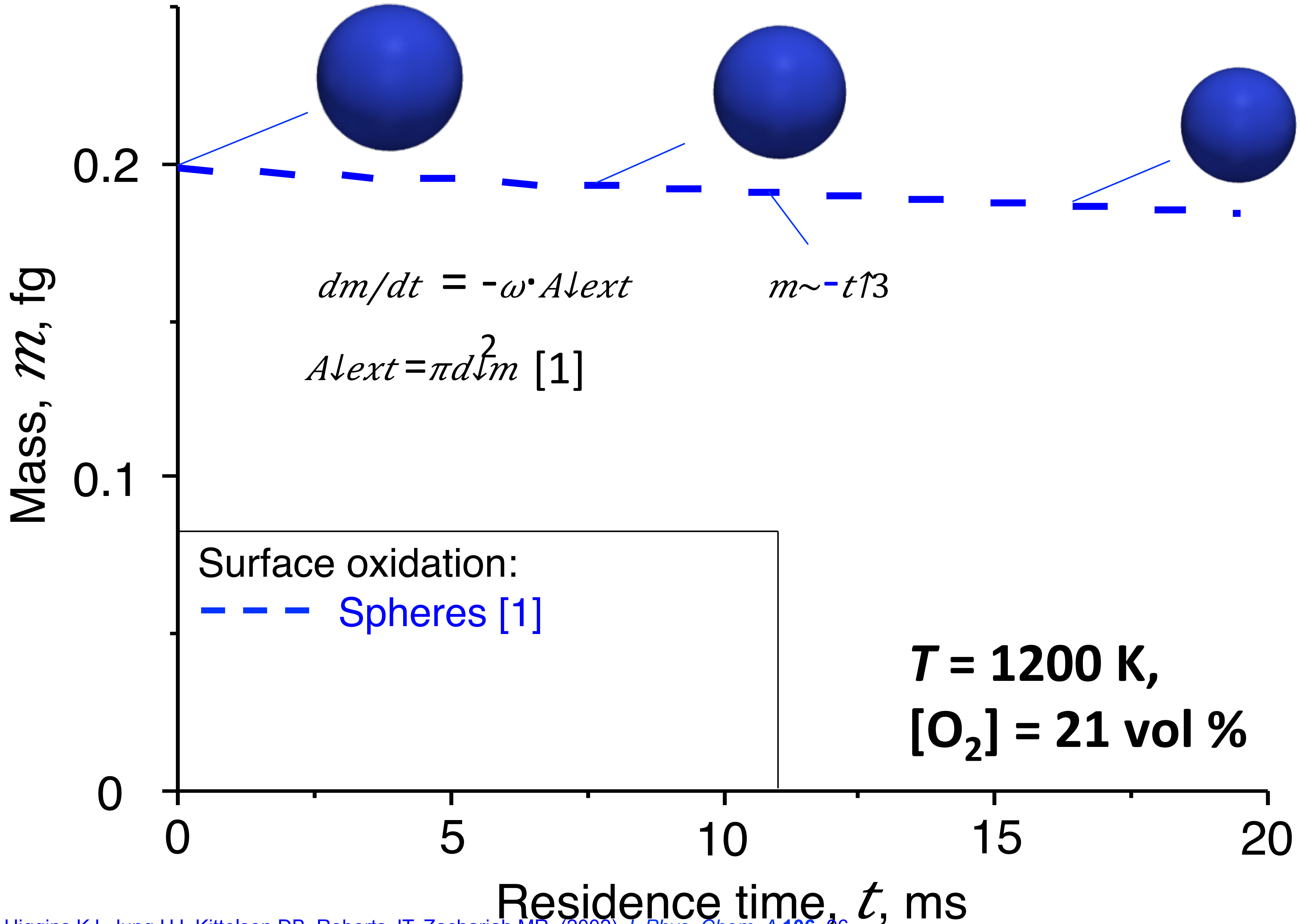


$$dm/dt = -\omega \cdot A_{ext}$$

$$A_{ext} = \pi d_m^2 \text{ [1]}$$

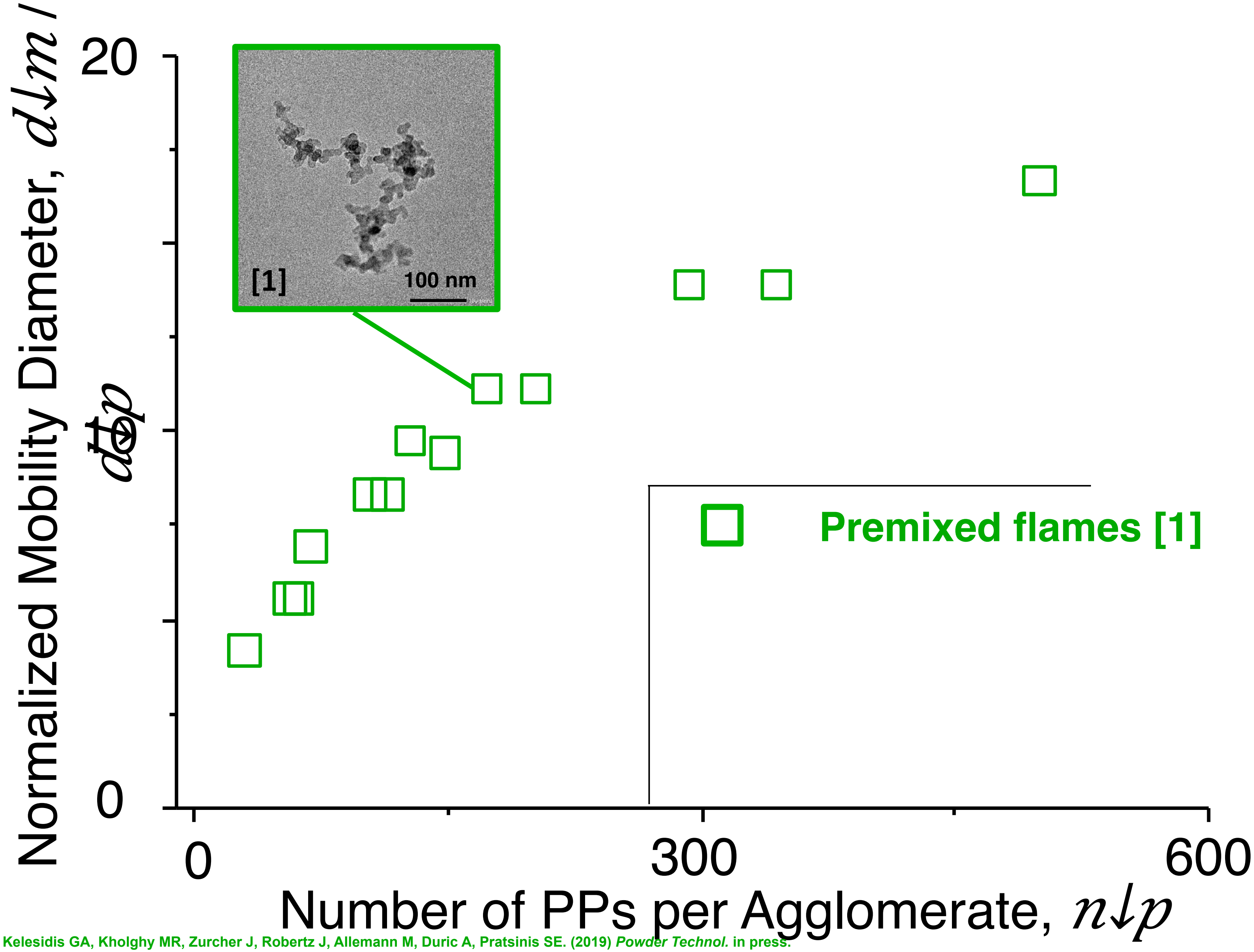
[1] Higgins KJ, Jung HJ, Kittelson DB, Roberts JT, Zachariah MR. (2002) *J. Phys. Chem. A* **106**, 96.

Soot oxidation dynamics



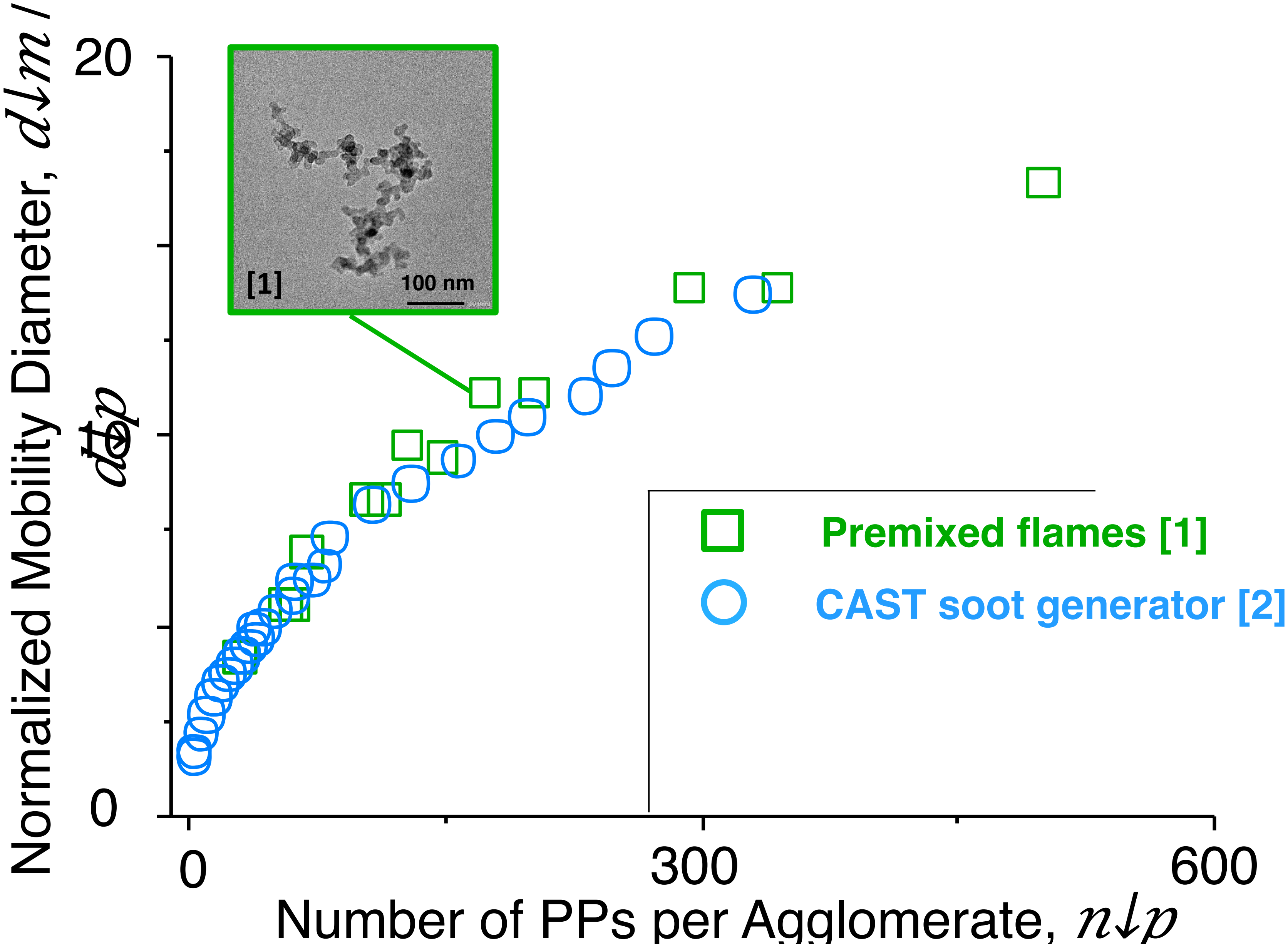
[1] Higgins KJ, Jung HJ, Kittelson DB, Roberts JT, Zachariah MR. (2002) *J. Phys. Chem. A* **106**, 96.

Soot agglomerate morphology



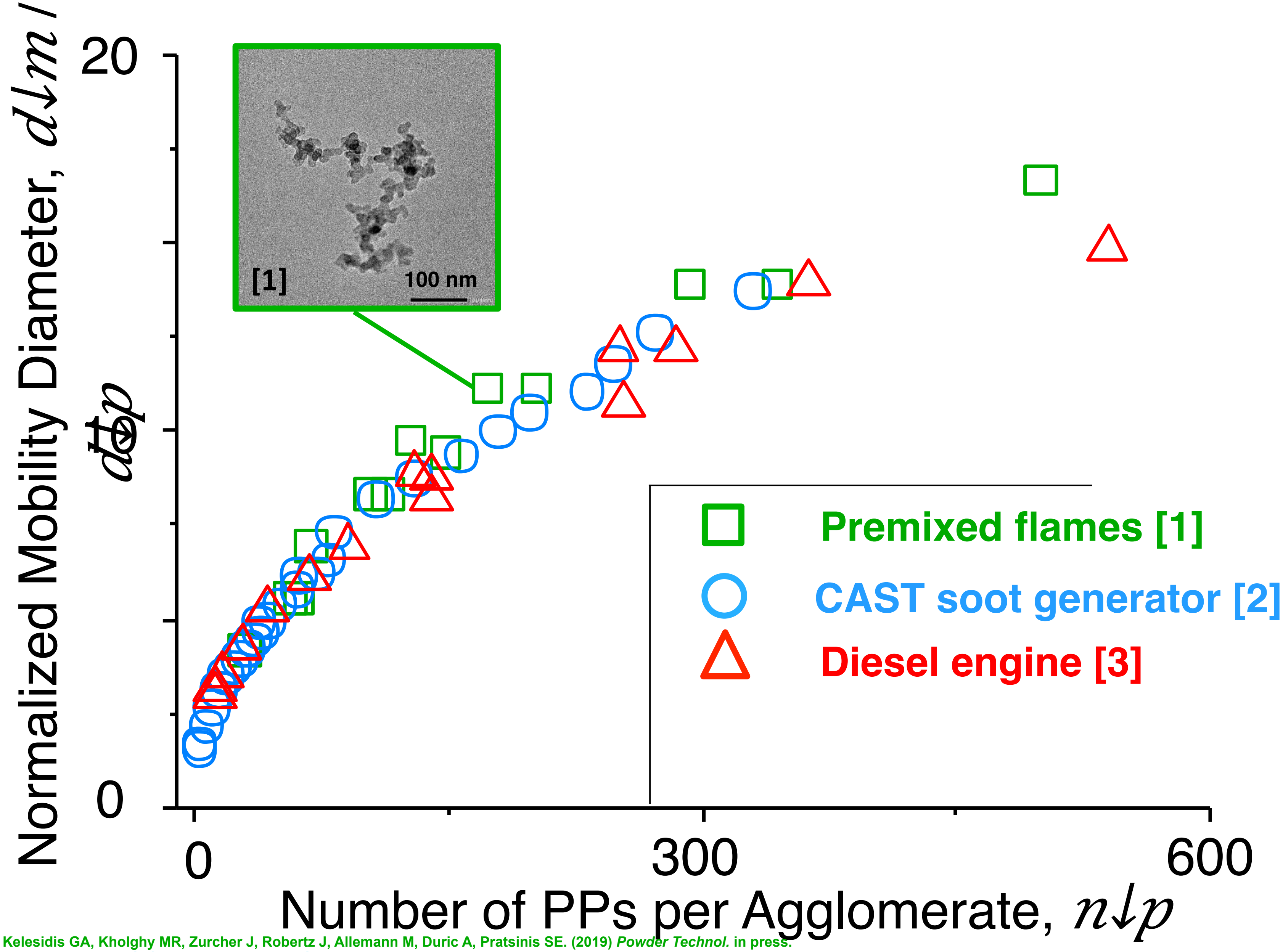
[1] Kelesidis GA, Kholghy MR, Zurcher J, Robertz J, Allemann M, Duric A, Pratsinis SE. (2019) *Powder Technol.* in press.

Soot agglomerate morphology



[1] Kelesidis GA, Kholghy MR, Zurcher J, Robertz J, Allemann M, Duric A, Pratsinis SE. (2019) *Powder Technol.* in press.
[2] Yon J, Bescond A, Ouf FX. (2015) *J. Aerosol Sci.* 87, 28.

Soot agglomerate morphology



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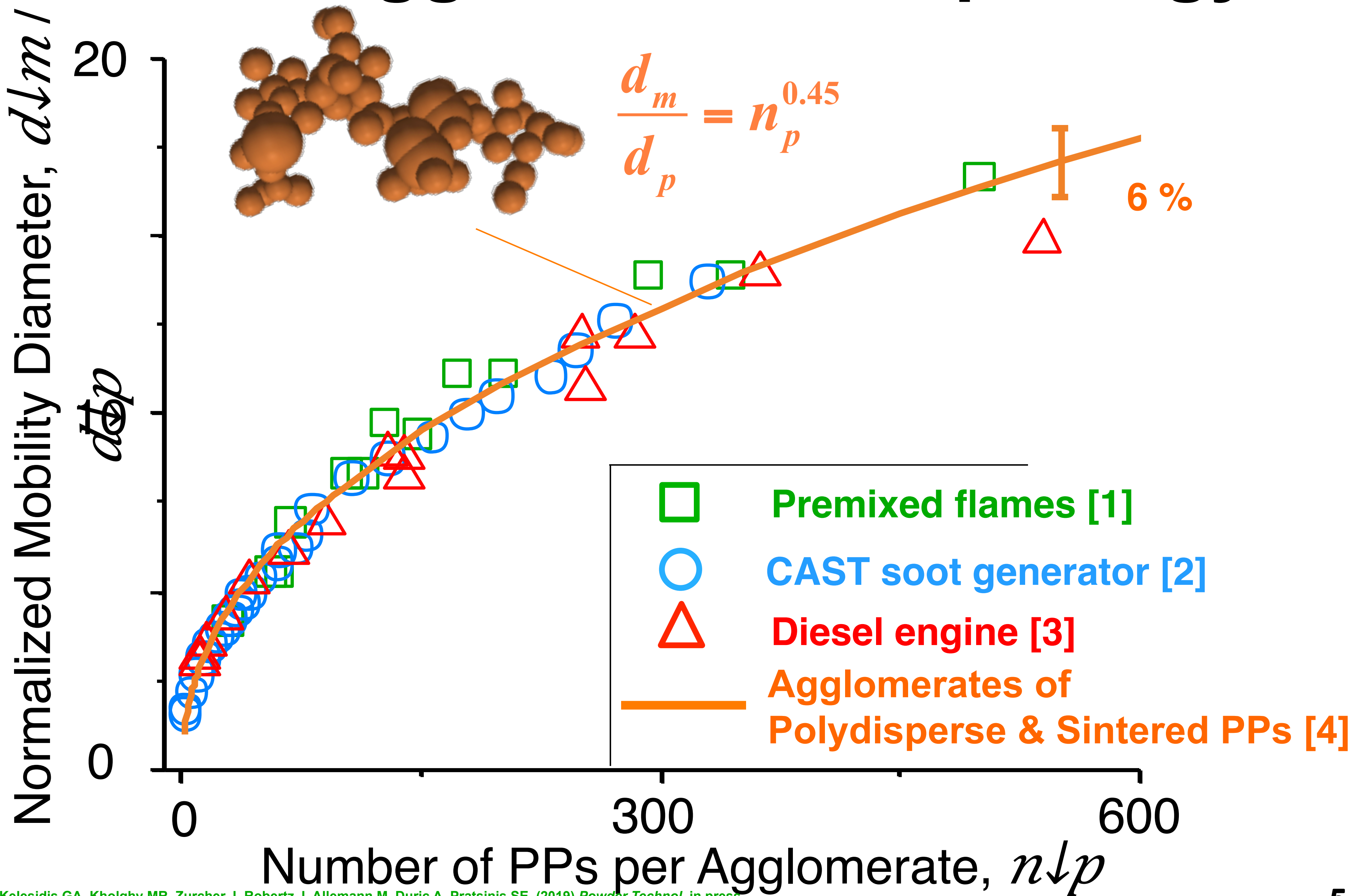
[2] Yon J, Bescond A, Ouf FX. (2015) *J. Aerosol Sci.* 87, 28.
[3] Rissler J, Messing ME, Malik AI, Nilsson PT, Nordin EZ, Bohgard M, Sanati M, Pagels JH. (2013) *Aerosol Sci. Technol.* 47, 792.

Soot agglomerate morphology



[1] Kelesidis GA, Kholghy MR, Zurcher J, Robertz J, Allemann M, Duric A, Pratsinis SE. (2019) *Powder Technol.* in press.
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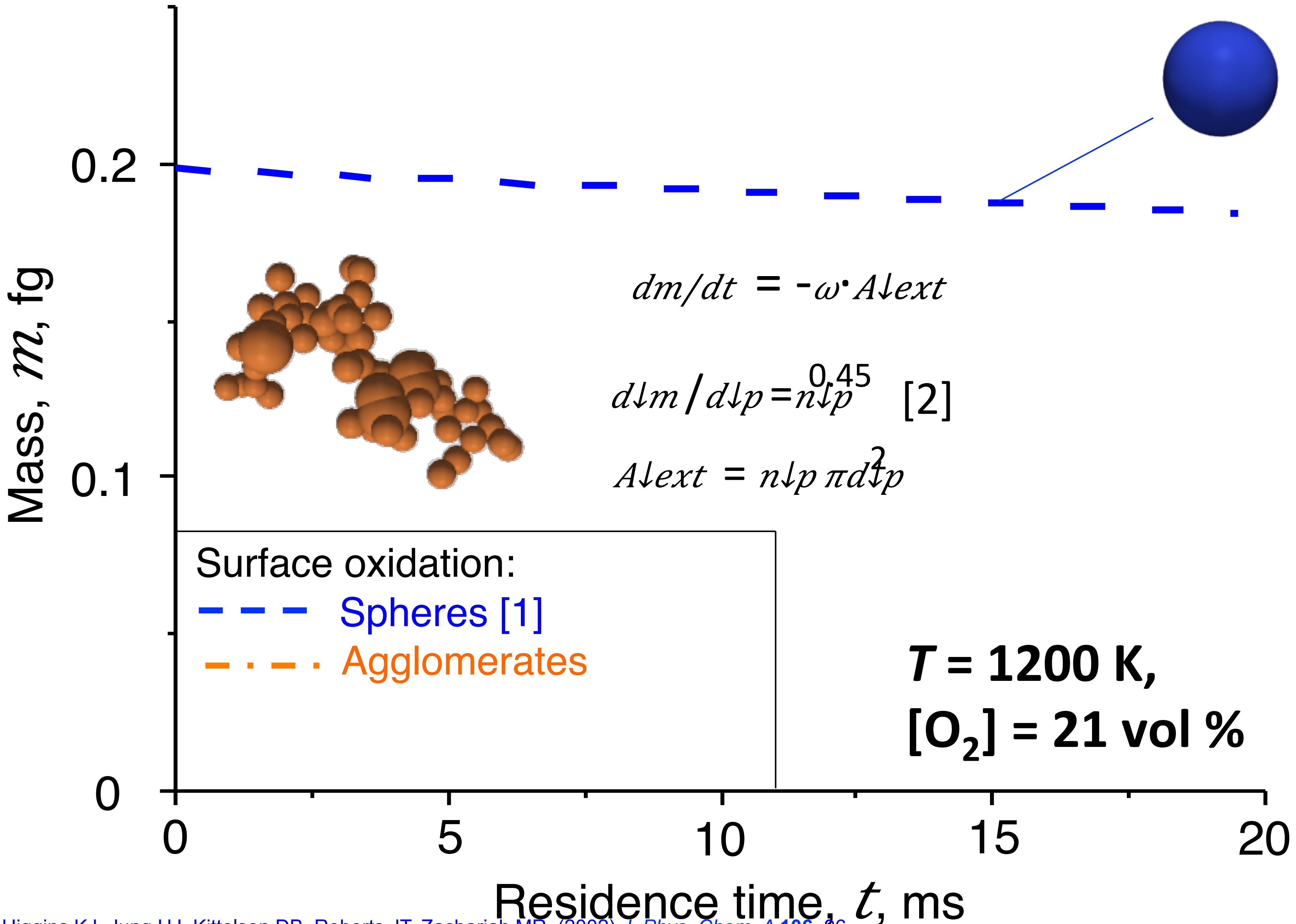
[4] Kelesidis GA, Goudeli E, Pratsinis SE. *Carbon* (2017) 121, 527.

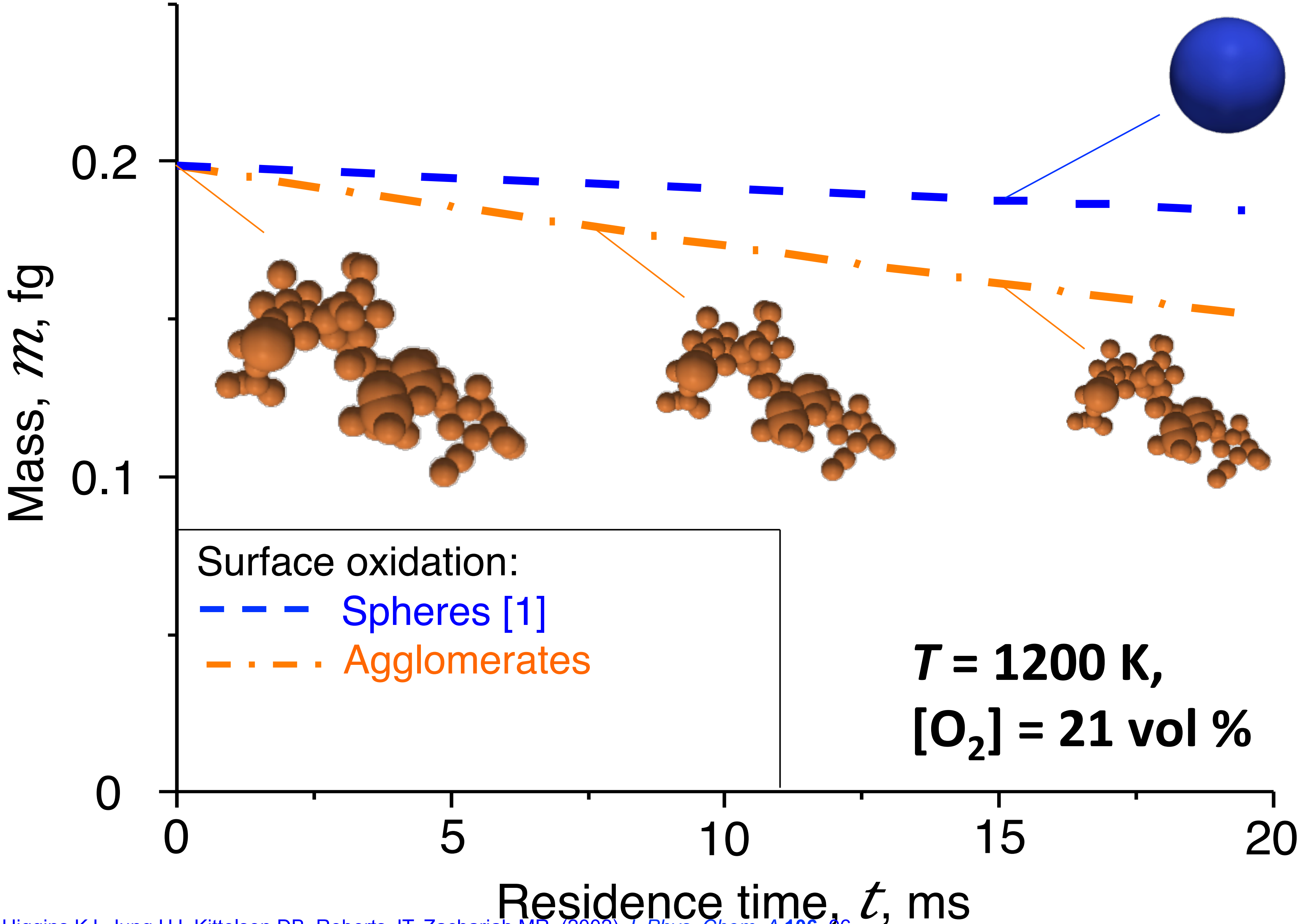
Soot oxidation dynamics



[1] Higgins KJ, Jung HJ, Kittelson DB, Roberts JT, Zachariah MR. (2002) *J. Phys. Chem. A* **106**, 96.

[2] Kelesidis GA, Goudeli E, Pratsinis SE. *Carbon* (2017) **121**, 527.

Soot oxidation dynamics



[1] Higgins KJ, Jung HJ, Kittelson DB, Roberts JT, Zachariah MR. (2002) *J. Phys. Chem. A* **106**, 96.

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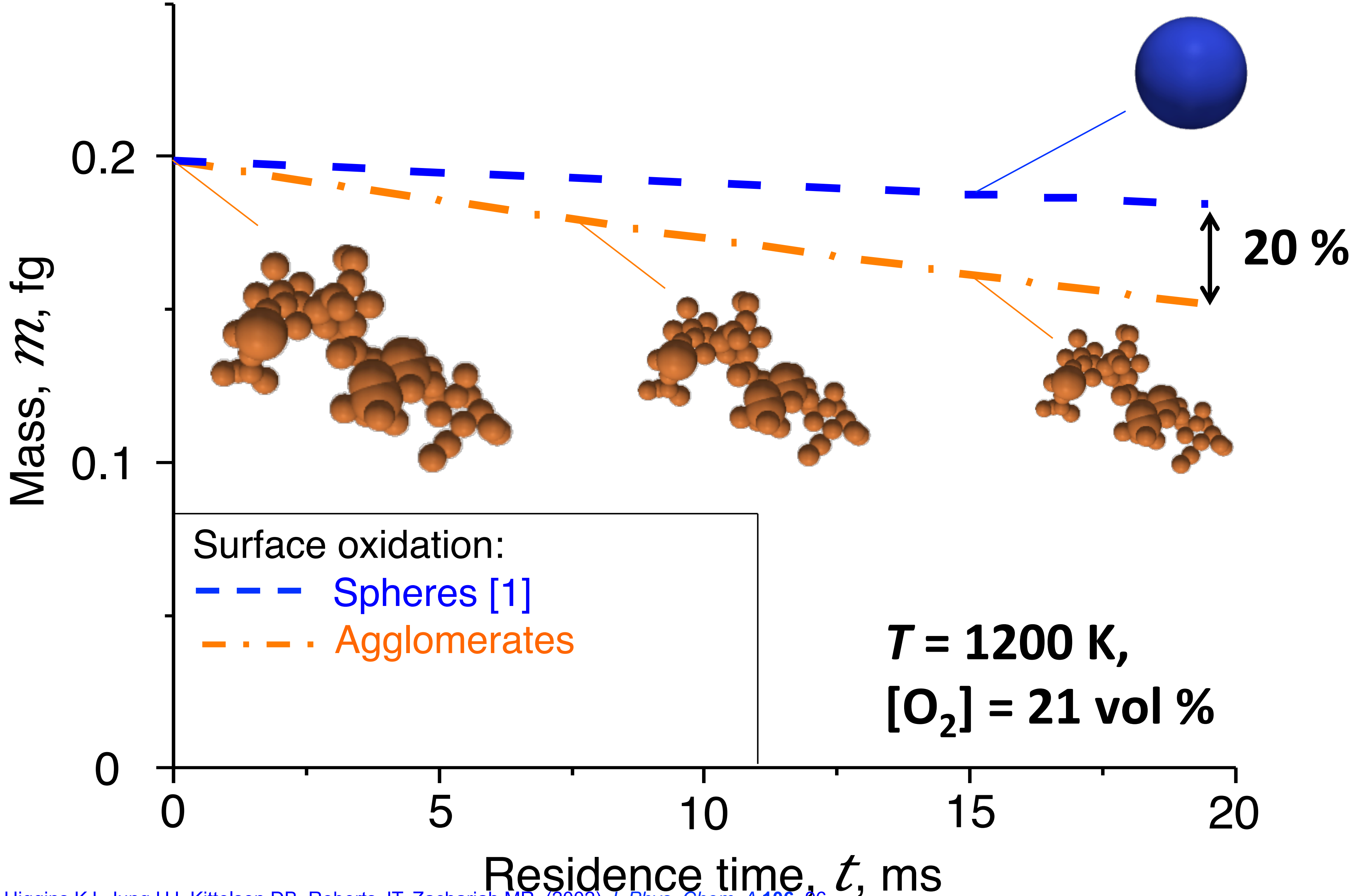
Soot oxidation dynamics



[1] Higgins KJ, Jung HJ, Kittelson DB, Roberts JT, Zachariah MR. (2002) *J. Phys. Chem. A* **106**, 96.

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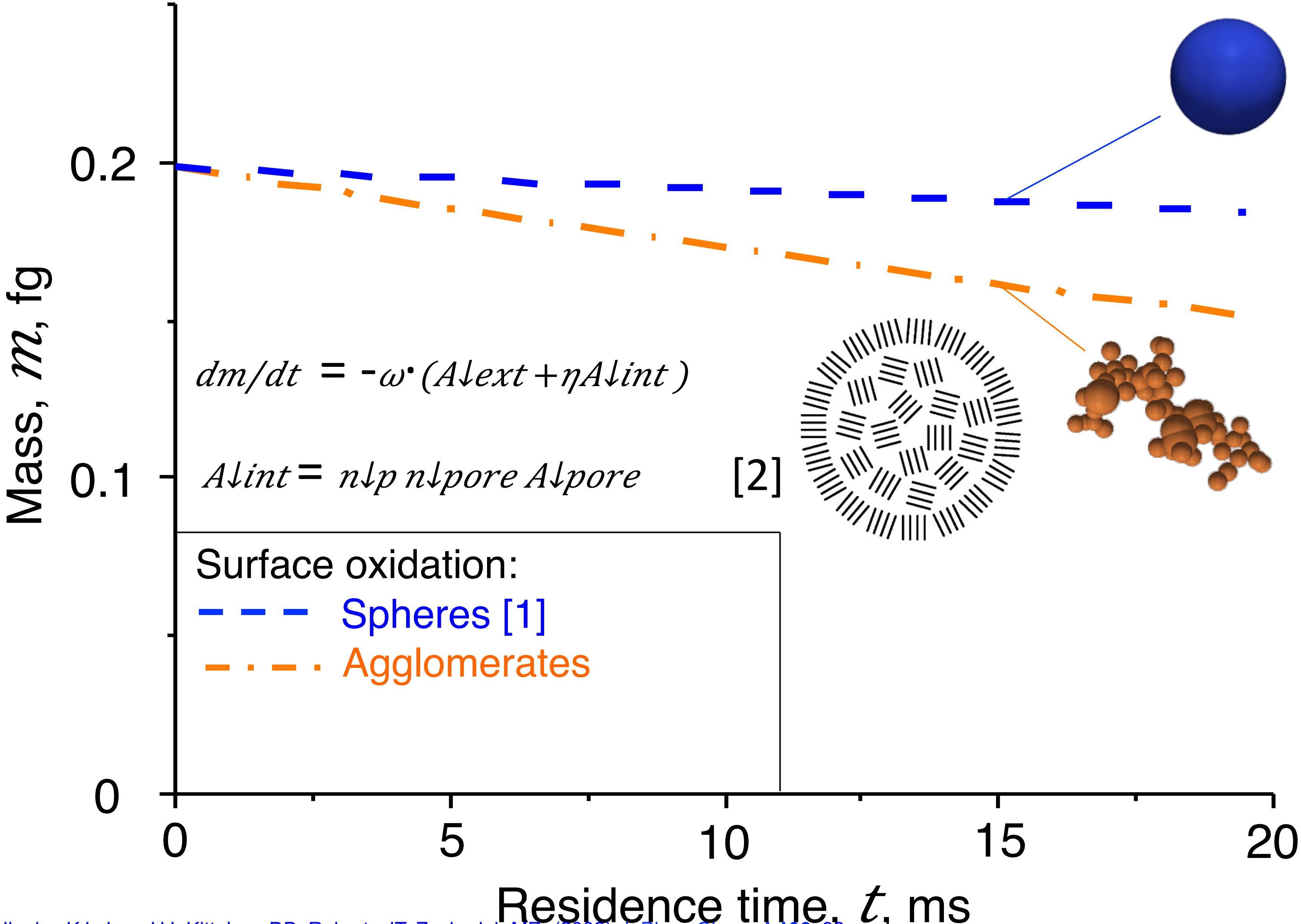
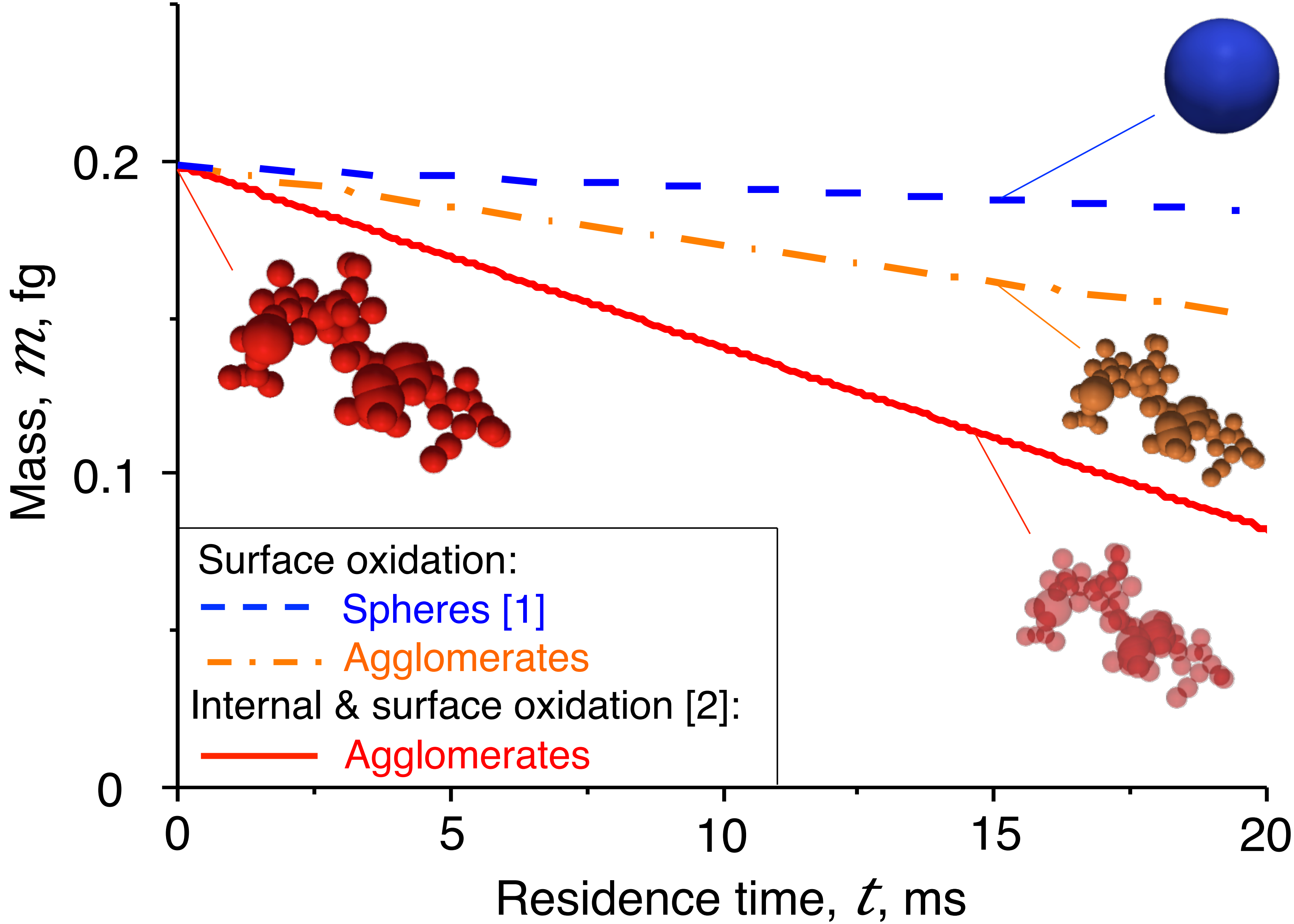


[1] Higgins KJ, Jung HJ, Kittelson DB, Roberts JT, Zachariah MR. (2002) *J. Phys. Chem. A* **106**, 96.

[2] Sirignano M, Kent J, D'Anna A. (2013) *Energy Fuels* **27**, 2303.

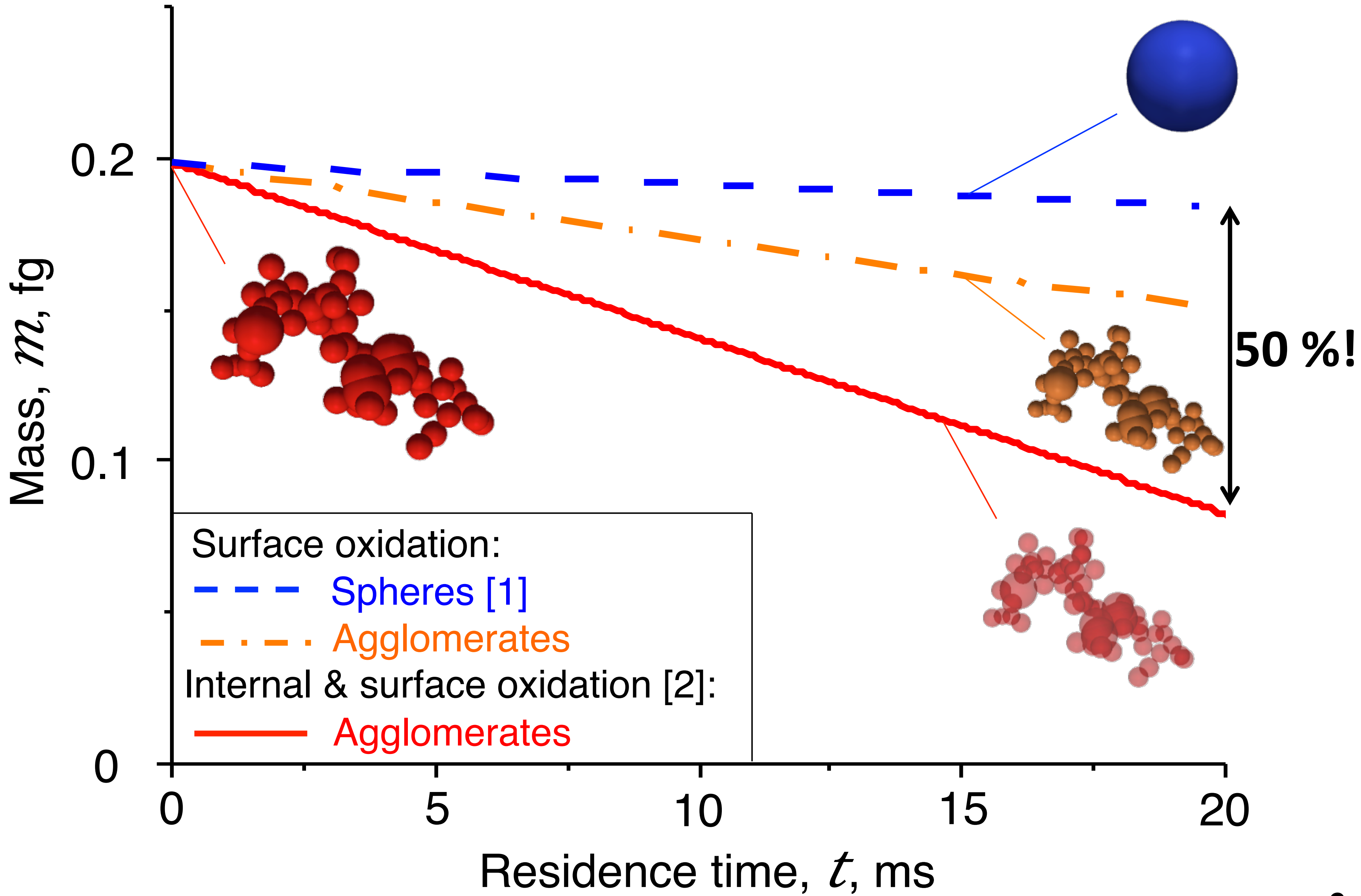
Soot oxidation dynamics



[1] Higgins KJ, Jung HJ, Kittelson DB, Roberts JT, Zachariah MR. (2002) *J. Phys. Chem. A* **106**, 96.

[2] Kelesidis GA, Pratsinis SE. *Combust. Flame*, under peer review.

Soot oxidation dynamics



[1] Higgins KJ, Jung HJ, Kittelson DB, Roberts JT, Zachariah MR. (2002) *J. Phys. Chem. A* **106**, 96.

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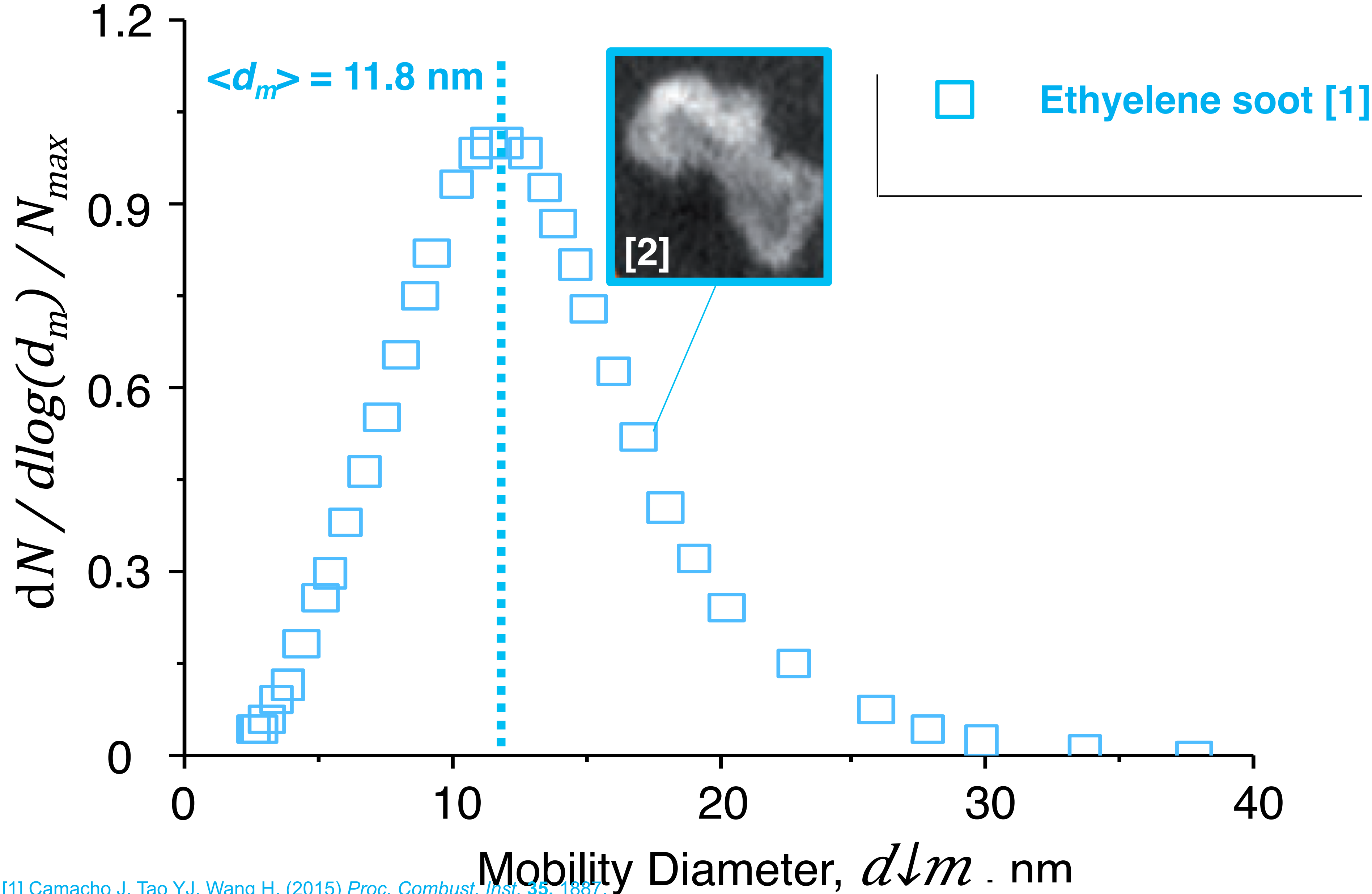
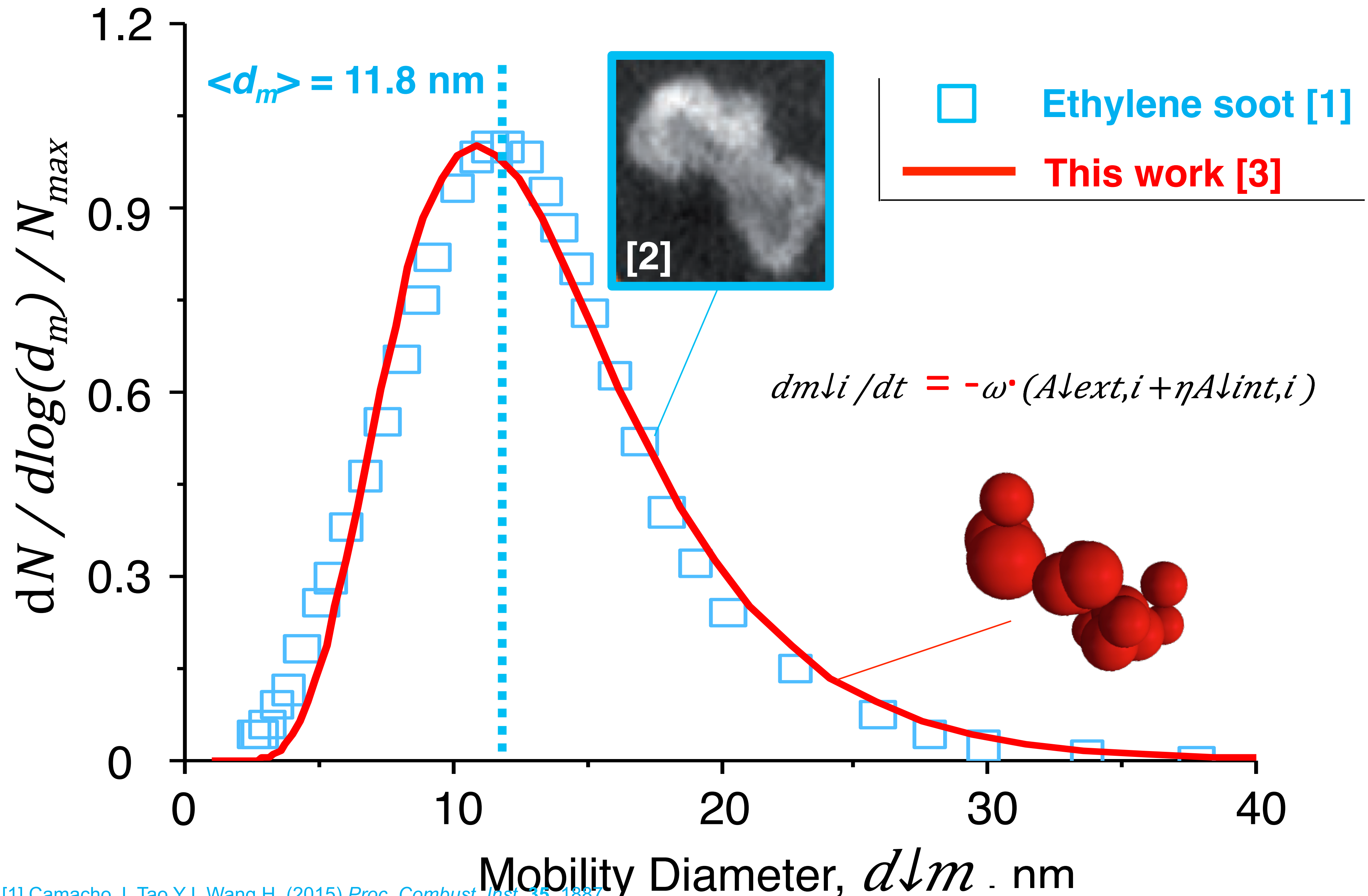
Oxidation of Nascent Soot, *t* = 0 ms



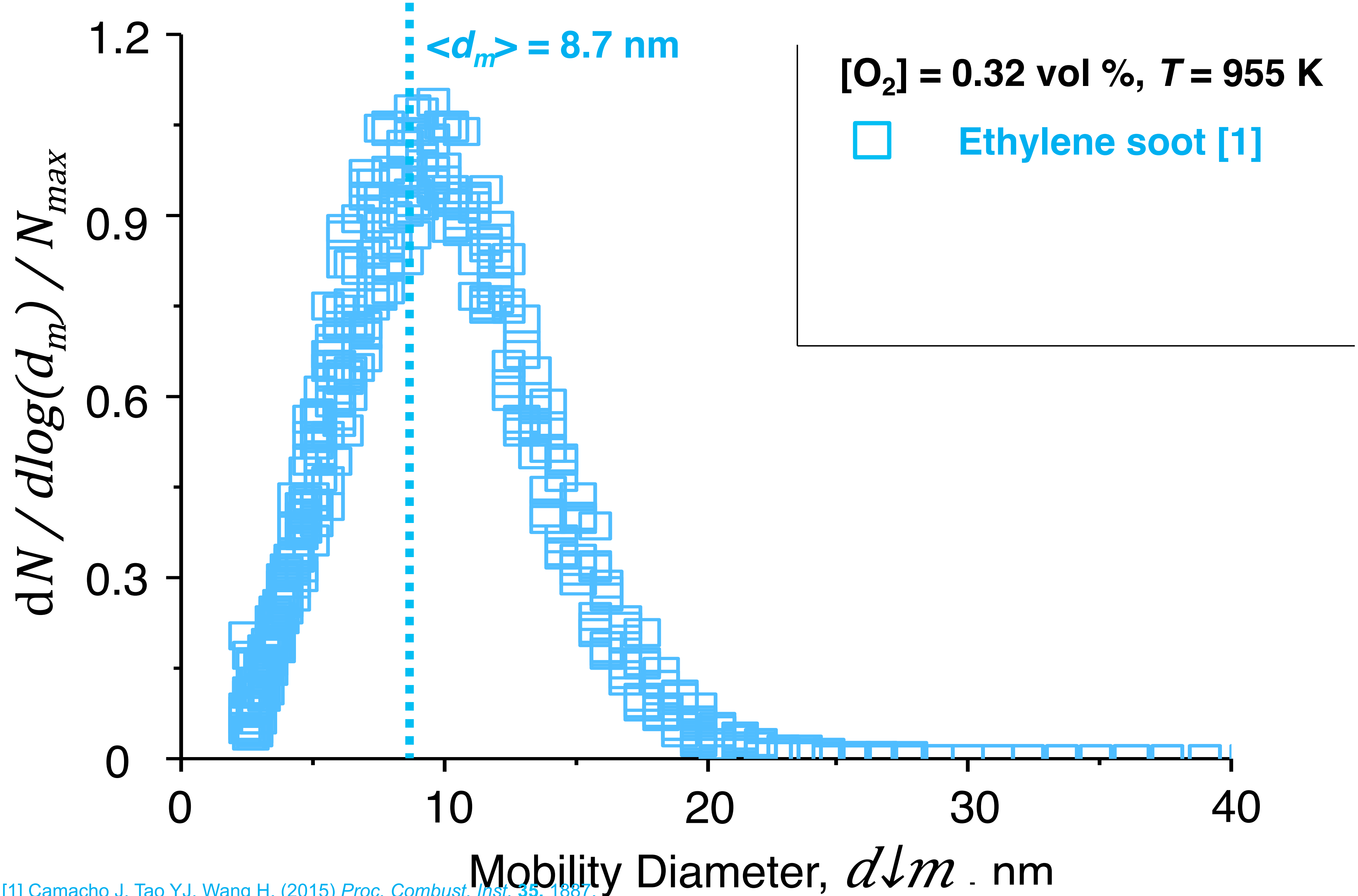
[1] Camacho J, Tao YJ, Wang H. (2015) *Proc. Combust. Inst.* **35**, 1887.
[2] Schenk M, Lieb S, Vieker H, Beyer A, Golzhauser A, Wang H, Kohse-Hoinghaus K. (2013) *ChemPhysChem* **14**, 3248.

Oxidation of Nascent Soot, *t* = 0 ms



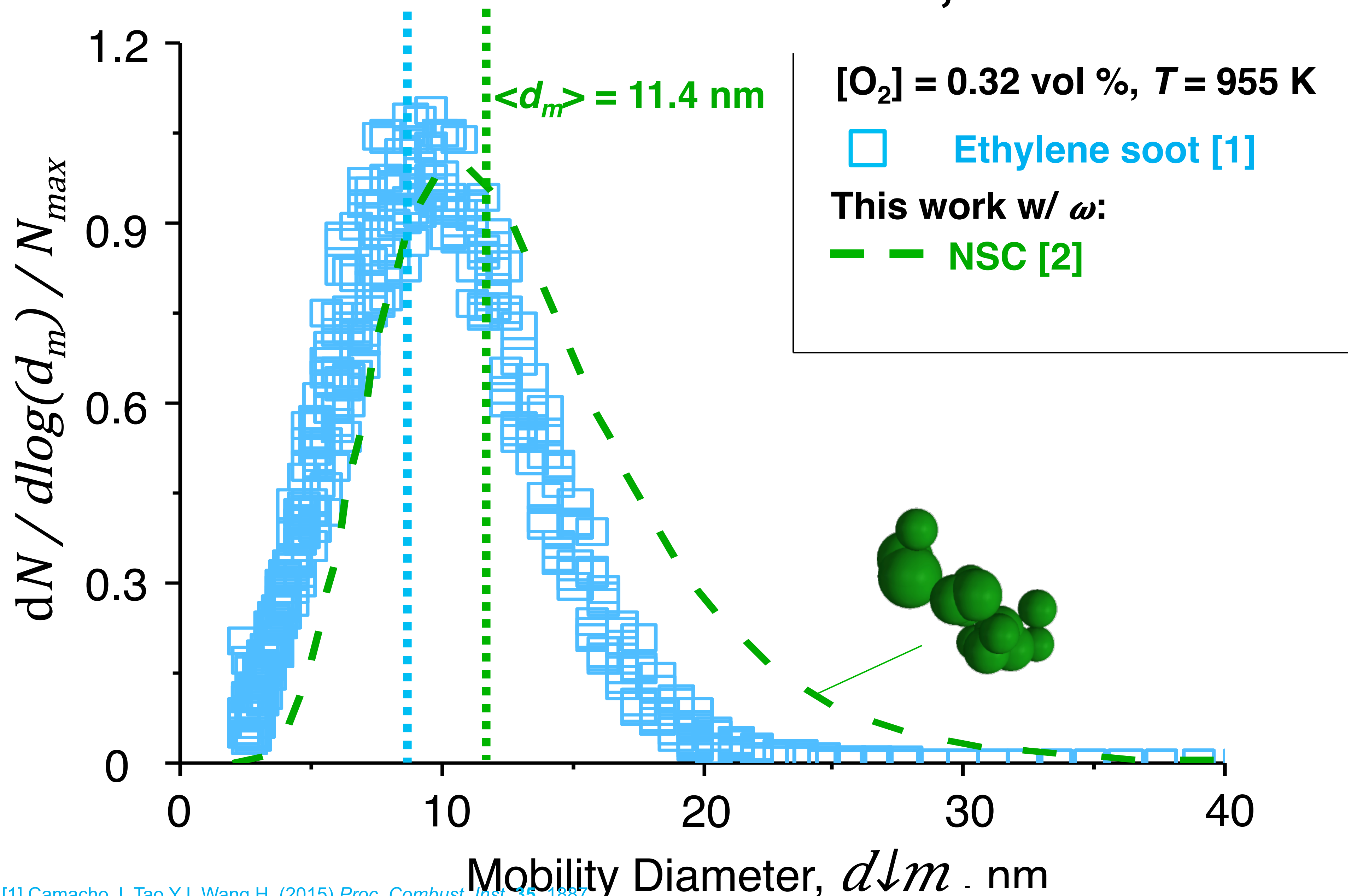
[1] Camacho J, Tao YJ, Wang H. (2015) *Proc. Combust. Inst.* **35**, 1887.
[2] Schenk M, Lieb S, Vieker H, Beyer A, Golzhauser A, Wang H, Kohse-Hoinghaus K. (2013) *ChemPhysChem* **14**, 3248.
[3] Kelesidis GA, Pratsinis SE. *Combust. Flame*, under peer review.

Oxidation of Nascent Soot, t = 217 ms



[1] Camacho J, Tao YJ, Wang H. (2015) *Proc. Combust. Inst.* 35, 1887.

Oxidation of Nascent Soot, t = 217 ms



[1] Camacho J, Tao YJ, Wang H. (2015) *Proc. Combust. Inst.* **35**, 1887.
[2] Nagle J, Strickland-Constable RF. (1961) *Proceedings of the Fifth Conference on Carbon*, **1**, 154.

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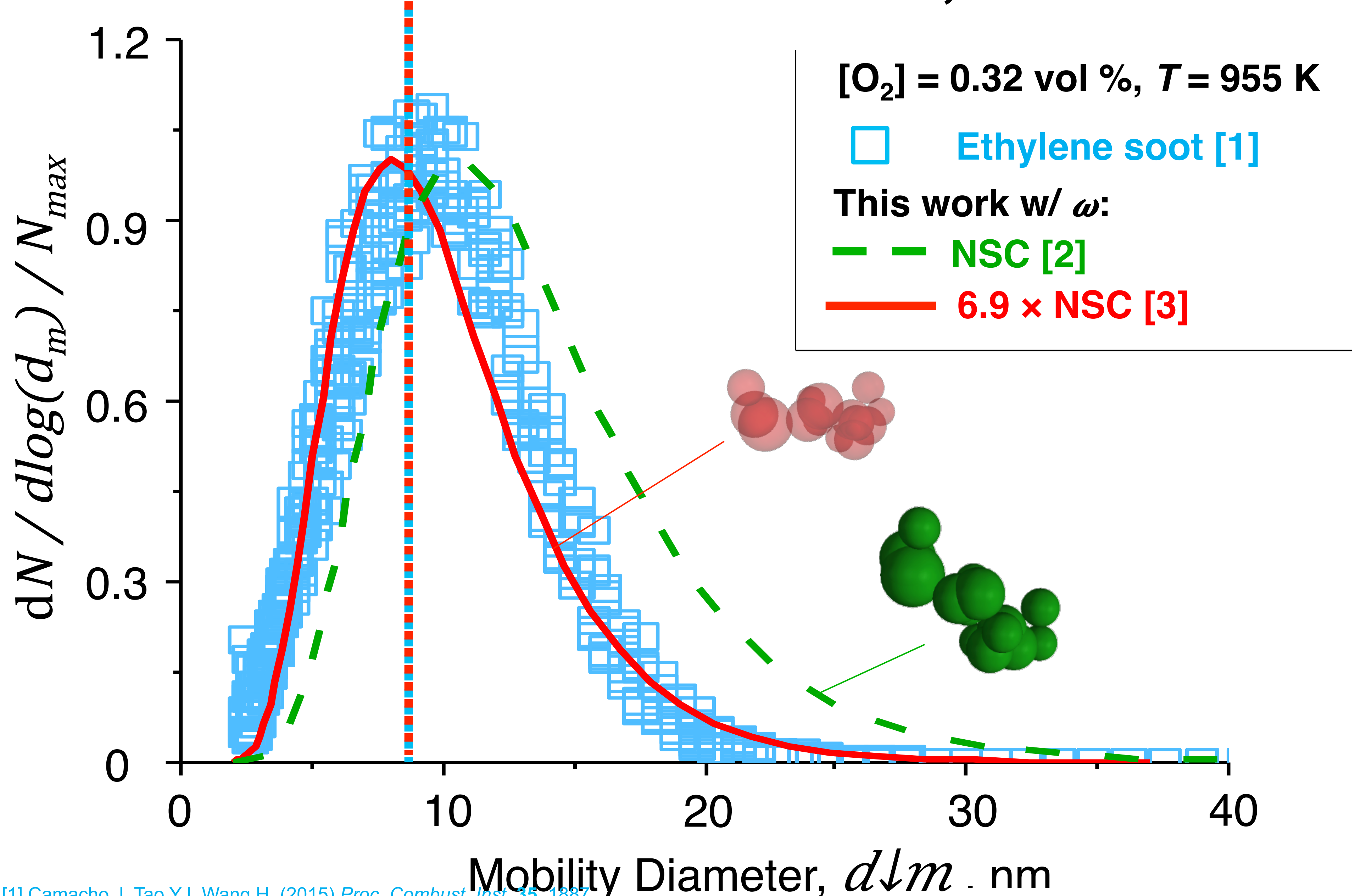
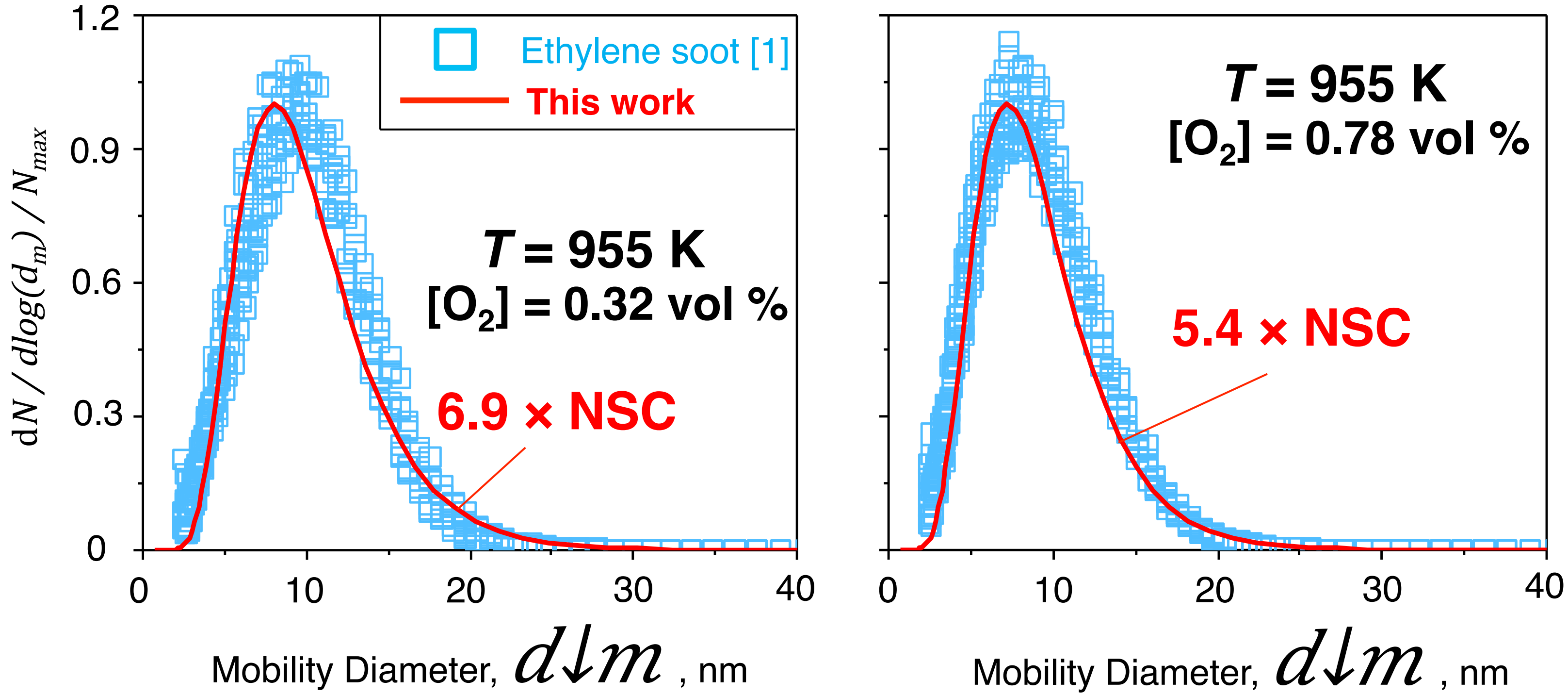


[1] Camacho J, Tao YJ, Wang H. (2015) *Proc. Combust. Inst.* **35**, 1887.
[2] Nagle J, Strickland-Constable RF. (1961) *Proceedings of the Fifth Conference on Carbon*, **1**, 154.
[3] Kelesidis GA, Pratsinis SE. *Combust. Flame*, under peer review.

Impact of Combustion Conditions



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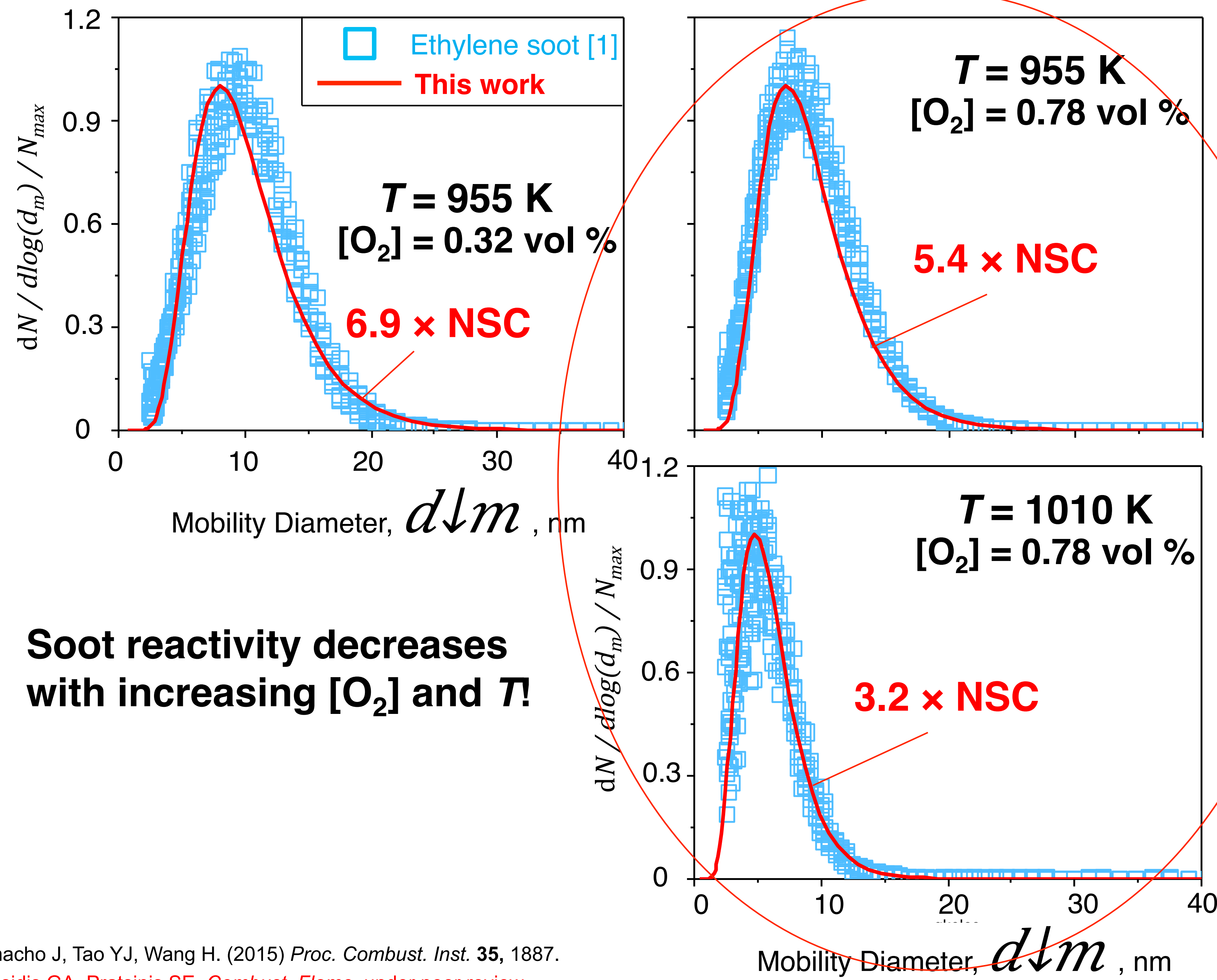
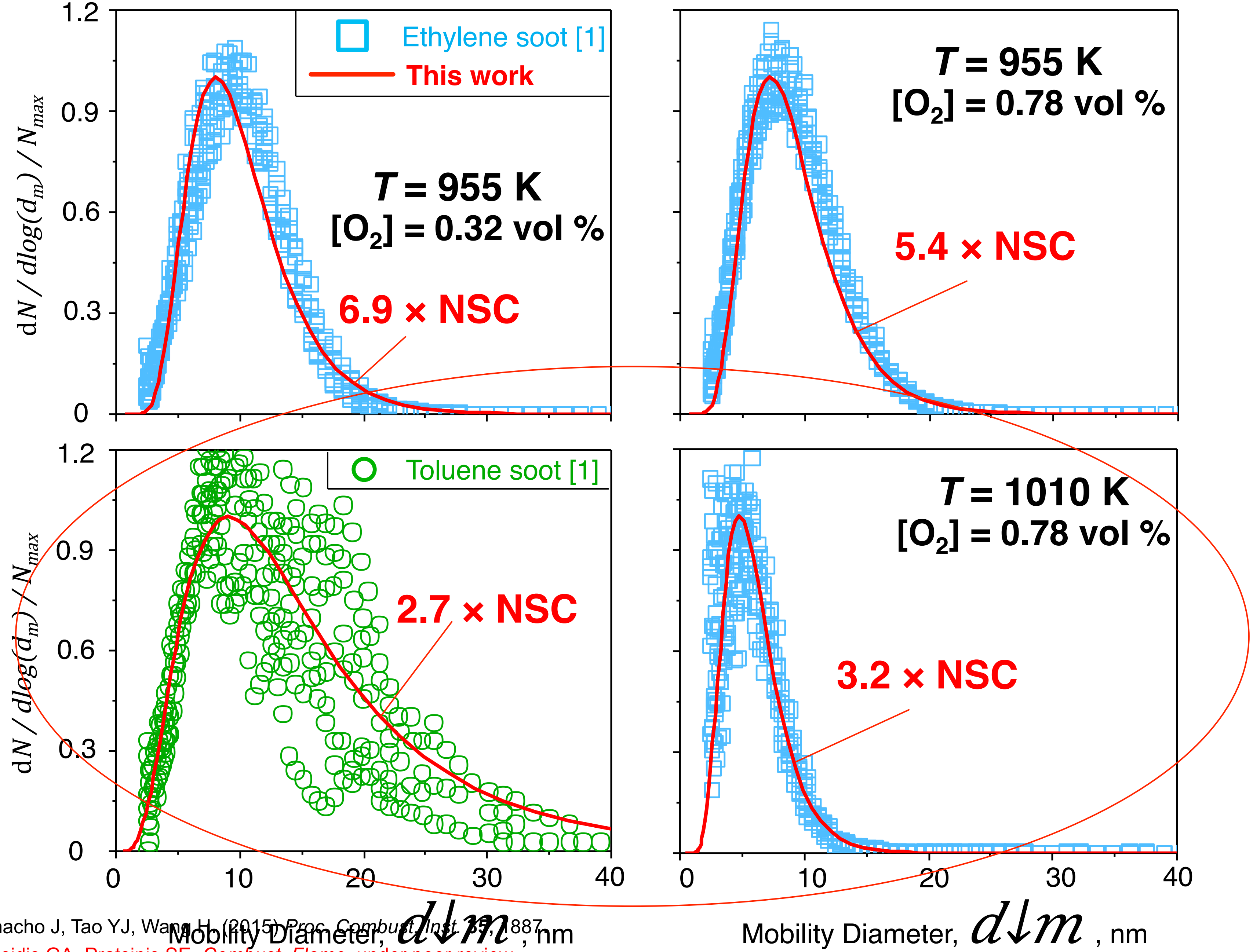


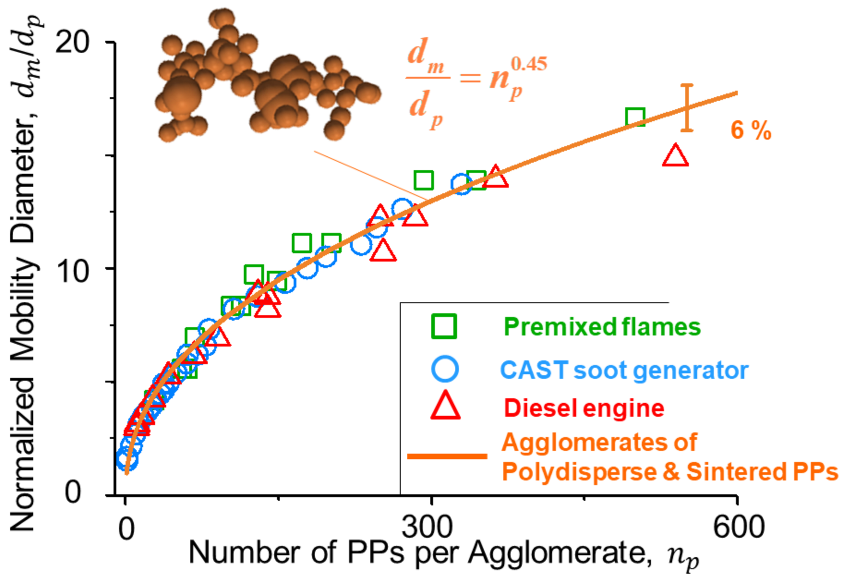
Soot reactivity decreases with increasing $[O_2]$ and *T*!

[1] Camacho J, Tao YJ, Wang H. (2015) *Proc. Combust. Inst.* **35,** 1887.
[2] Kelesidis GA, Pratsinis SE. *Combust. Flame*, under peer review.

Impact of Combustion Conditions



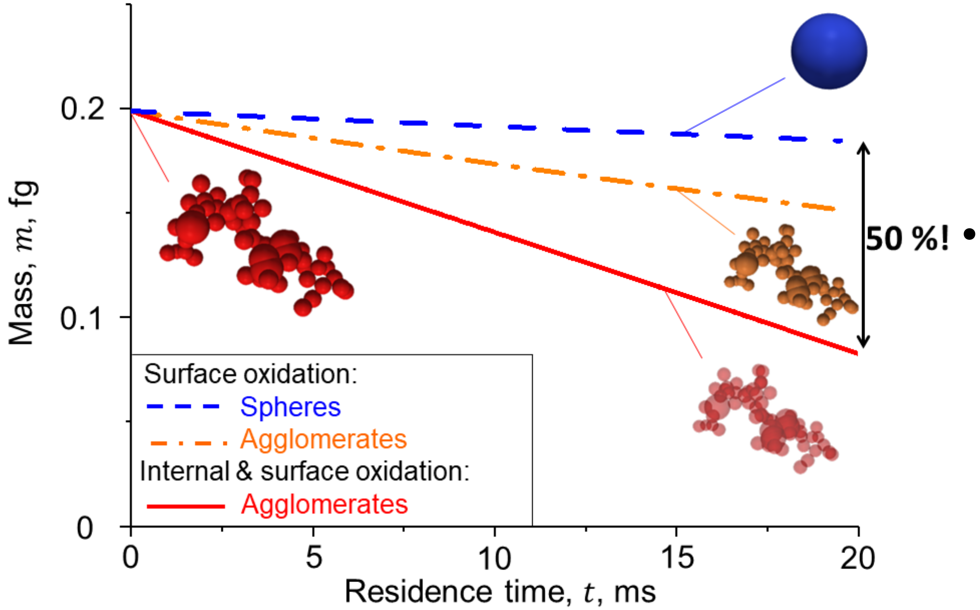
[1] Camacho J, Tao YJ, Wang H. (2015) *Proc. Combust. Inst.* 35, 1887.
[2] Kelesidis GA, Pratsinis SE. *Combust. Flame*, under peer review.



Conclusions

- Soot morphology is given by a universal power law [1]:

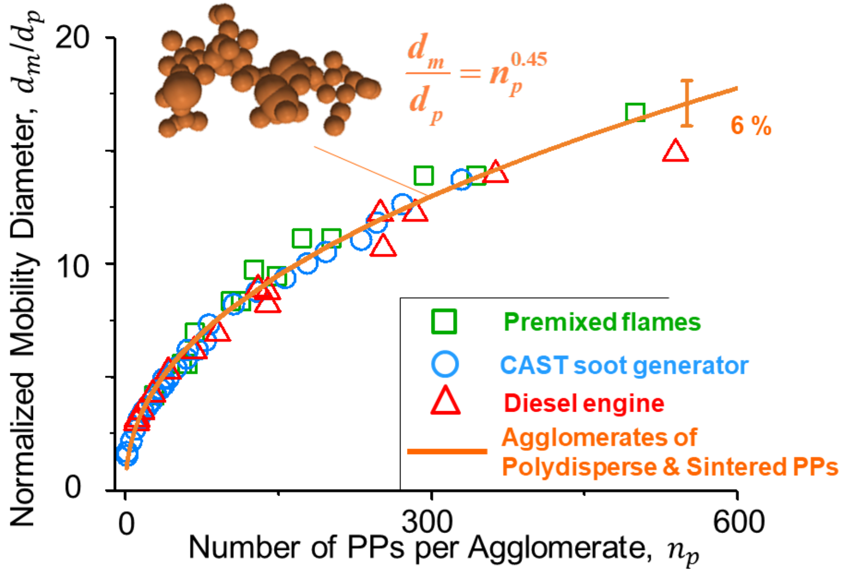
$$\frac{d_m}{d_p} = n_p^{0.45}$$



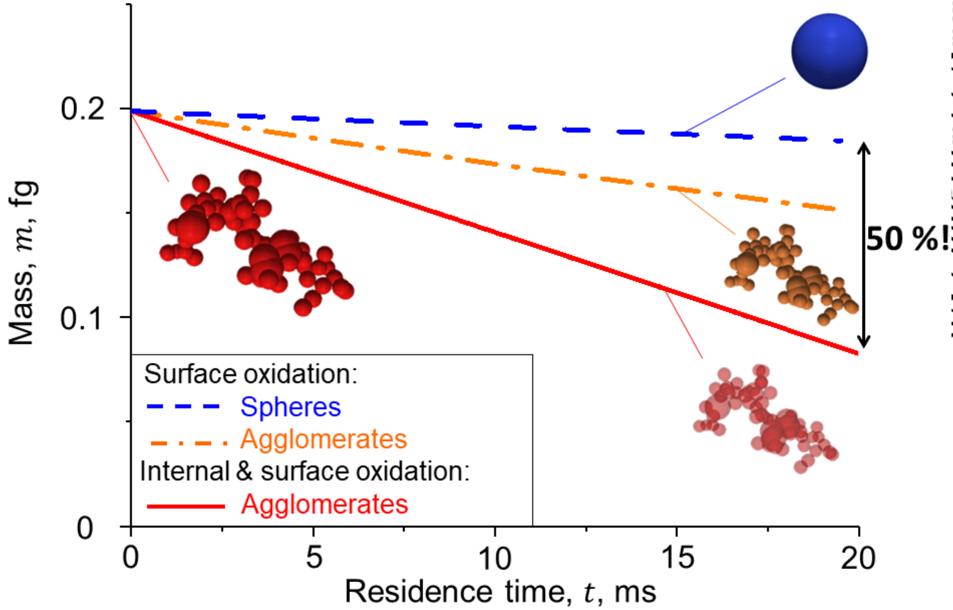
- Soot structure along with internal AND external soot surface area drive its oxidation!

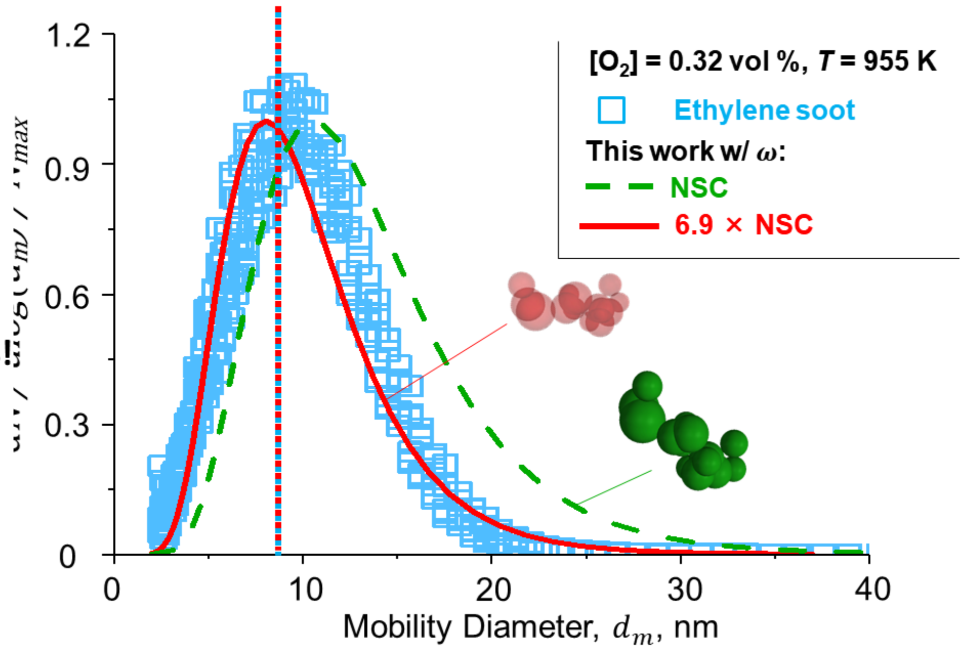
[1] Kelesidis GA, Goudeli E, Pratsinis SE. *Carbon* (2017) **121**, 527.

Conclusions



- The classic NSC correlation increasingly underestimates (**3 - 7 times**) the soot oxidation rate with decreasing T and/or $[O_2]$!



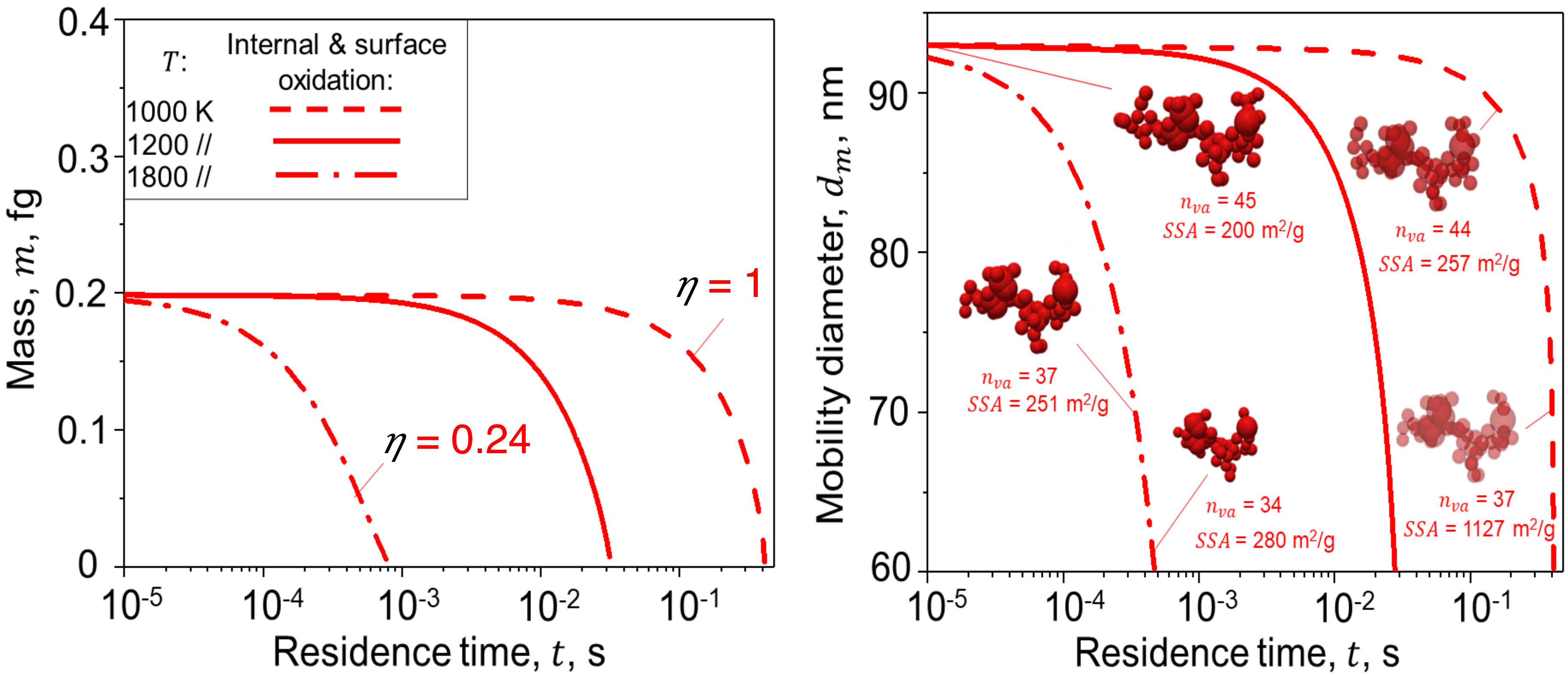


[1] Kelesidis GA, Goudeli E, Pratsinis SE. *Carbon* (2017) **121**, 527.

Thank you for your attention!

Oxidation Back-up Slides

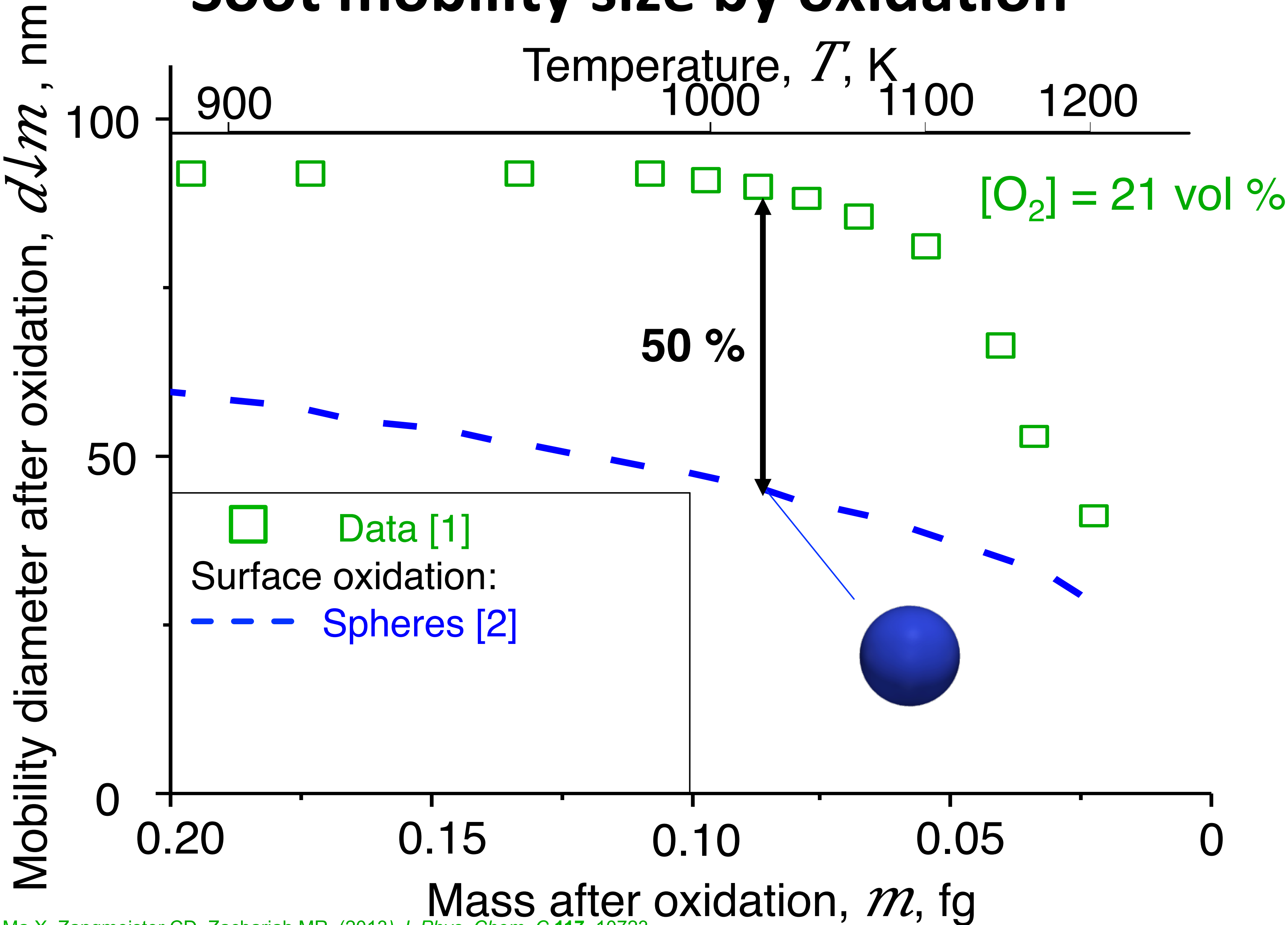
Impact of *T* on oxidation dynamics



Thiele effectiveness factor: $\eta = 3/\varphi\,(1/\tanh(\varphi) - 1/\varphi)$

Thiele modulus: $\varphi = 0.5 d_p \sqrt{k_{O2}/D_{O2}} \sim \dfrac{O_2 \text{ diffusion time}}{O_2 \text{ reaction } //}$

Soot mobility size by oxidation



[1] Ma X, Zangmeister CD, Zachariah MR. (2013) *J. Phys. Chem. C* **117**, 10723.

[2] Higgins KJ, Jung HJ, Kittelson DB, Roberts JT, Zachariah MR. (2002) *J. Phys. Chem. A* **106**, 96.

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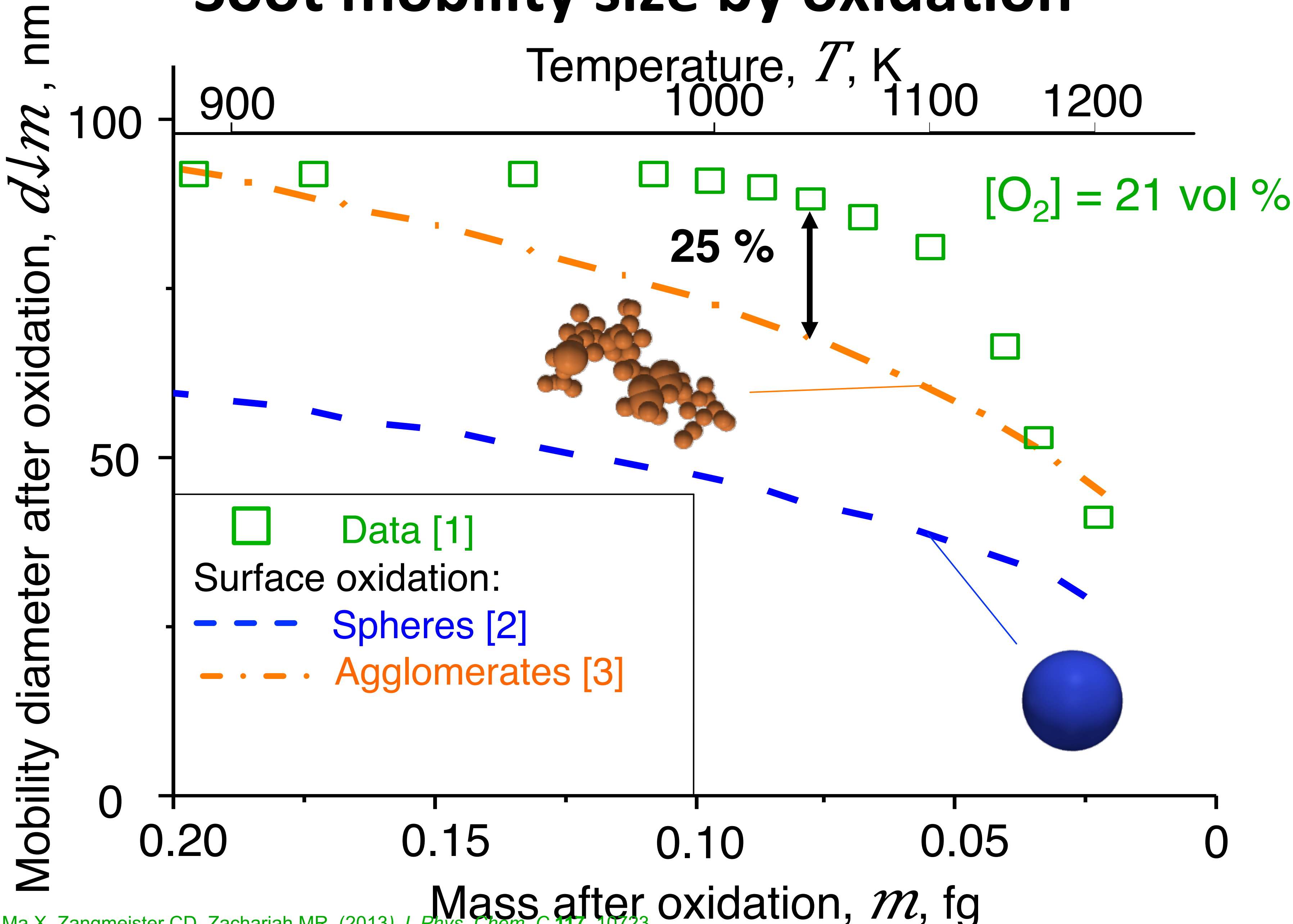

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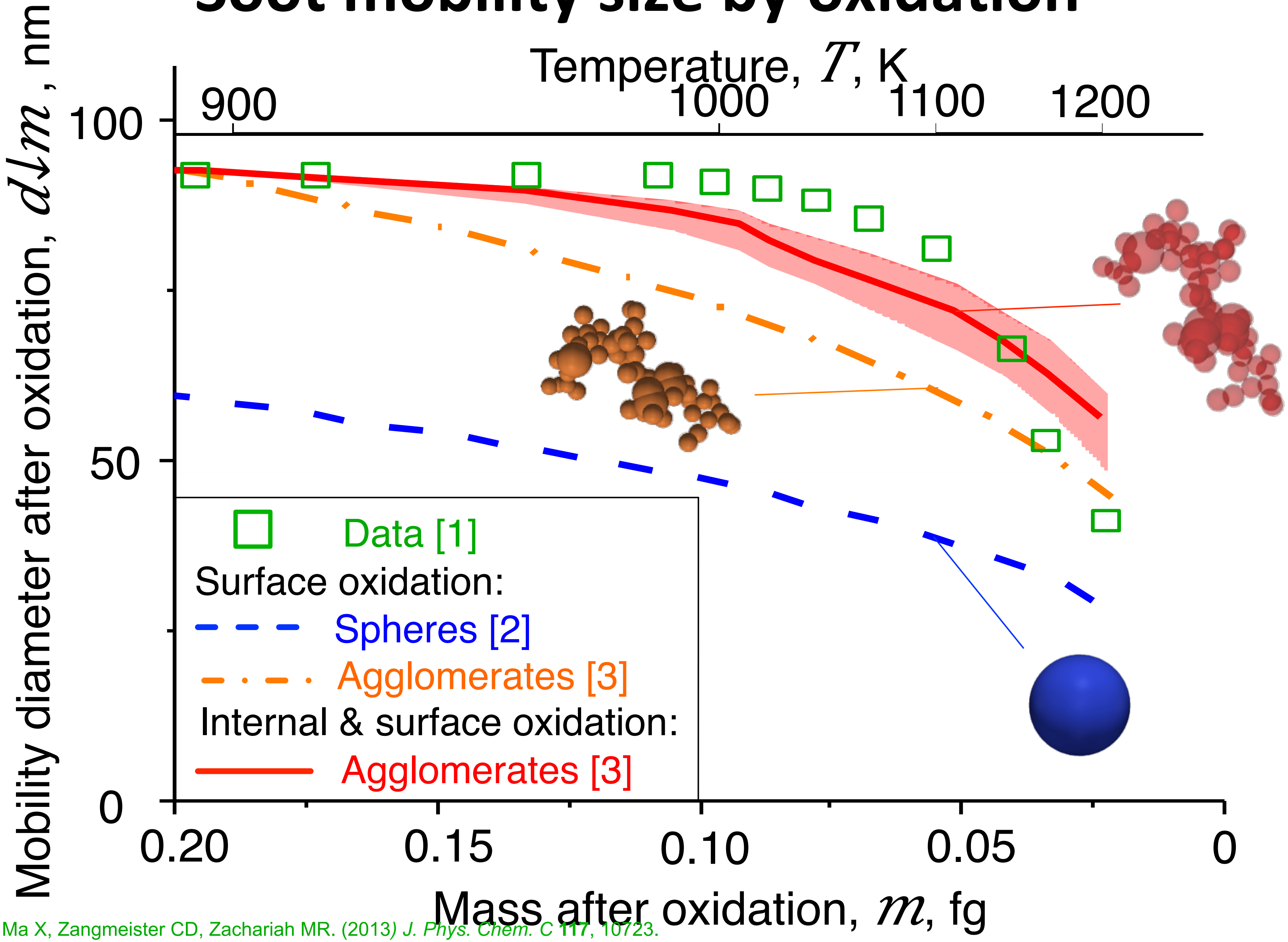
Soot mobility size by oxidation



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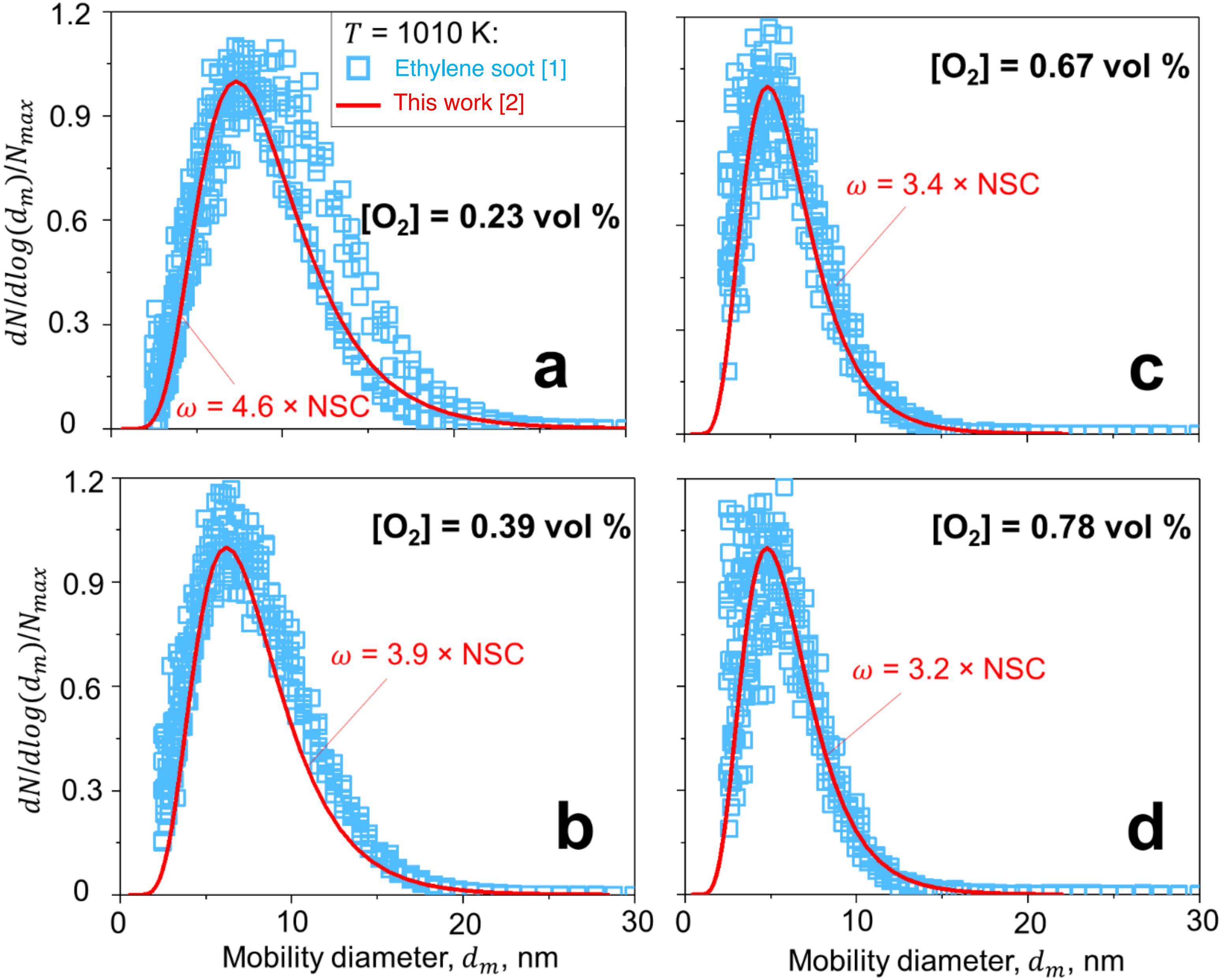
[3] Kelesidis GA, Pratsinis SE. *Combust. Flame*, under peer review.

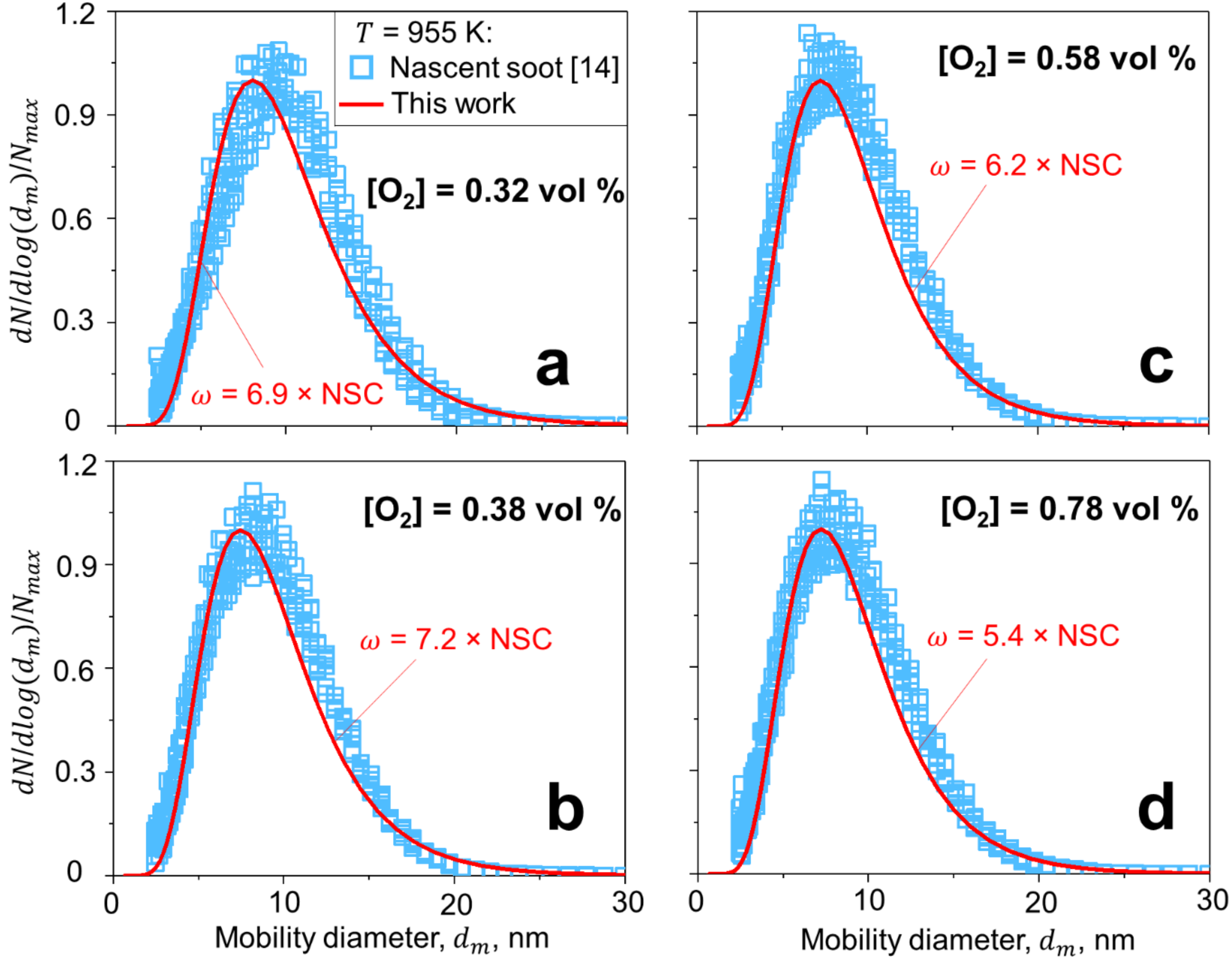
Oxidation at different $[O_2]$



[1] Camacho J, Tao YJ, Wang H. (2015) *Proc. Combust. Inst.* **35,** 1887.

[2] Kelesidis GA, Pratsinis SE. *Combust. Flame*, under peer review.

Oxidation at different T



[1] Camacho J, Tao YJ, Wang H. (2015) *Proc. Combust. Inst.* **35,** 1887.

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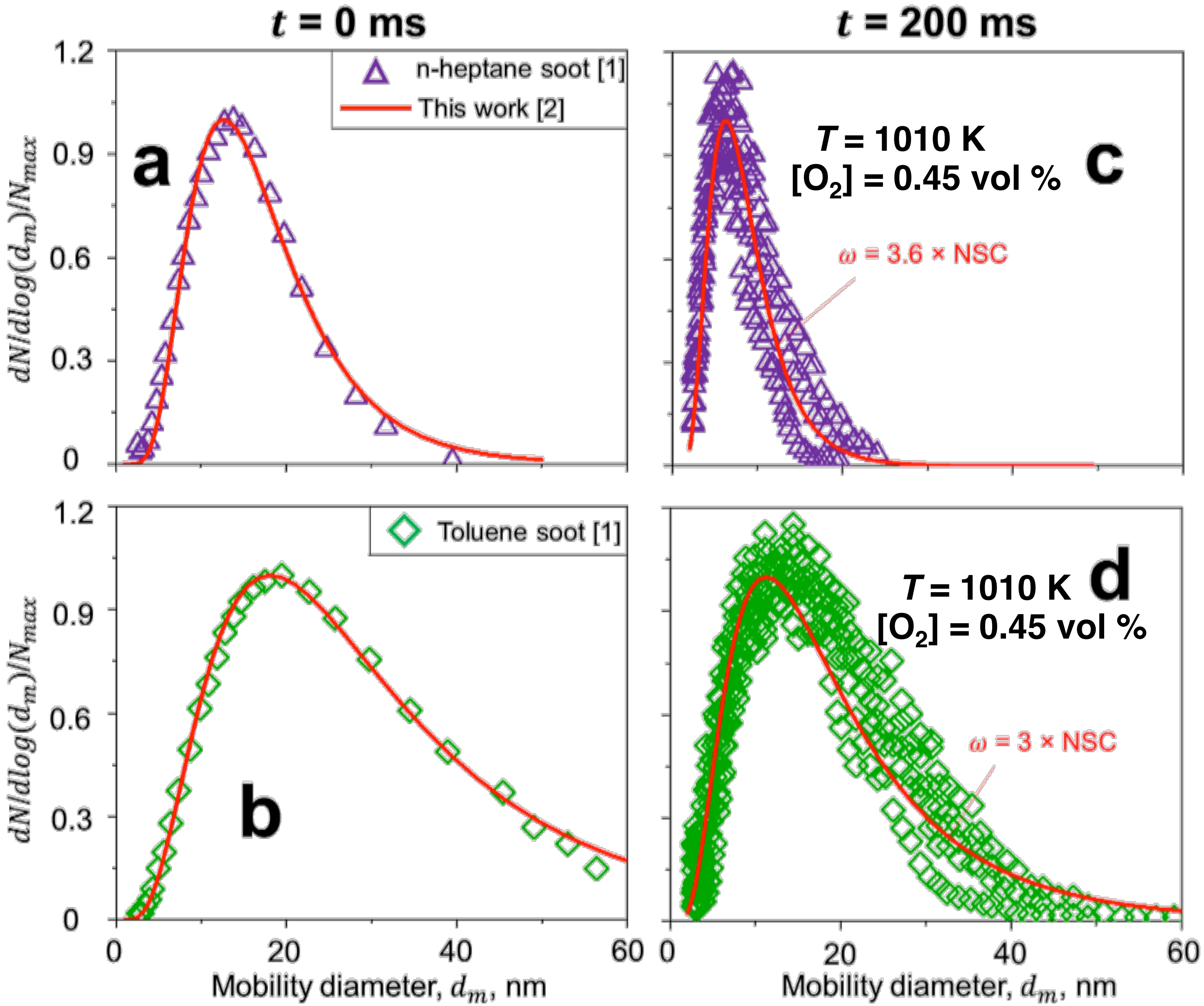
Impact of fuel on soot oxidation



[1] Camacho J, Tao YJ, Wang H. (2015) *Proc. Combust. Inst.* **35,** 1887.
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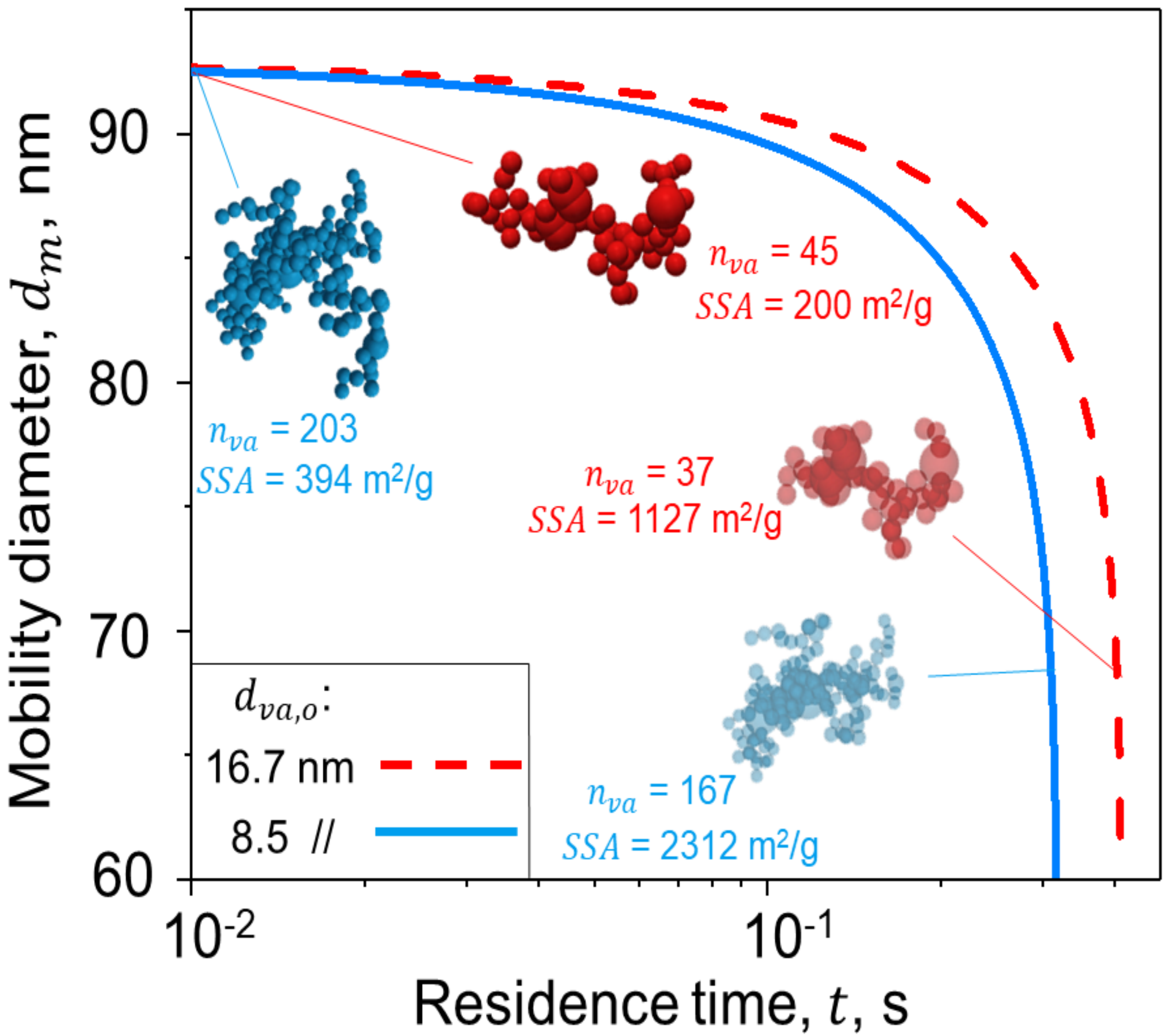
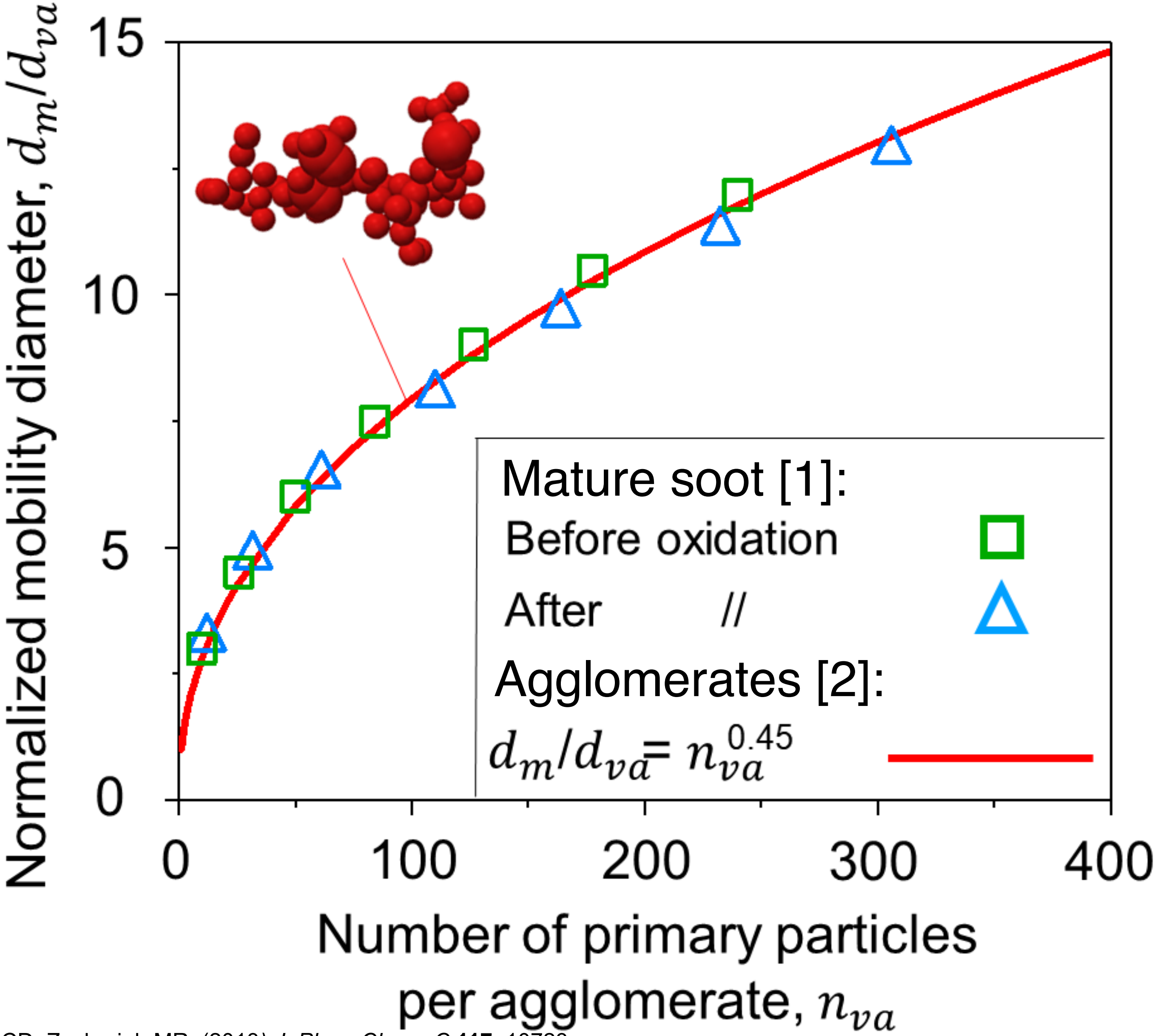
Impact of PP diameter on oxidation



Impact of oxidation on morphology



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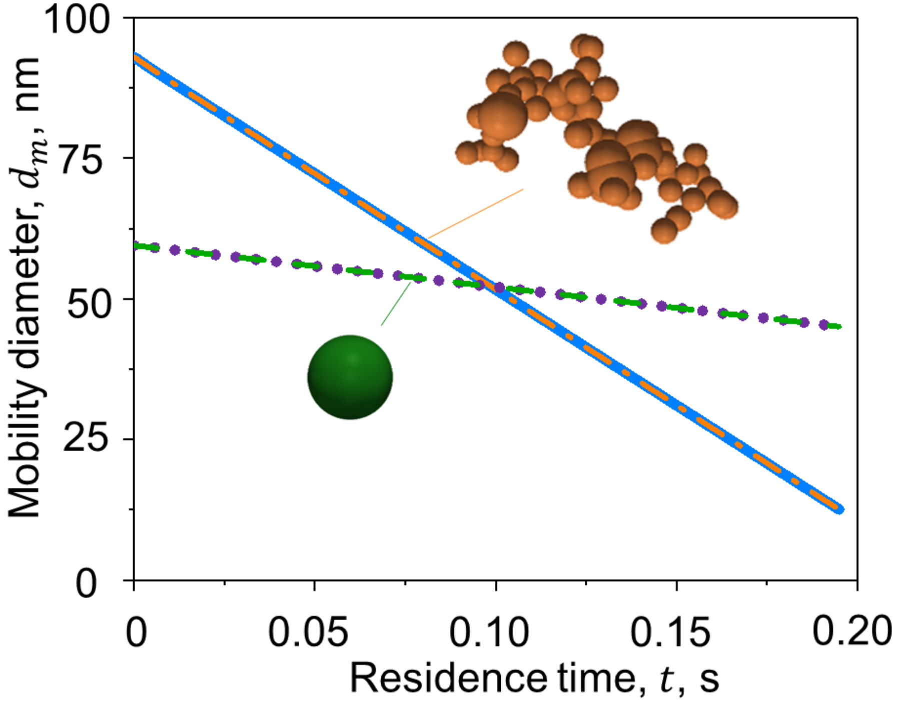
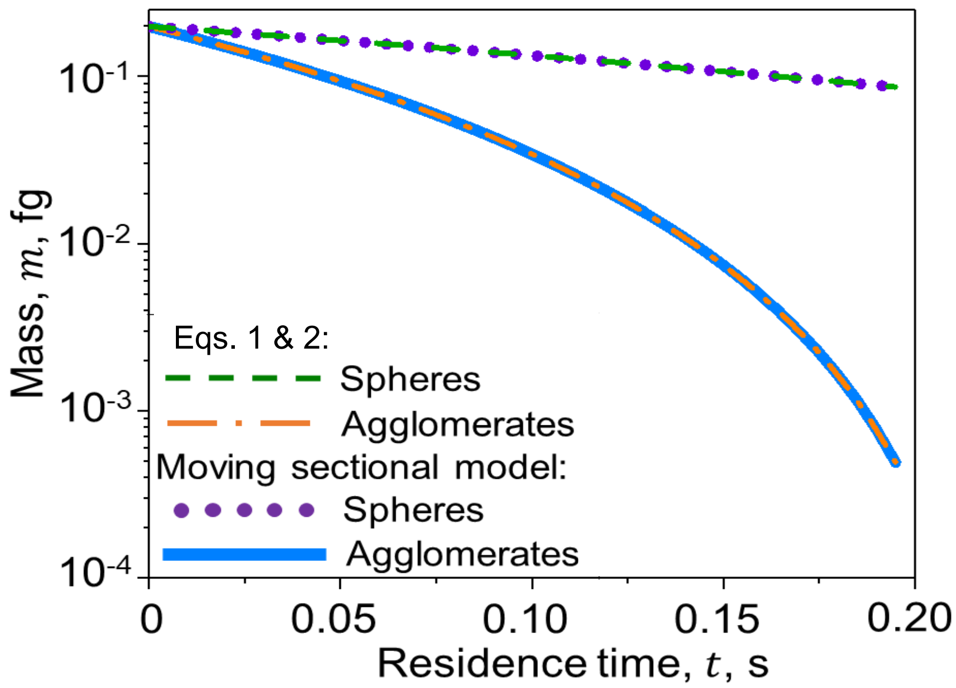
Validation of surface oxidation





Eq. 1: $$d_m = d_{m,o} - \frac{2\omega}{\rho_o}\Delta t$$

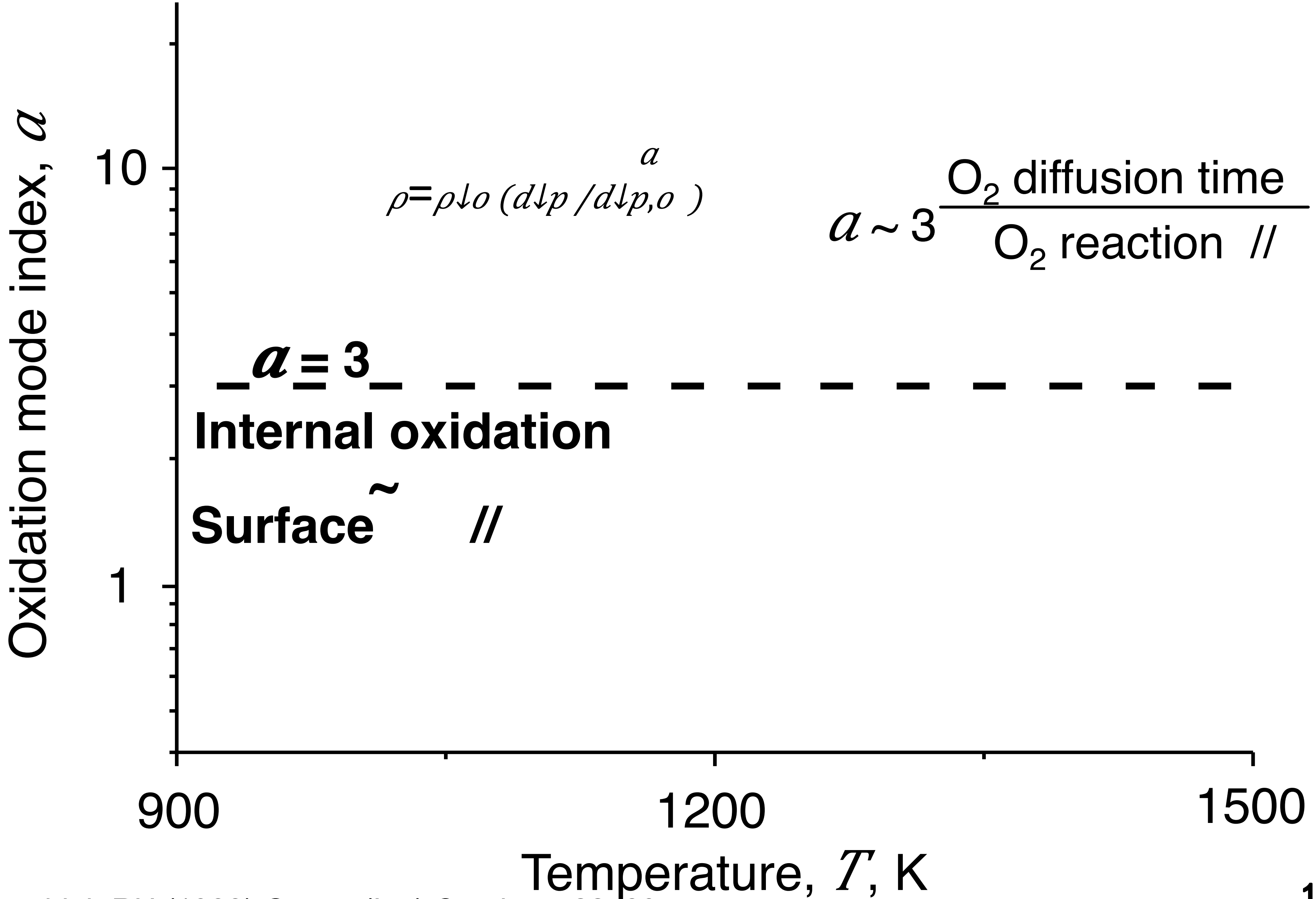
Eq. 2: $$d_m = d_{m,o} - \frac{2\omega}{\rho_o}\frac{d_{m,o}}{d_{va,o}}\Delta t$$

Impact of Oxidation on Density

$$\rho = \rho_o \left(d_p / d_{p,o} \right)^a$$

Essenhigh RH (1988) *Symp. (Int.) Combust.* **22,** 89.

Impact of Oxidation on Density



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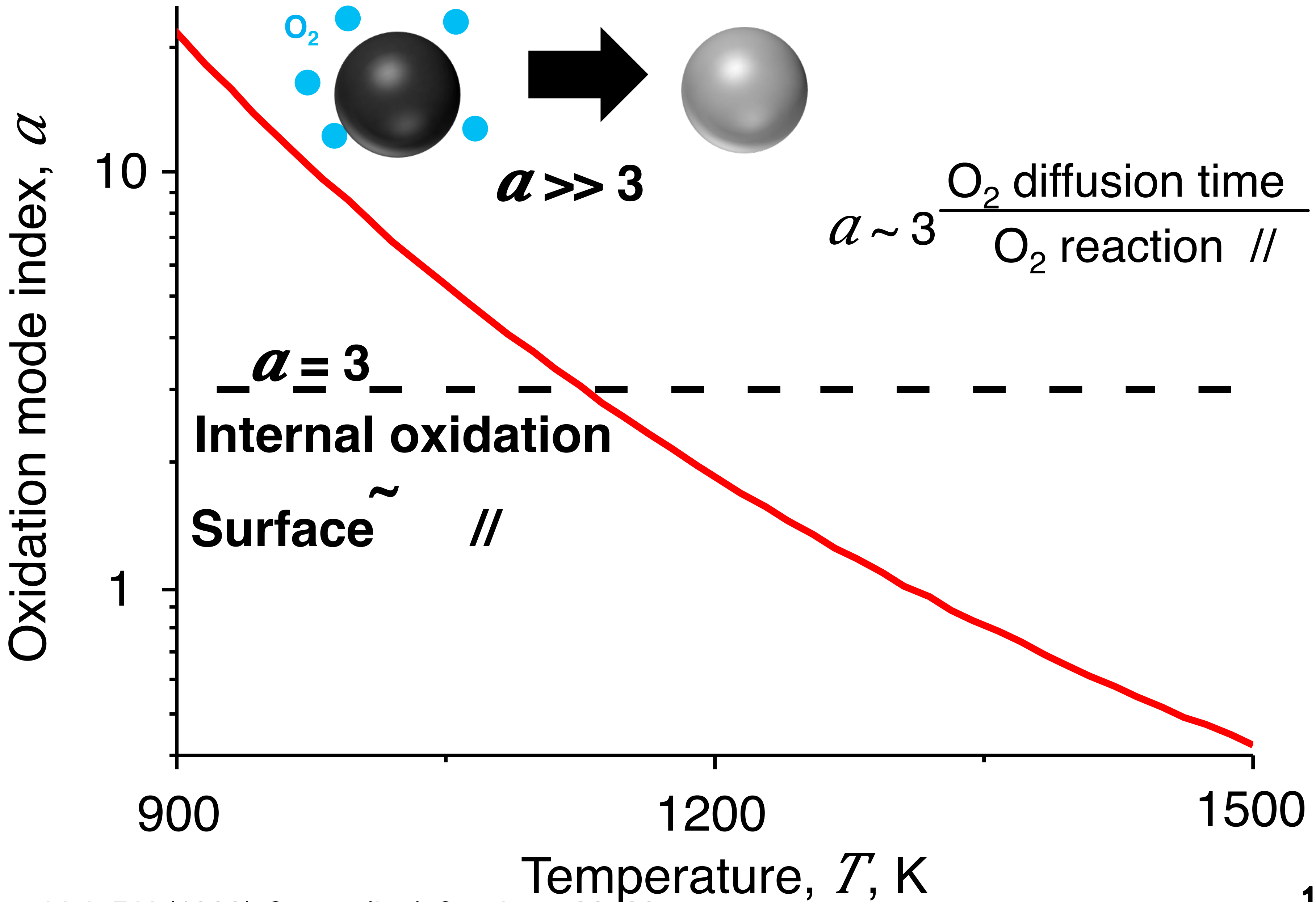
Impact of Oxidation on Density



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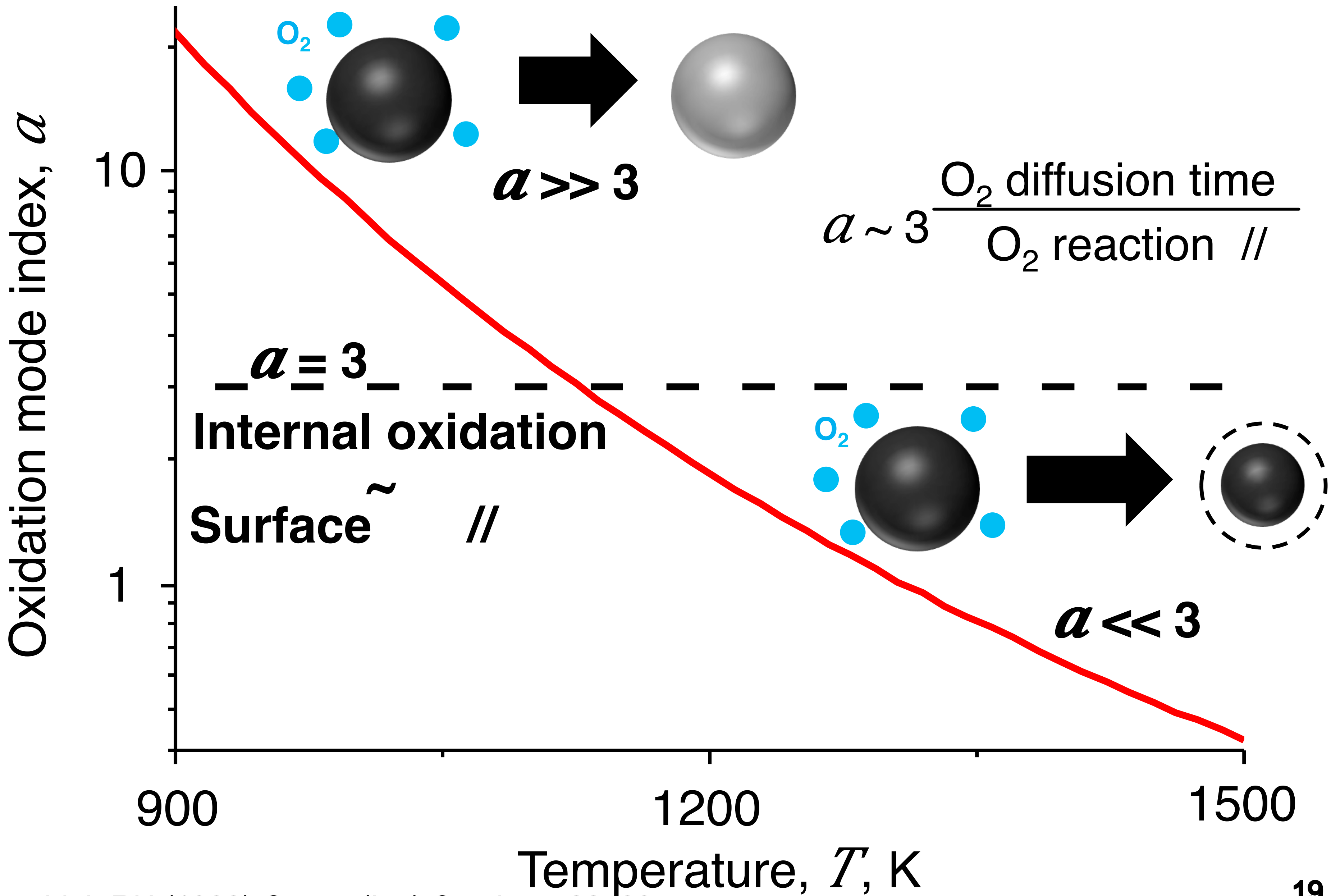
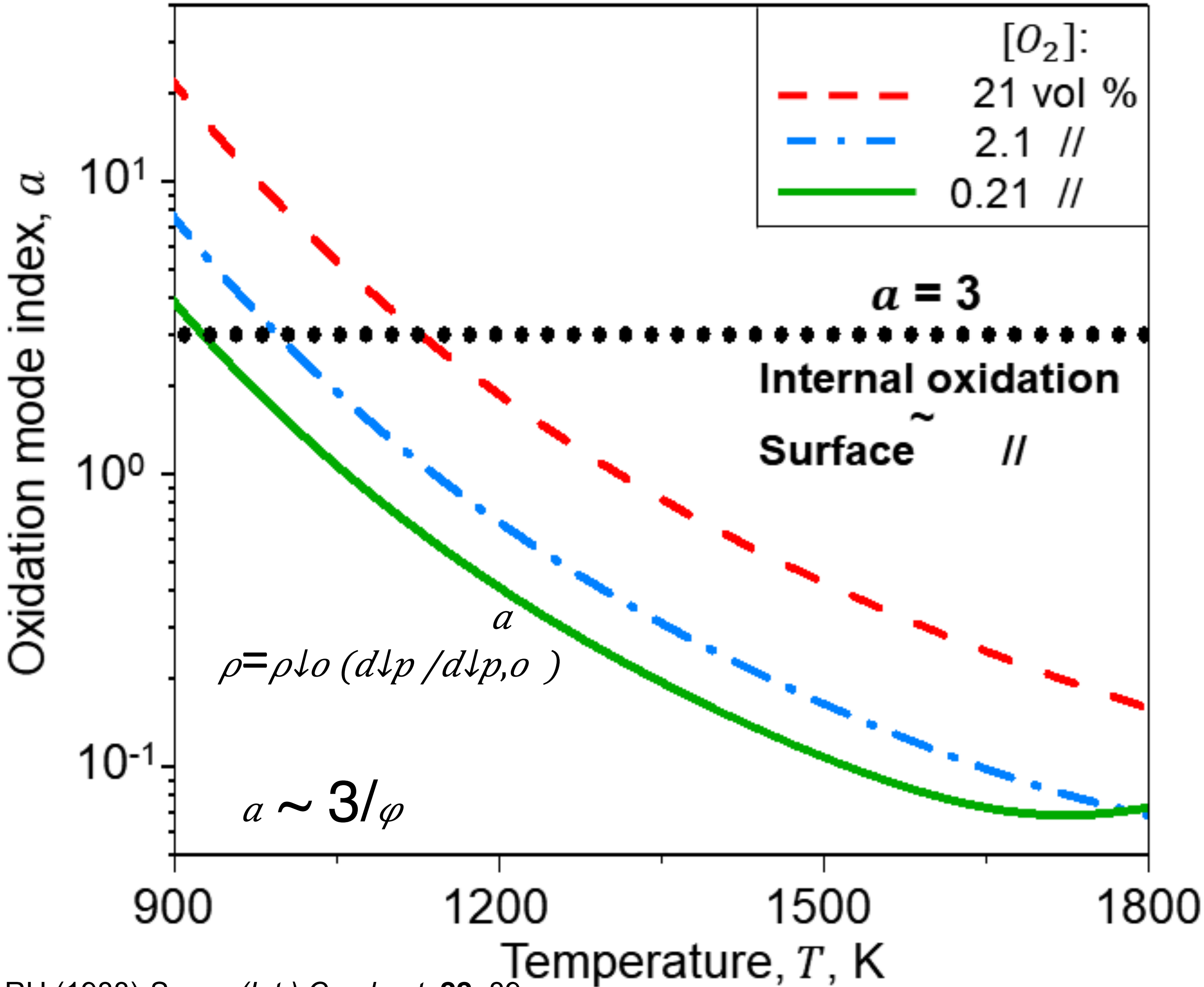
Impact of Oxidation on Density



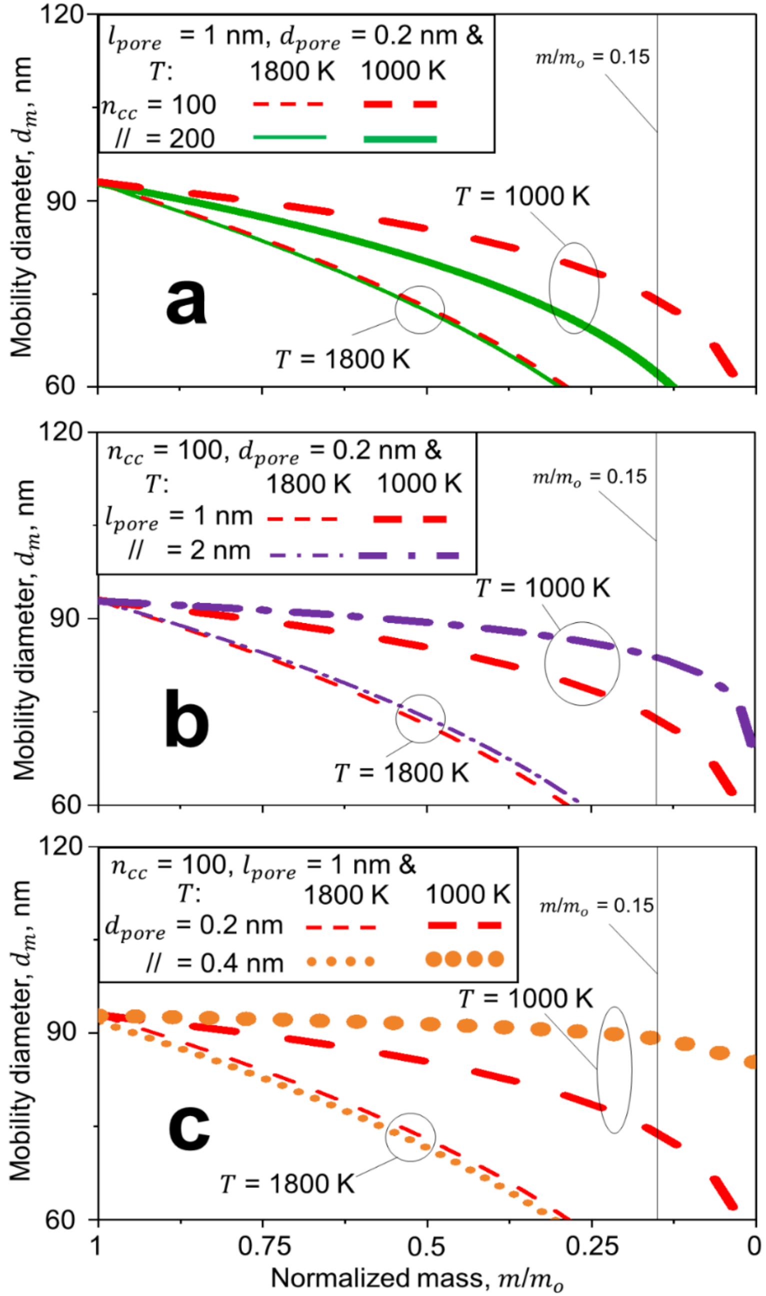
Essenhigh RH (1988) *Symp. (Int.) Combust.* **22,** 89.

Impact of Oxidation on Density

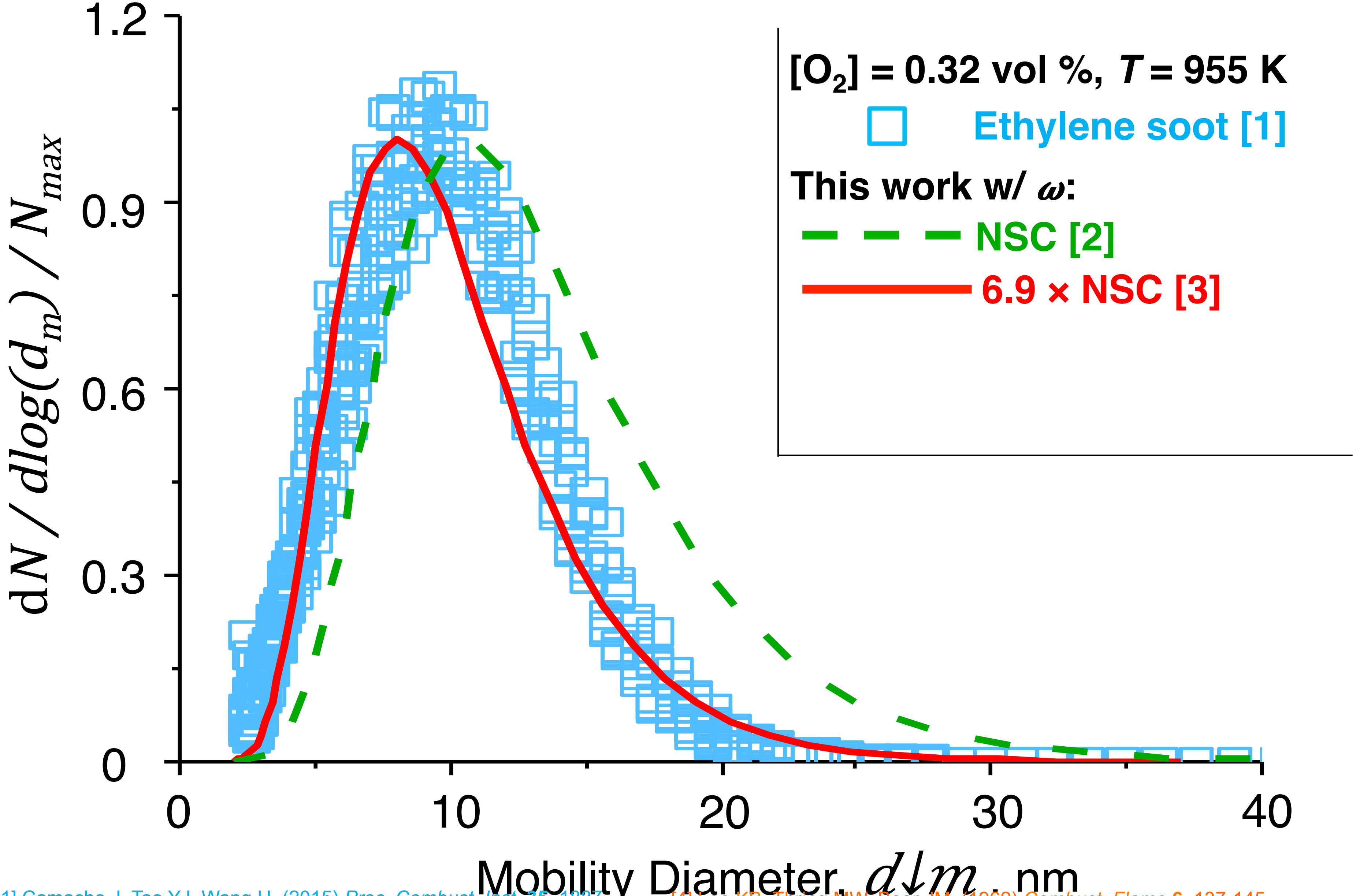


Essenhigh RH (1988) *Symp. (Int.) Combust.* **22,** 89.

Sensitivity on internal structure

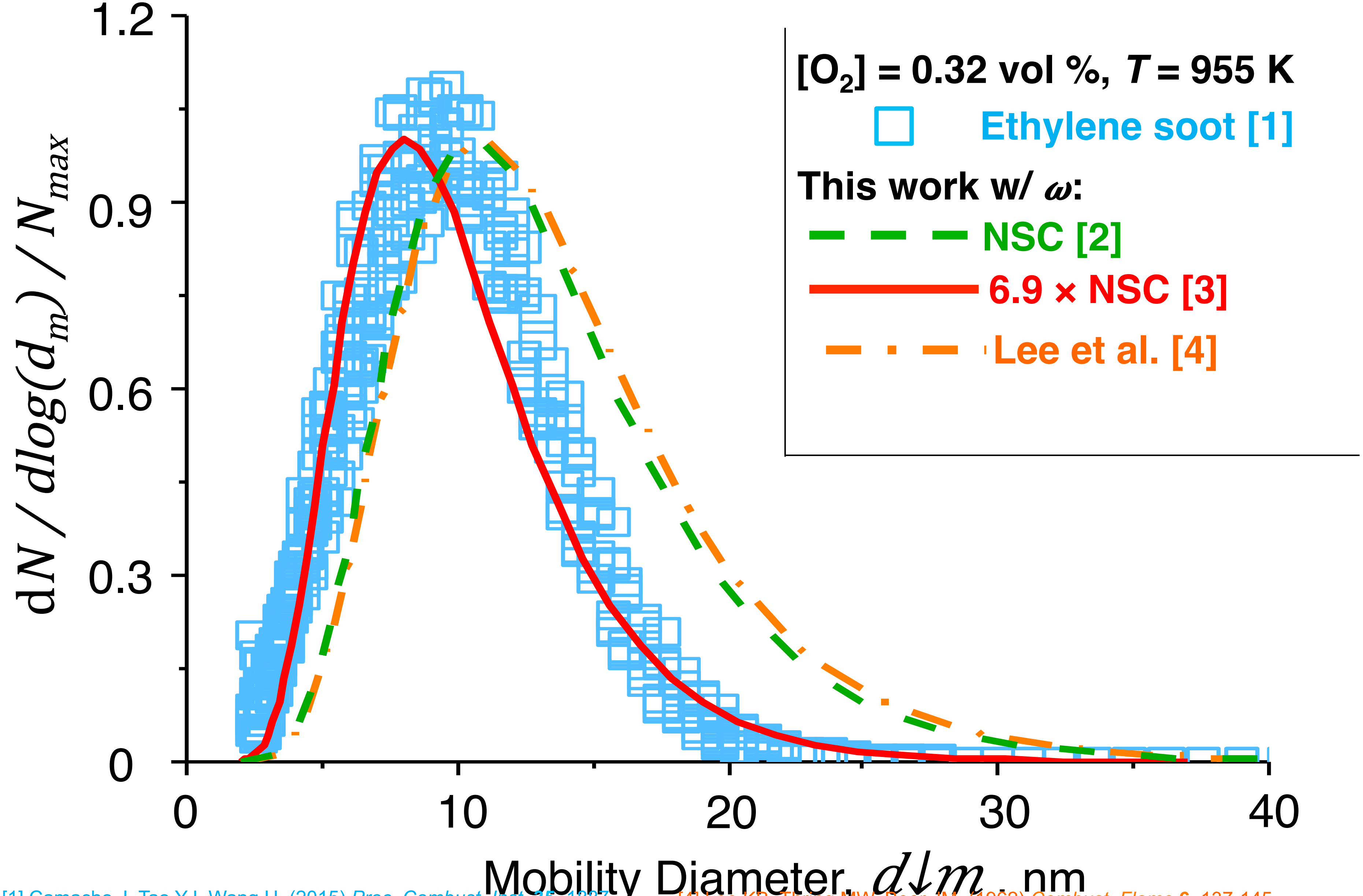


Comparison to other oxidation rates



[1] Camacho J, Tao YJ, Wang H. (2015) *Proc. Combust. Inst.* **35**, 1887.
[2] Nagle J, Strickland-Constable RF. (1961) *Proceedings of the Fifth Conference on Carbon*, **1**, 154.
[3] Kelesidis GA, Pratsinis SE. *Combust. Flame*, under peer review.
[4] Lee KB, Thring MW, Beer JM. (1962) *Combust. Flame* **6**, 137-145.

Comparison to other oxidation rates



[1] Camacho J, Tao YJ, Wang H. (2015) *Proc. Combust. Inst.* **35**, 1887.
[2] Nagle J, Strickland-Constable RF. (1961) *Proceedings of the Fifth Conference on Carbon*, **1**, 154.
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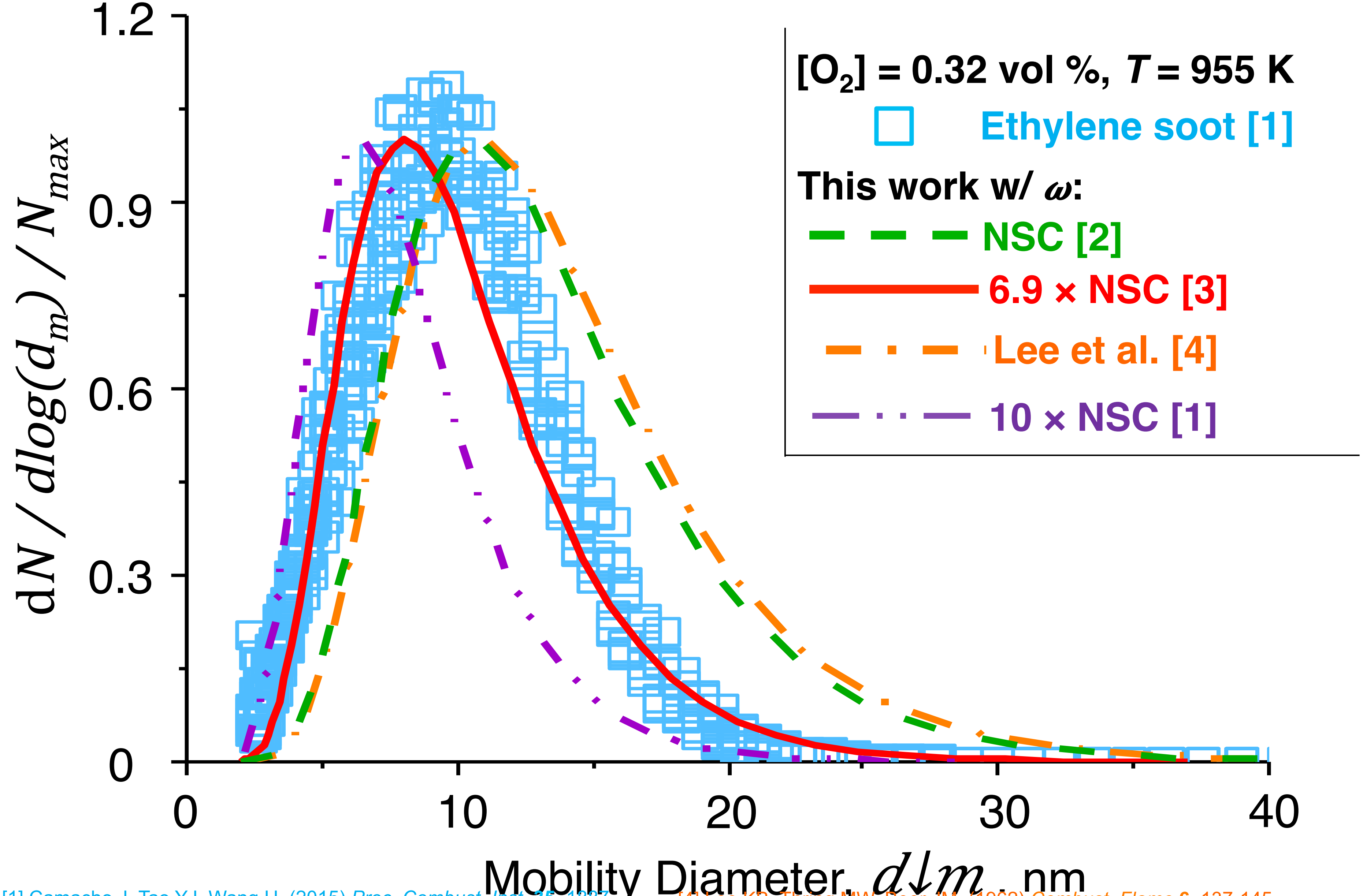
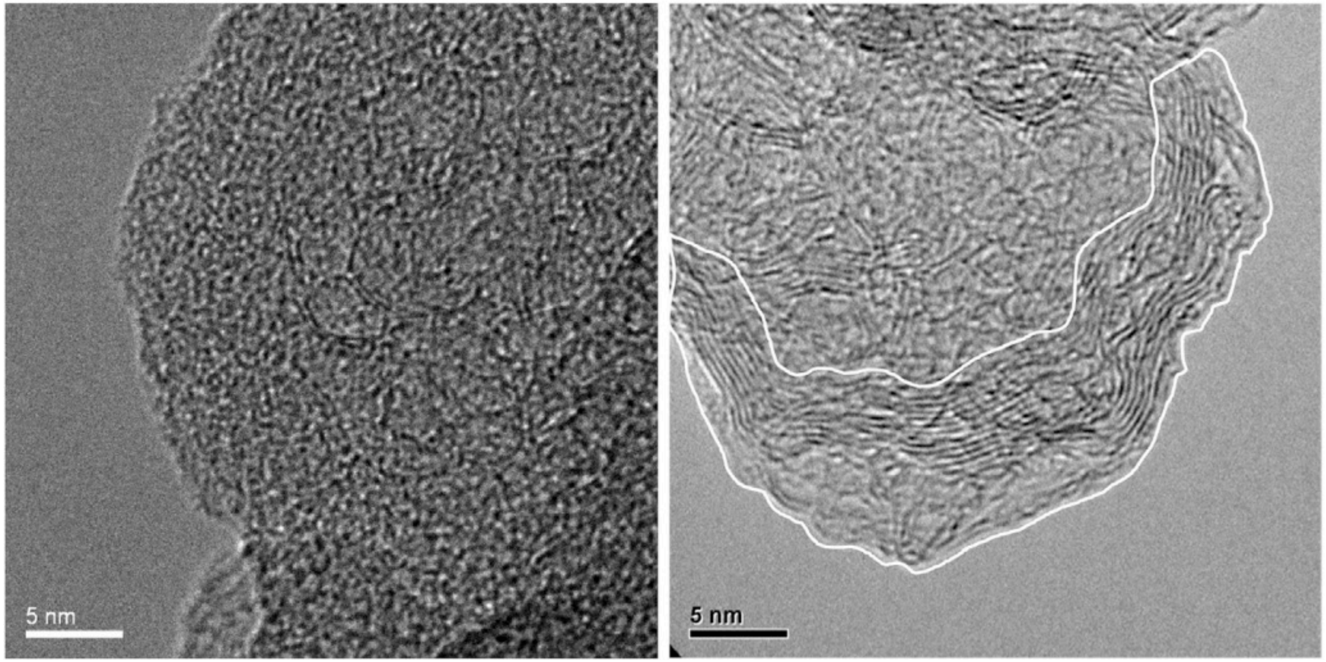
[4] Lee KB, Thring MW, Beer JM. (1962) *Combust. Flame* **6**, 137-145.

Comparison to other oxidation rates



[1] Camacho J, Tao YJ, Wang H. (2015) *Proc. Combust. Inst.* **35**, 1887.
[2] Nagle J, Strickland-Constable RF. (1961) *Proceedings of the Fifth Conference on Carbon*, **1**, 154.
[3] Kelesidis GA, Pratsinis SE. *Combust. Flame*, under peer review.
[4] Lee KB, Thring MW, Beer JM. (1962) *Combust. Flame* **6**, 137-145.

Reduction of soot reactivity



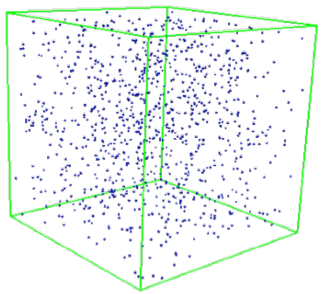
Oxidation

Gaddam et al. (2016) *Carbon* **98,** 545.

DEM Back-up Slides

Soot Dynamics by Discrete Element Modeling (DEM)

i) Initial configuration after inception has largely ended.



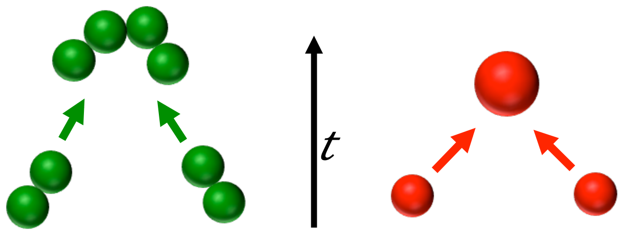
T = 1830 K

$d_{m,o}$ = 2 nm

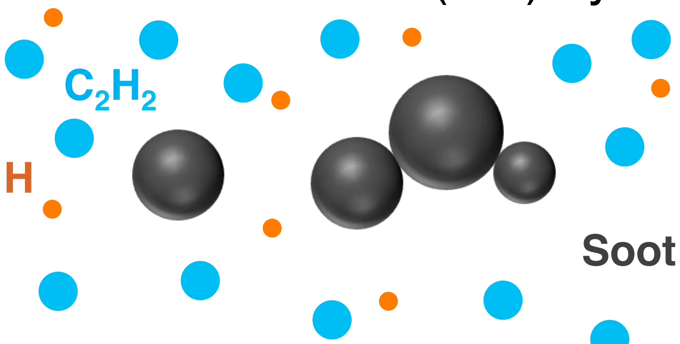
$N_{tot,o}$ = 4.5·10^{16} m^{-3}

[1,2]

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

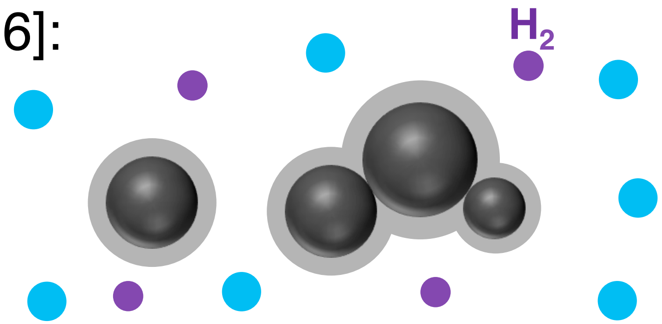


iii) **Surface Growth** (SG) by HACA mechanism [4-6]:



r_{HACA} [4]

β_{C2H2} [6]



Mass Balance for each C_2H_2 reaction:

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

[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 Dynamics by Discrete Element Modeling (DEM)

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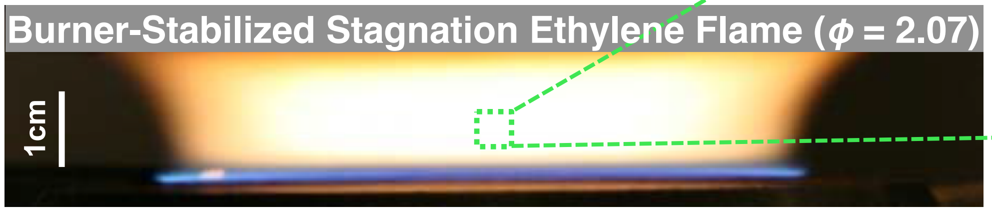
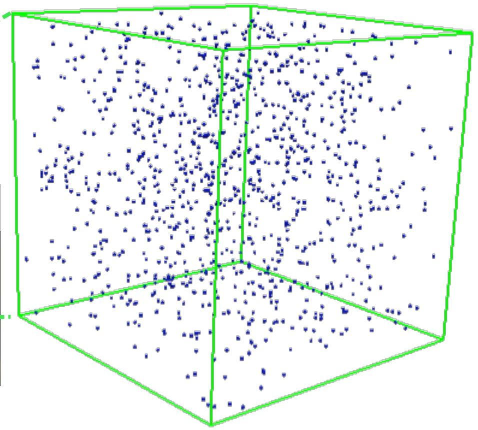




T = 1830 K

$d_{m,o}$ = 2 nm

$N_{tot,o}$ = 4.5·10^16 m

[1,2]

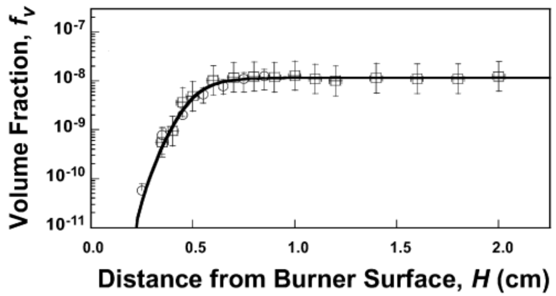
ii) Discrete Element Modeling (DEM) of **Particle Motion** and **Coagulation** [3]

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

$$C_{soot}\text{-}H + H \leftrightarrow C_{soot}^{\bullet} + H_2$$

$$C_{soot}^{\bullet} + H \rightarrow C_{soot}\text{-}H$$

$$C_{soot}^{\bullet} + C_2H_2 \rightarrow C_{soot}\text{-}H + H$$



$x_{C_2H_2}$ = 0.02

x_{H_2} = 0.1 [5]

x_H = 10^{-4} [2]

[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.

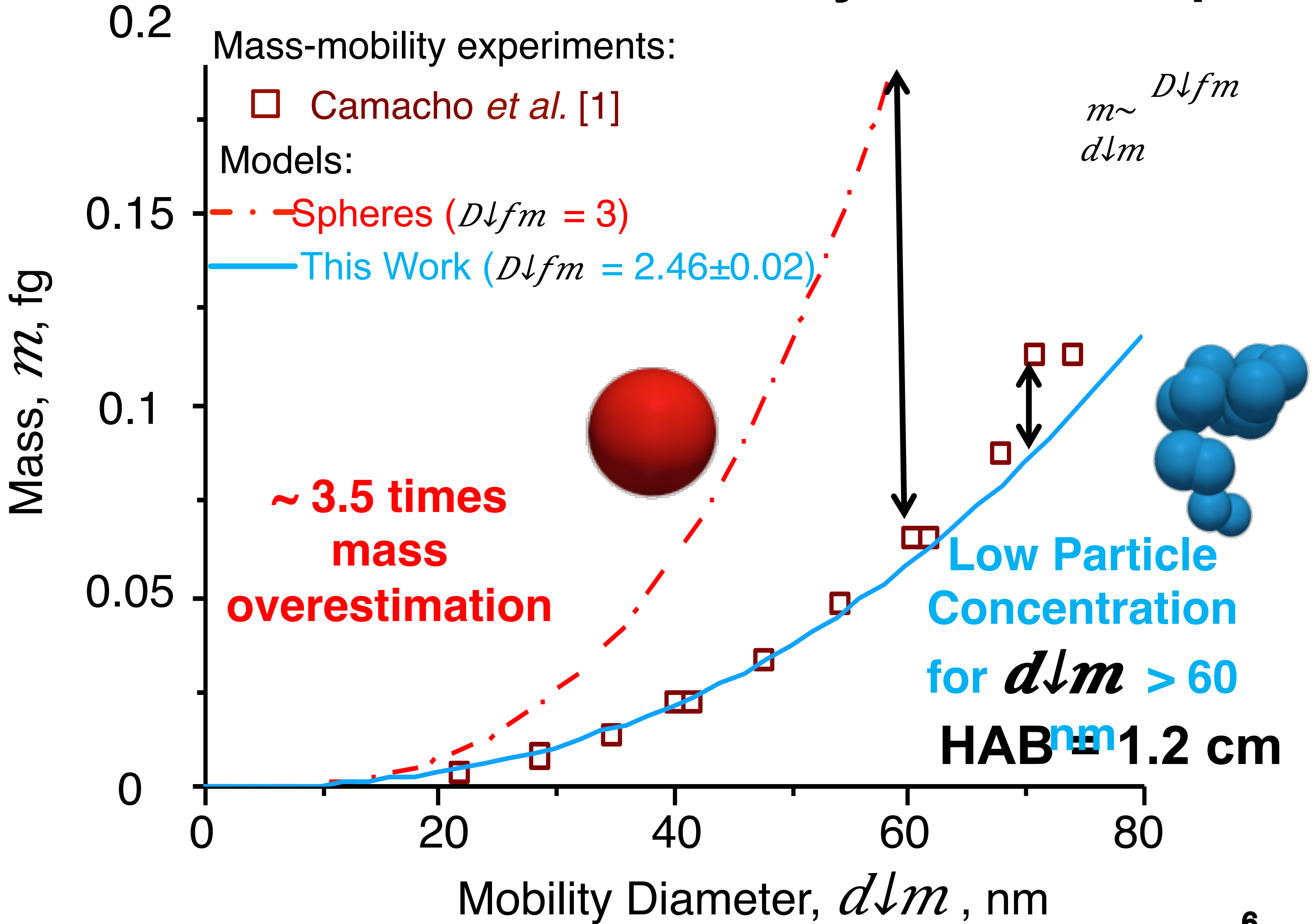
[3] Goudeli E, Eggersdorfer ML, Pratsinis SE. (2015) *Langmuir* **31**,1320.

[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.

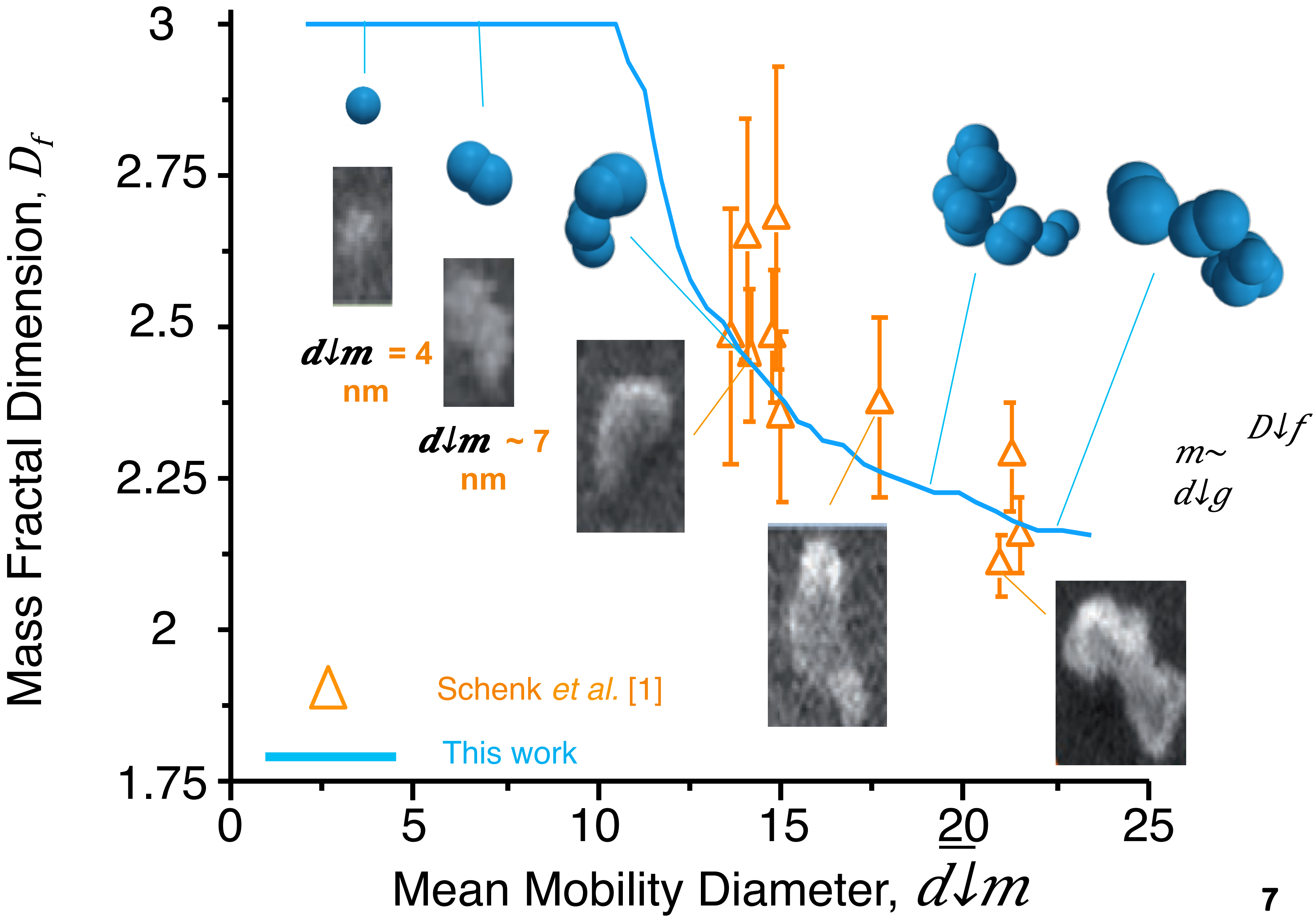
[6] Kelesidis GA, Goudeli E, Pratsinis SE. (2017) *Proc. Combust. Inst.* 36, 29.

Nascent Soot Mass-Mobility Relationship



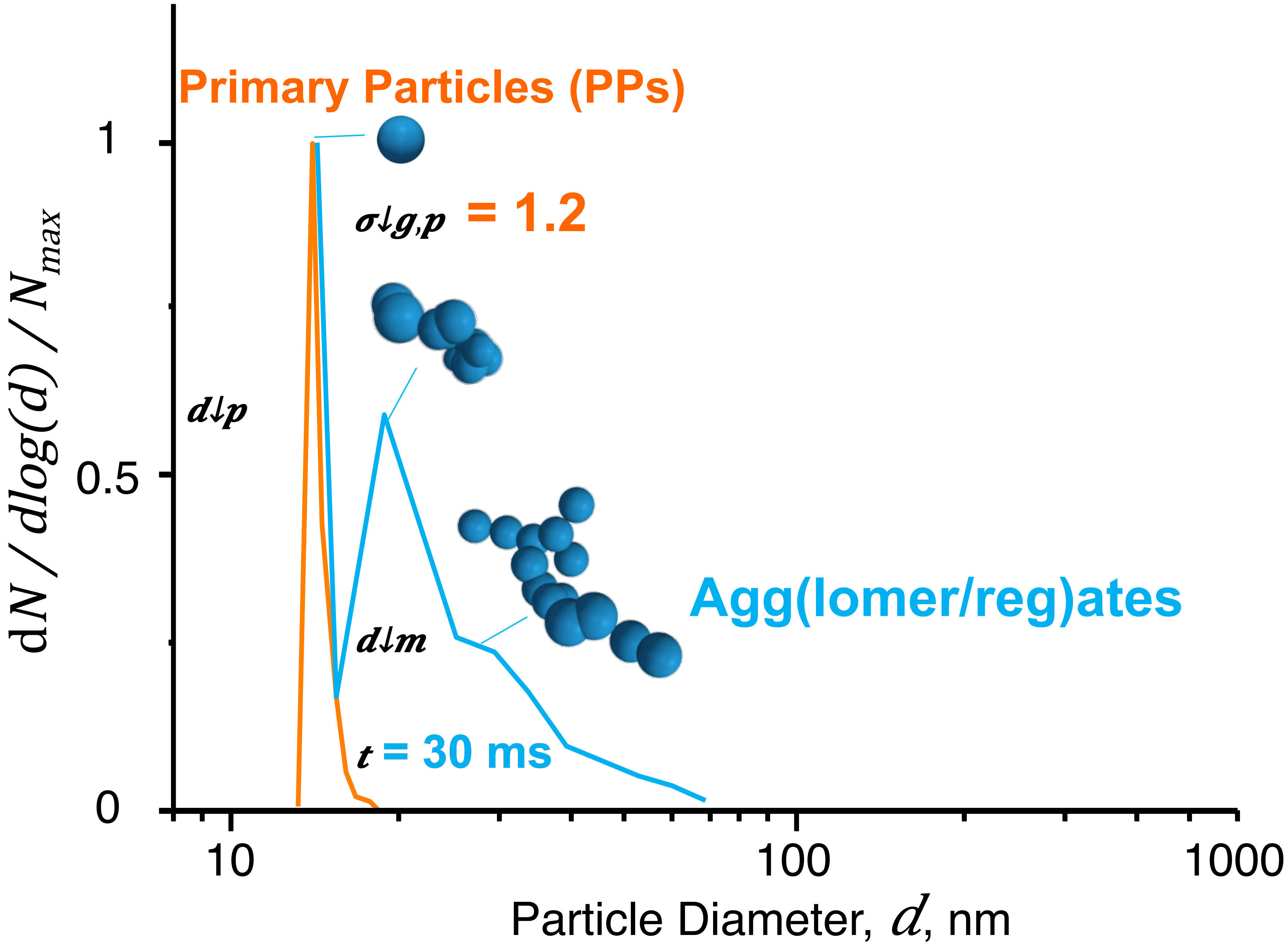
[1] Camacho J, Liu C, Gu C, Lin H, Huang Z, Tang Q, You X, Saggese C, Li Y, Jung H, Deng L, Wlokas I, Wang H. (2015) *Combust. Flame* **162**, 3810.

Evolution of Nascent Soot Morphology

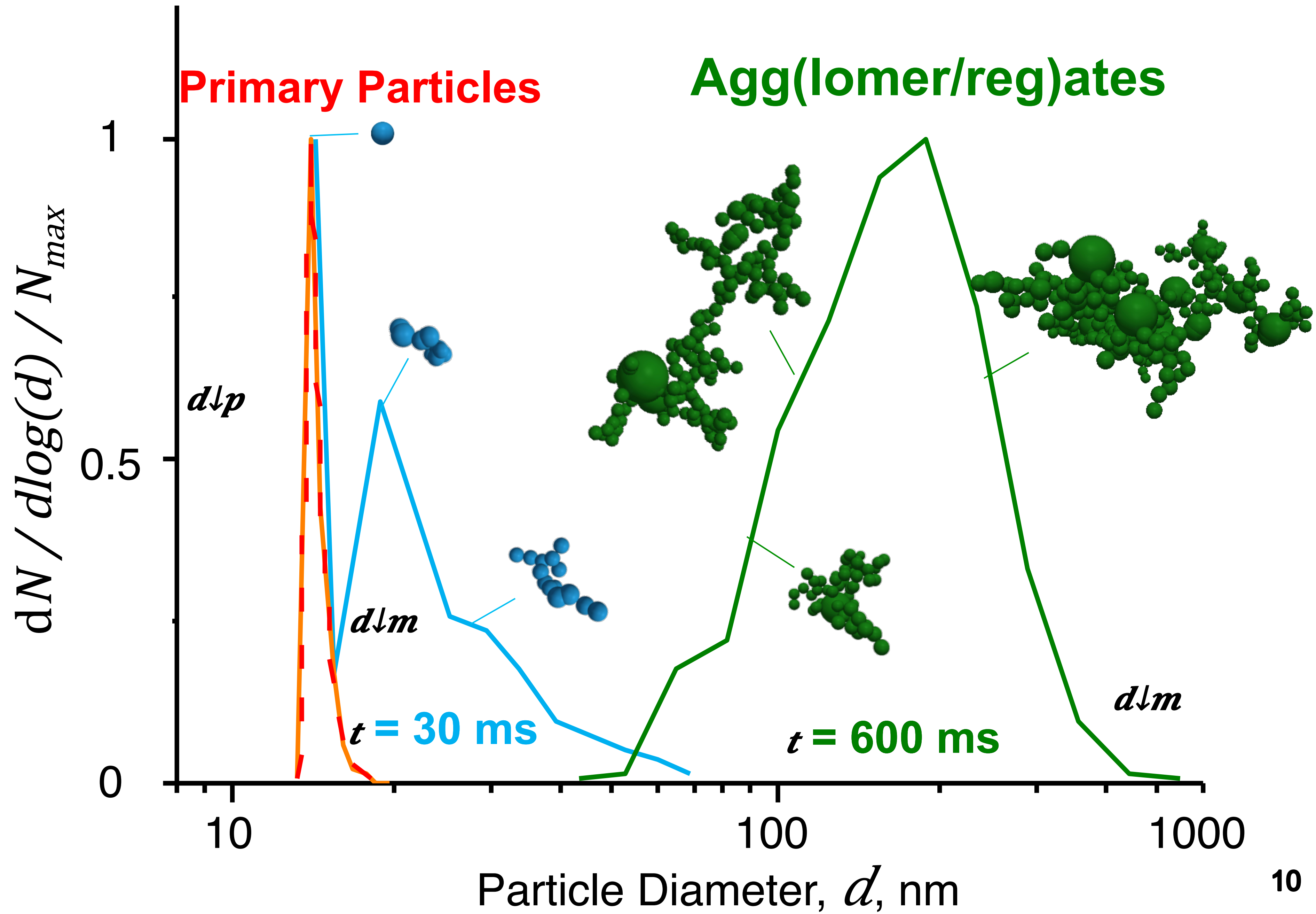


[1] Schenk M, Lieb S, Vieker H, Beyer A, Golzhauser A,Wang H, Kohse-Hoinghaus K. (2013) *PhysChemPhys* **14**, 3248.

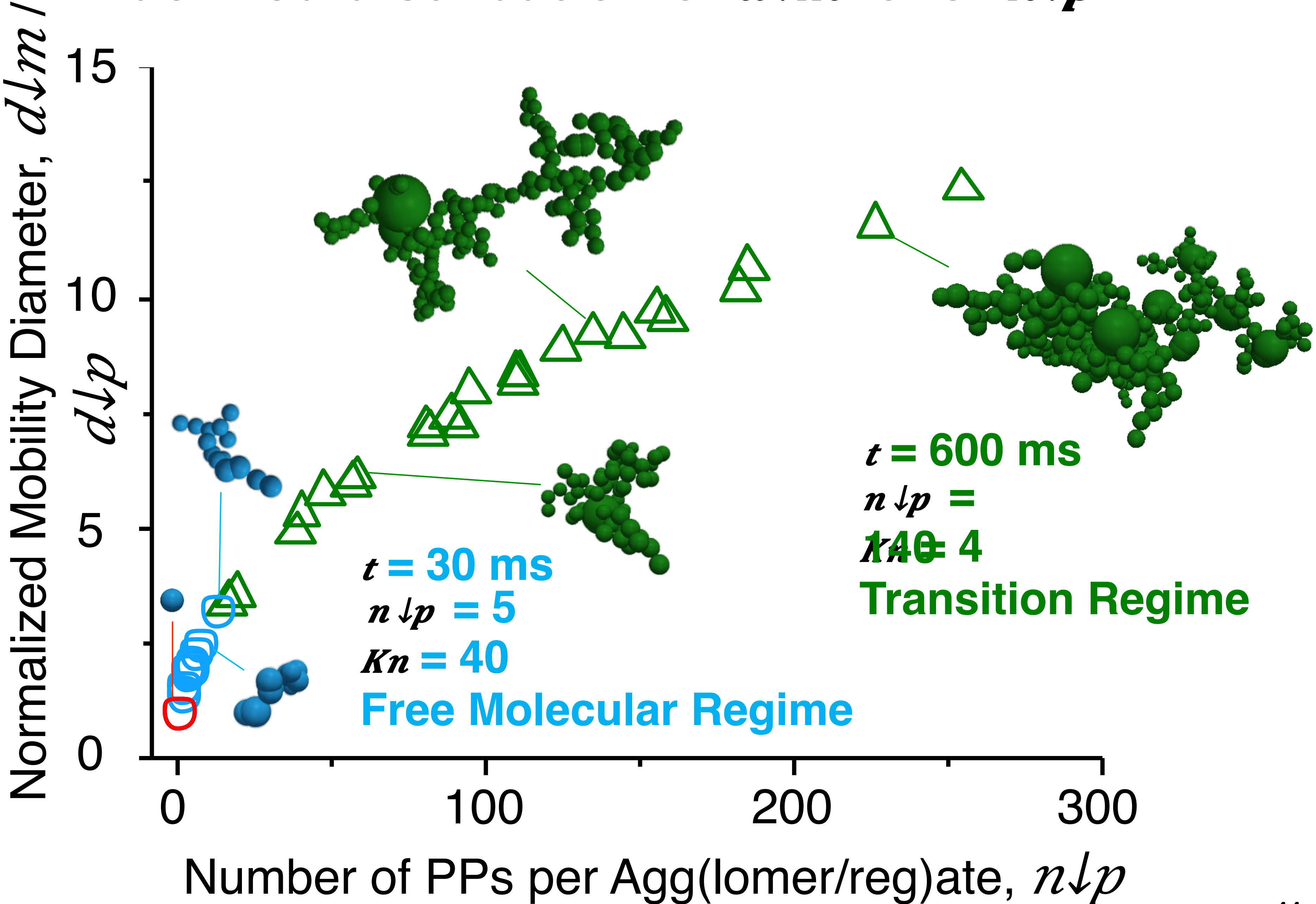
DEM-derived Soot Size Distributions



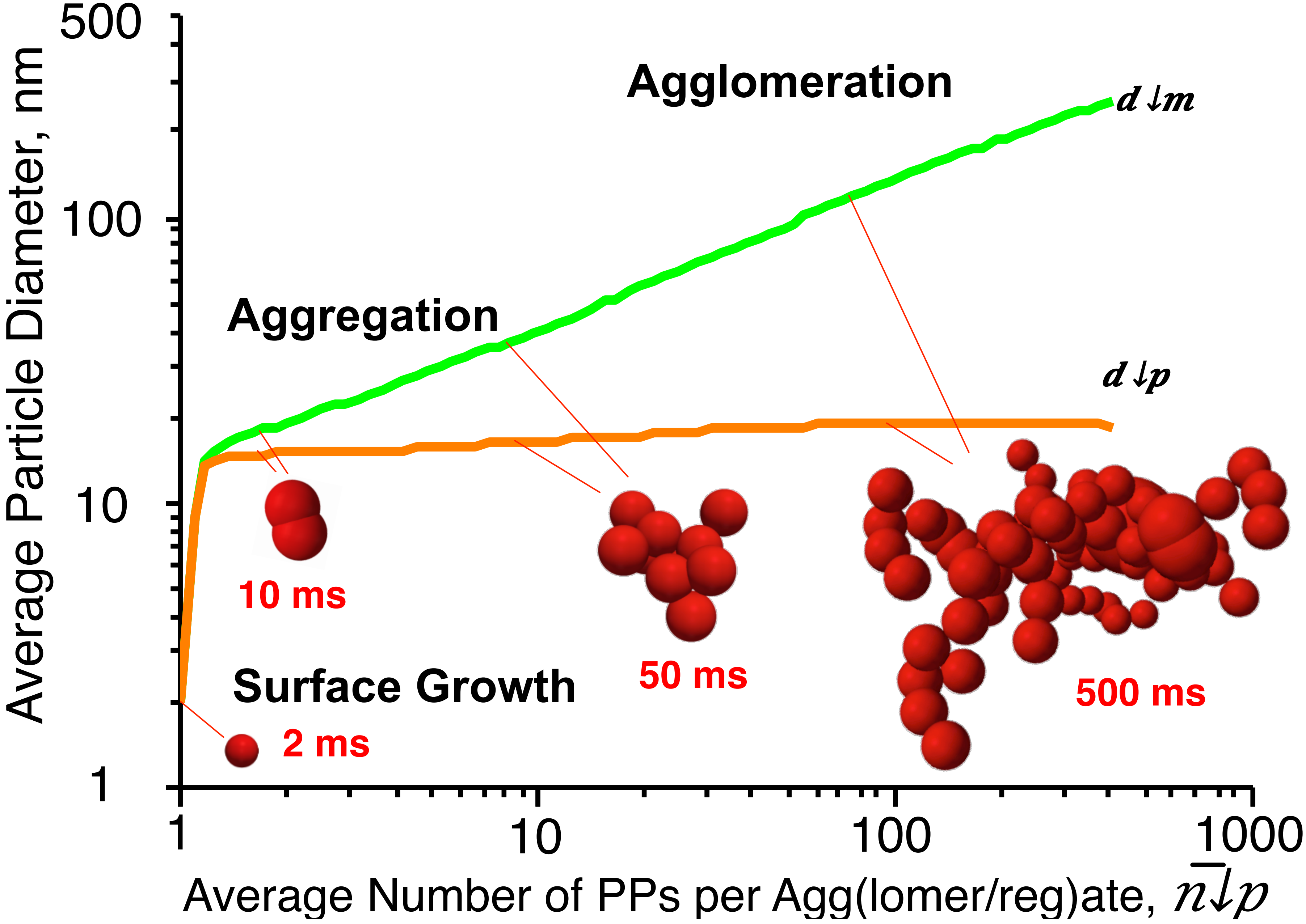
DEM-derived Soot Size Distributions



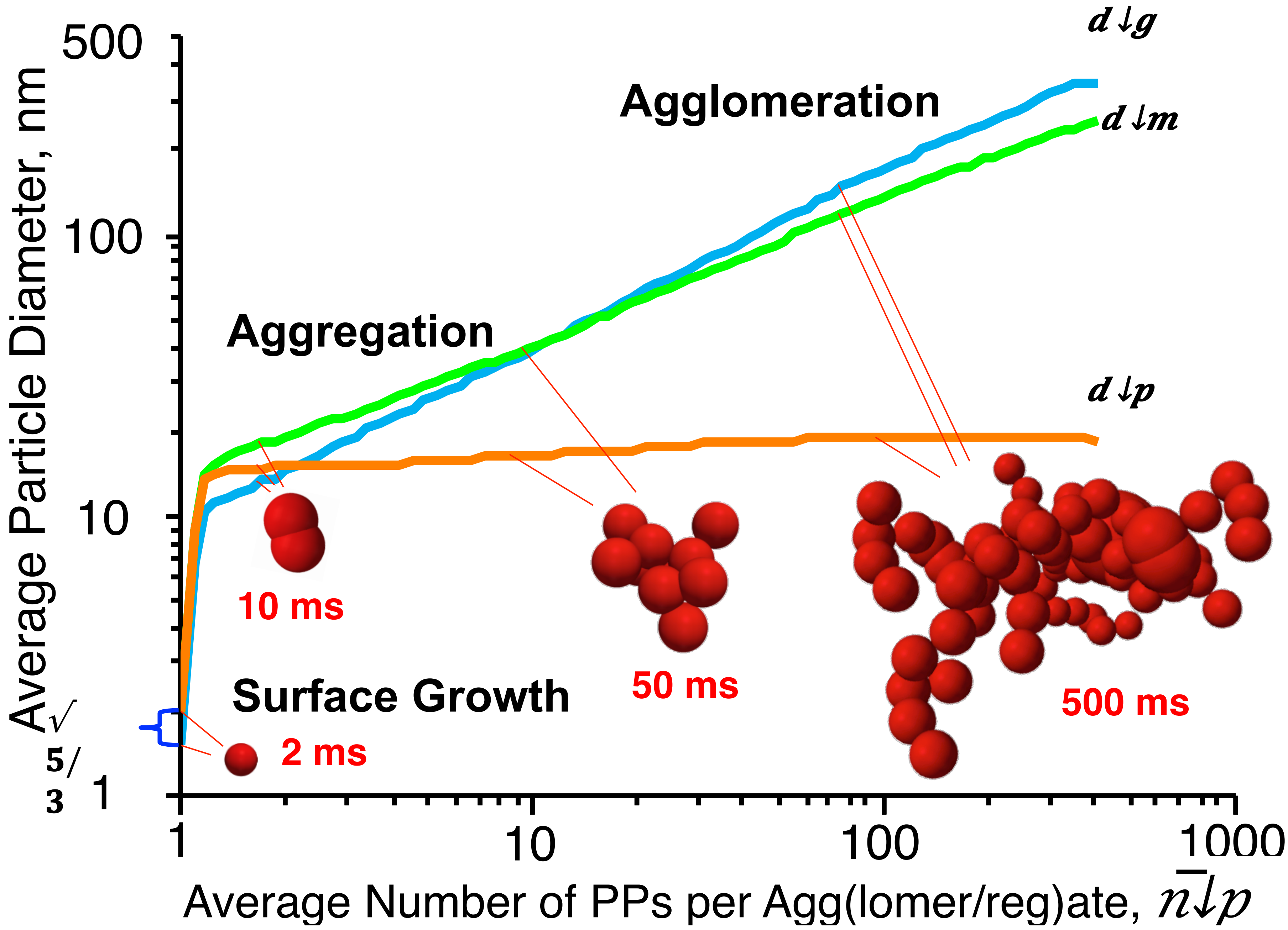
DEM-derived distribution of d_m over n_p

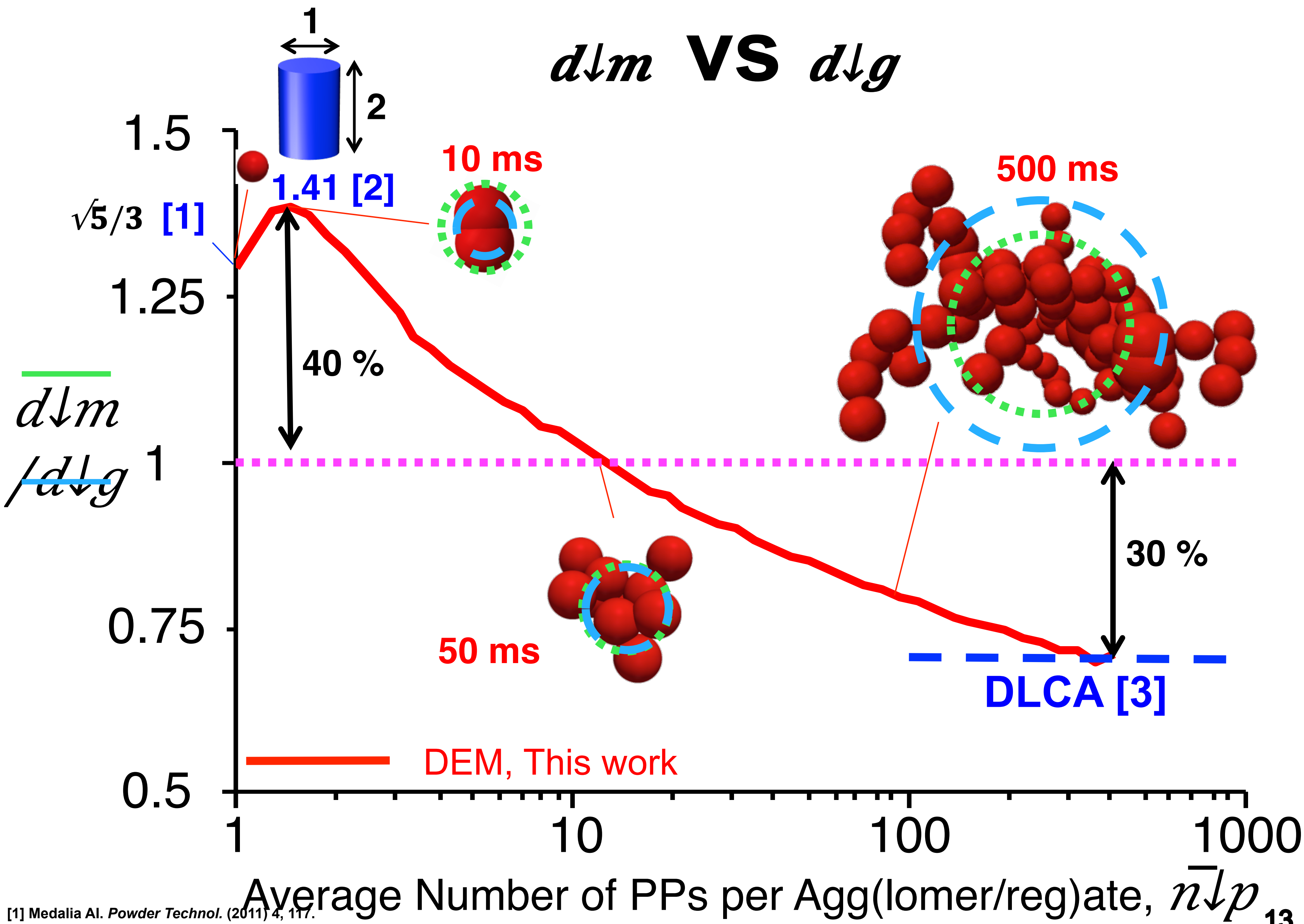


Soot Aggregation Dynamics by DEM



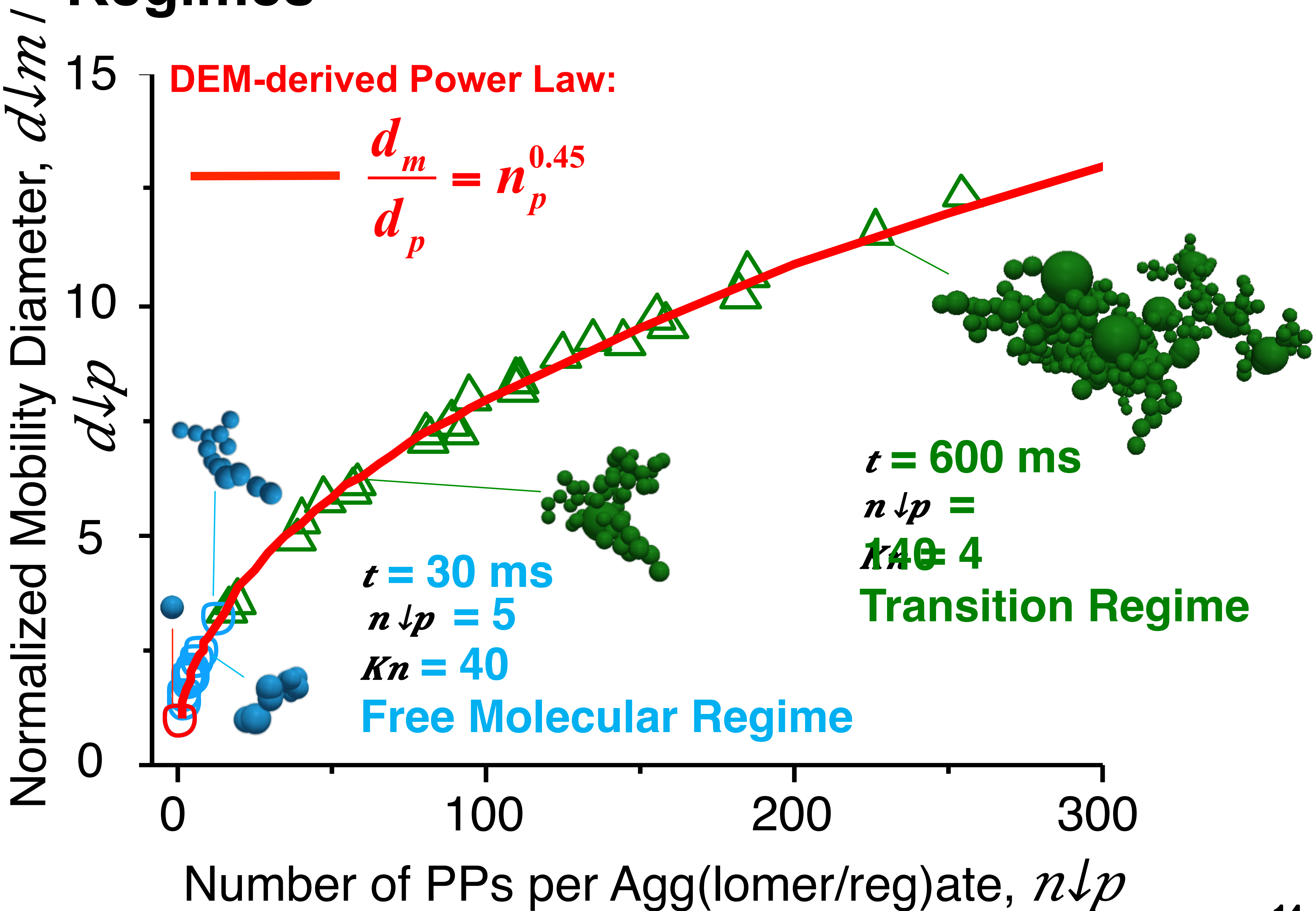
Soot Aggregation Dynamics by DEM





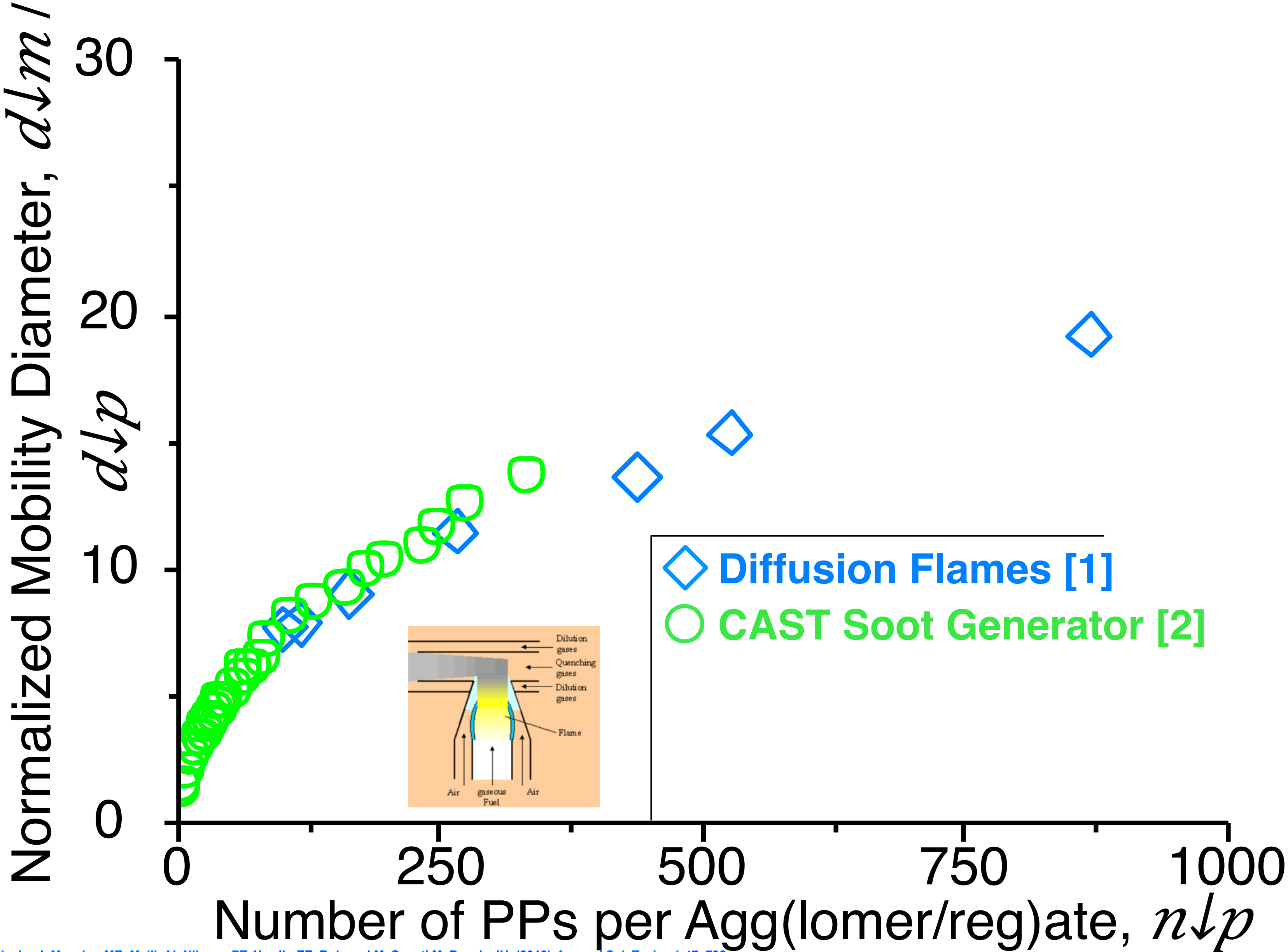
[1] Medalia AI. *Powder Technol.* (2011) 4, 117.
[2] Johnson DL, Leith D, Reist PC. *J. Aerosol Sci.* (1987) 18, 87.
[3] Wang GM, Sorensen CM. *Phys. Rev.* (1999) E60, 3036.

Regimes



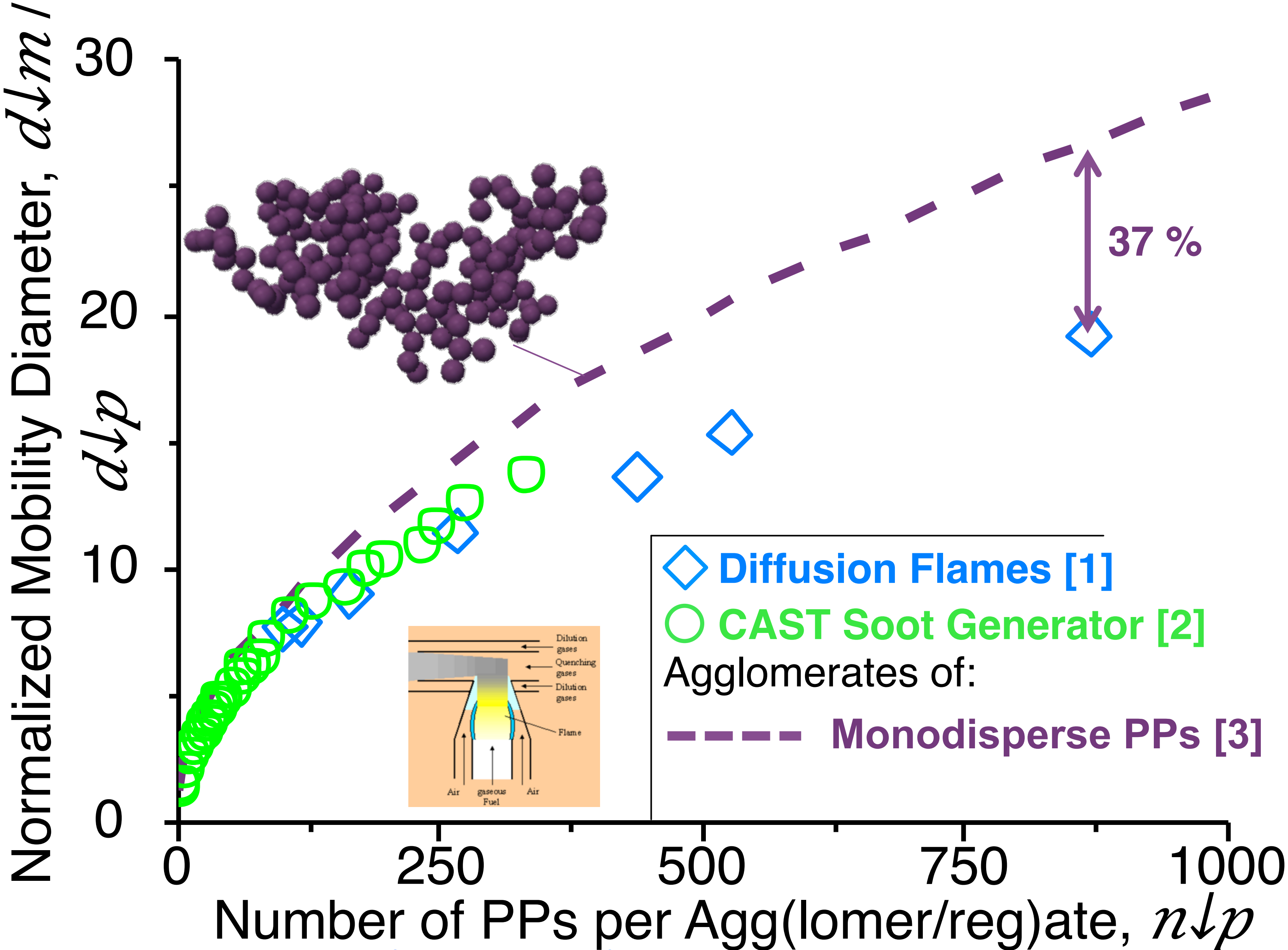
DEM-derived Power Law:
$\frac{d_m}{d_p} = n_p^{0.45}$
t = 600 ms
n↓p =
140
Kn = 4
Transition Regime
t = 30 ms
n↓p = 5
Kn = 40
Free Molecular Regime
Normalized Mobility Diameter, d↓m / d↓p
Number of PPs per Agg(lomer/reg)ate, n↓p
0
5
10
15
0
100
200
300

Comparison to Experiments:



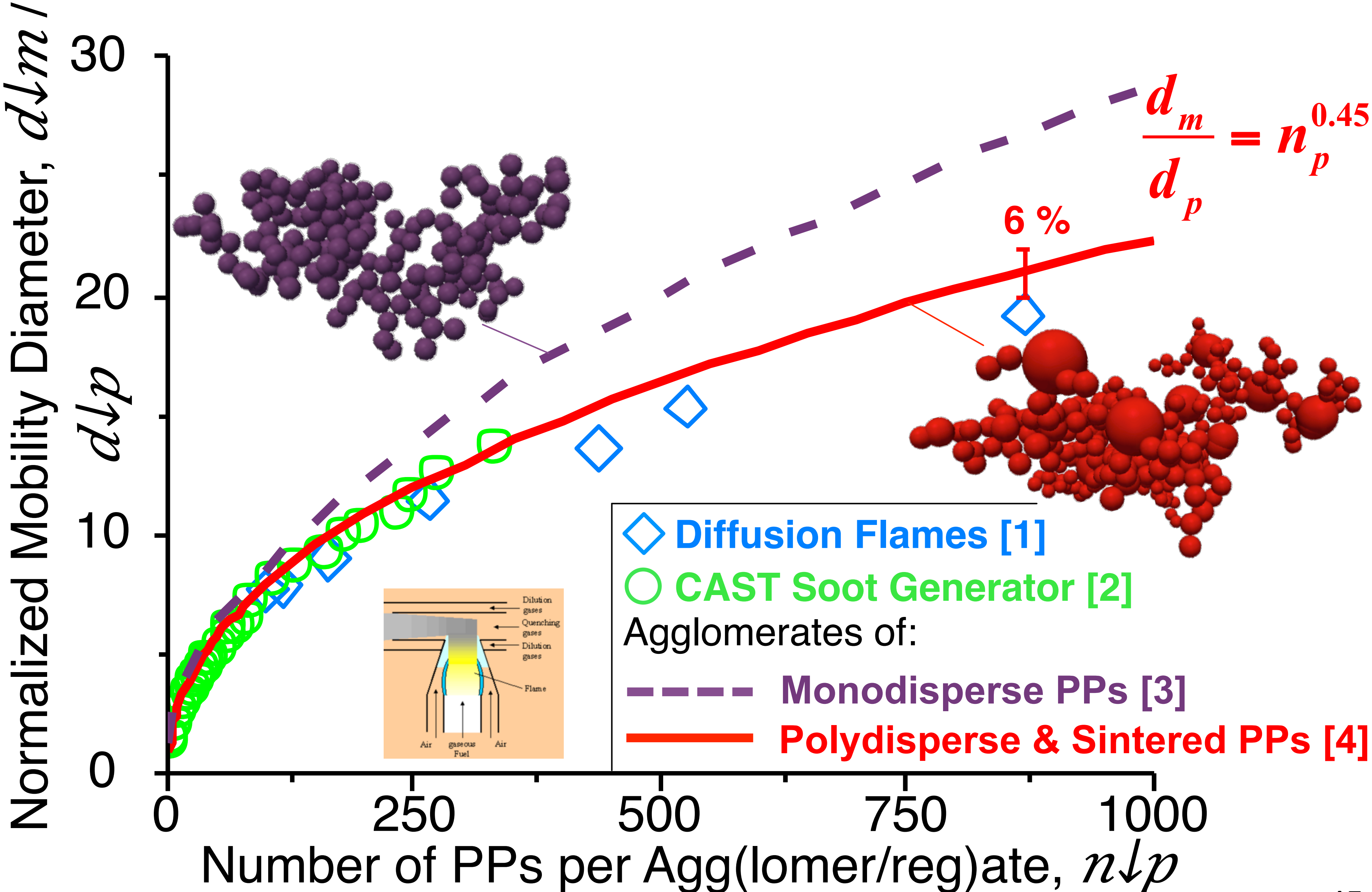
[1] Rissler J, Messing ME, Malik AI, Nilsson PT, Nordin EZ, Bohgard M, Sanati M, Pagels JH. (2013) *Aerosol Sci. Technol.* 47, 792.
[2] Yon J, Bescond A, Ouf FX. (2015) *J. Aerosol Sci.* 87, 28.

Comparison to Experiments:



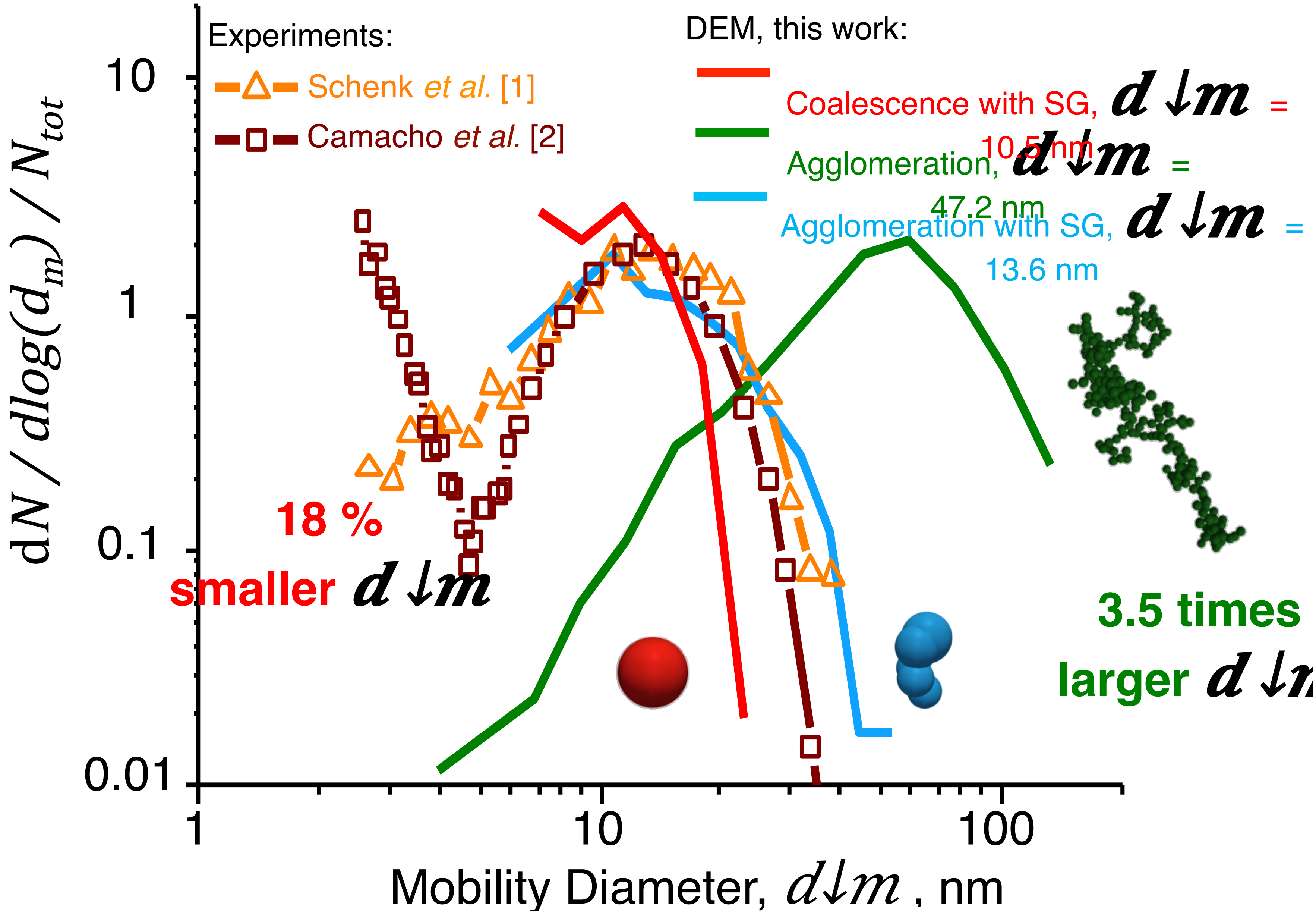
[1] Rissler J, Messing ME, Malik AI, Nilsson PT, Nordin EZ, Bohgard M, Sanati M, Pagels JH. (2013) *Aerosol Sci. Technol.* 47, 792.
[2] Yon J, Bescond A, Ouf FX. (2015) *J. Aerosol Sci.* 87, 28.
[3] Sorensen CM. *Aerosol Sci. Technol.* (2011) 45, 765.

Comparison to Experiments:



[1] Rissler J, Messing ME, Malik AI, Nilsson PT, Nordin EZ, Bohgard M, Sanati M, Pagels JH. (2013) *Aerosol Sci. Technol.* 47, 792.
[2] Yon J, Bescond A, Ouf FX. (2015) *J. Aerosol Sci.* 87, 28.
[3] Sorensen CM. *Aerosol Sci. Technol.* (2011) 45, 765.
[4] Kelesidis GA, Goudeli E, Pratsinis SE. *Carbon* (2017) 121, 527.

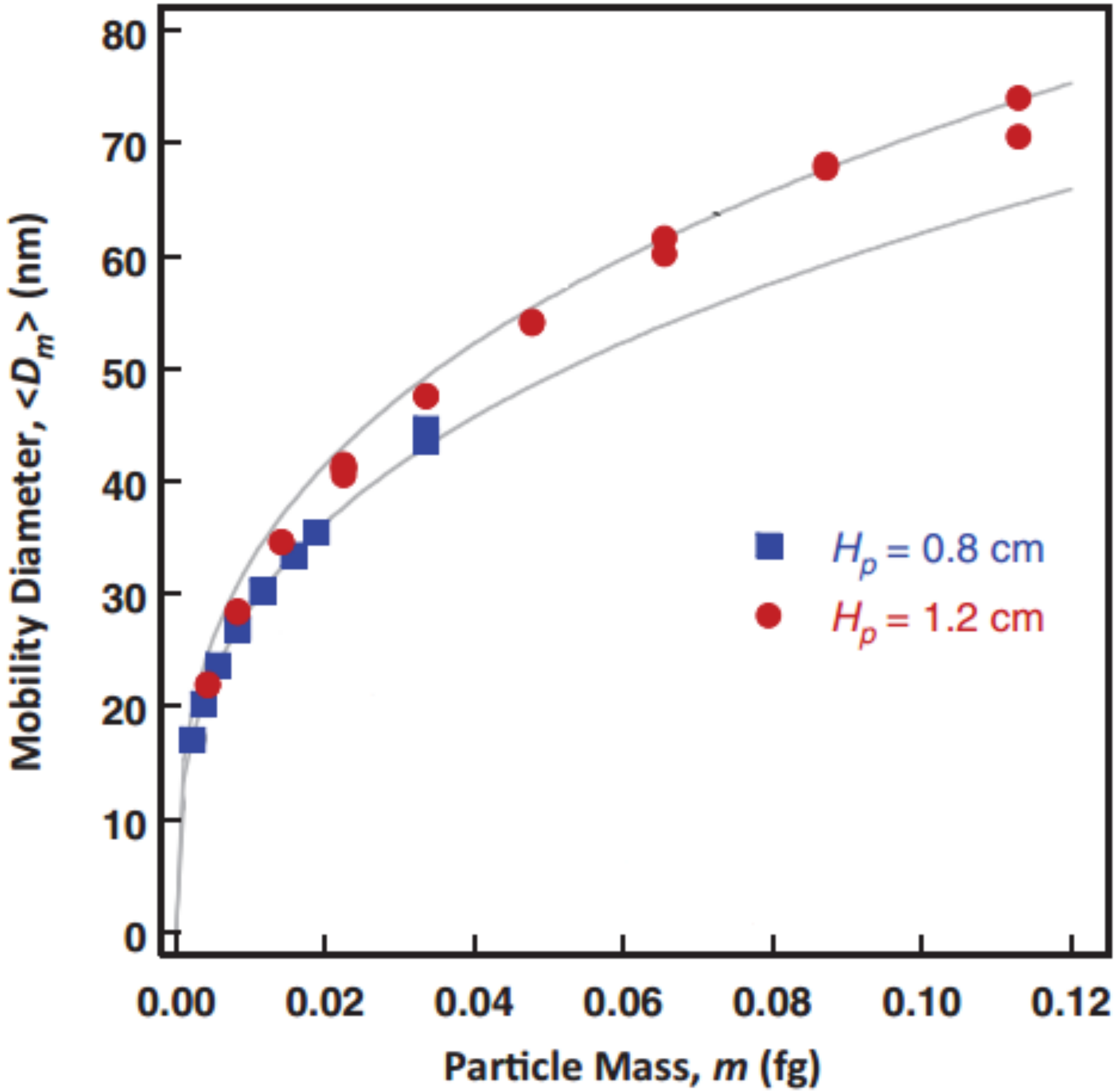
Soot Size Distribution, HAB = 0.8 cm



[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.

Nascent Soot Mass-Mobility Relationship



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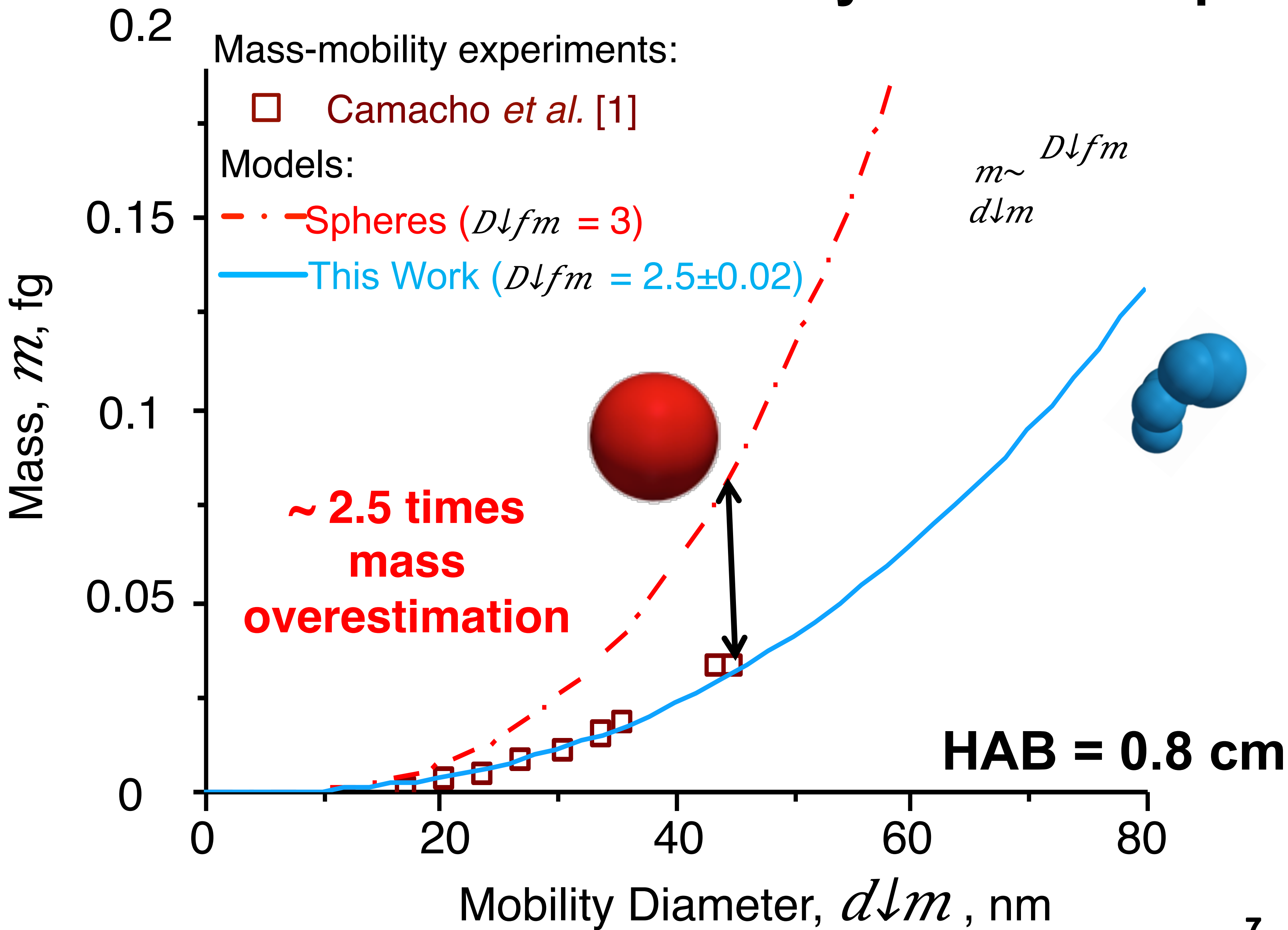

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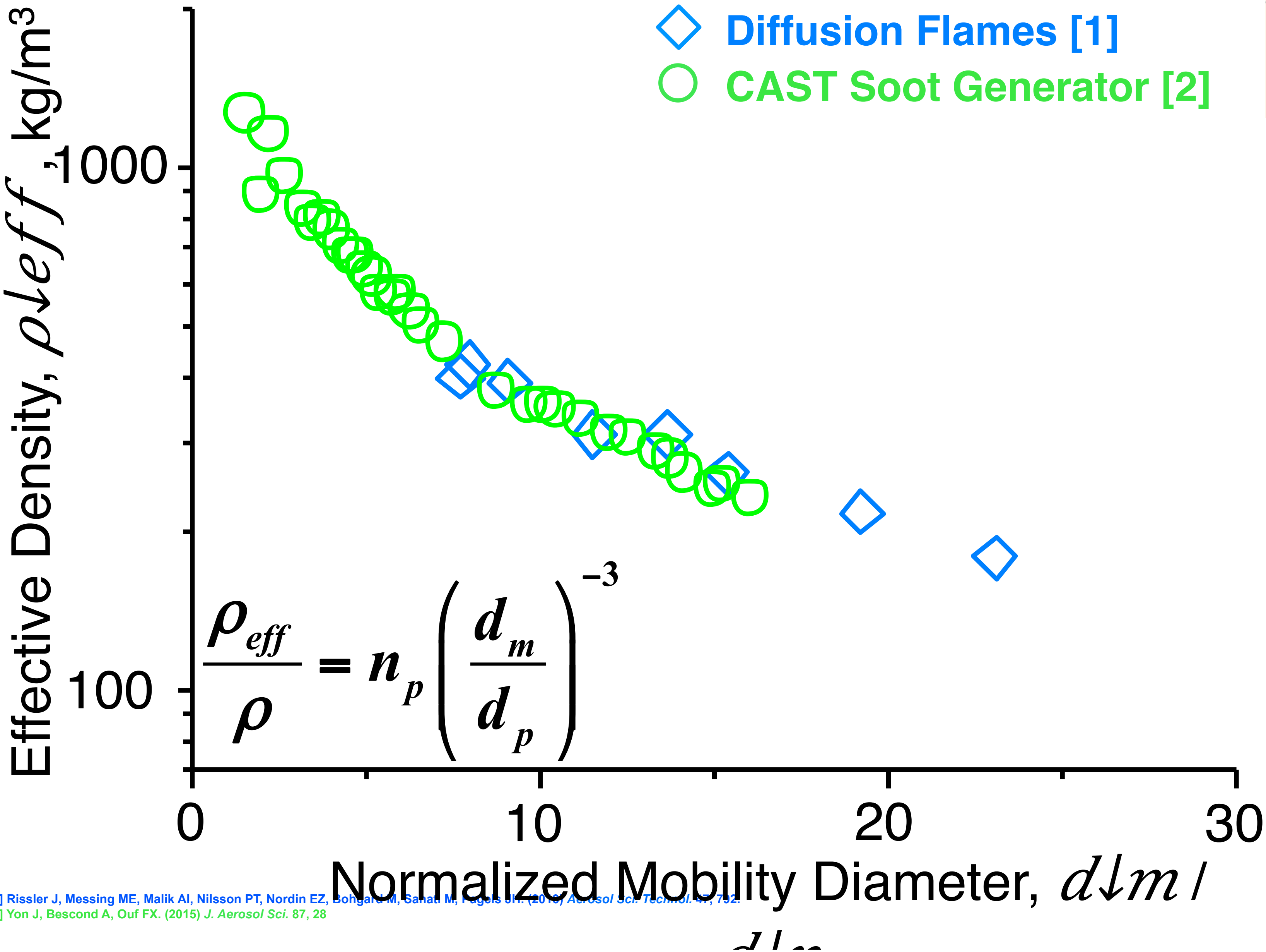
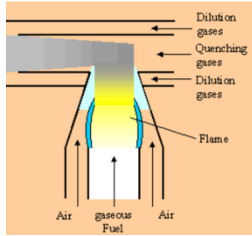
Characterization of Soot Morphology

Soot Effective Density





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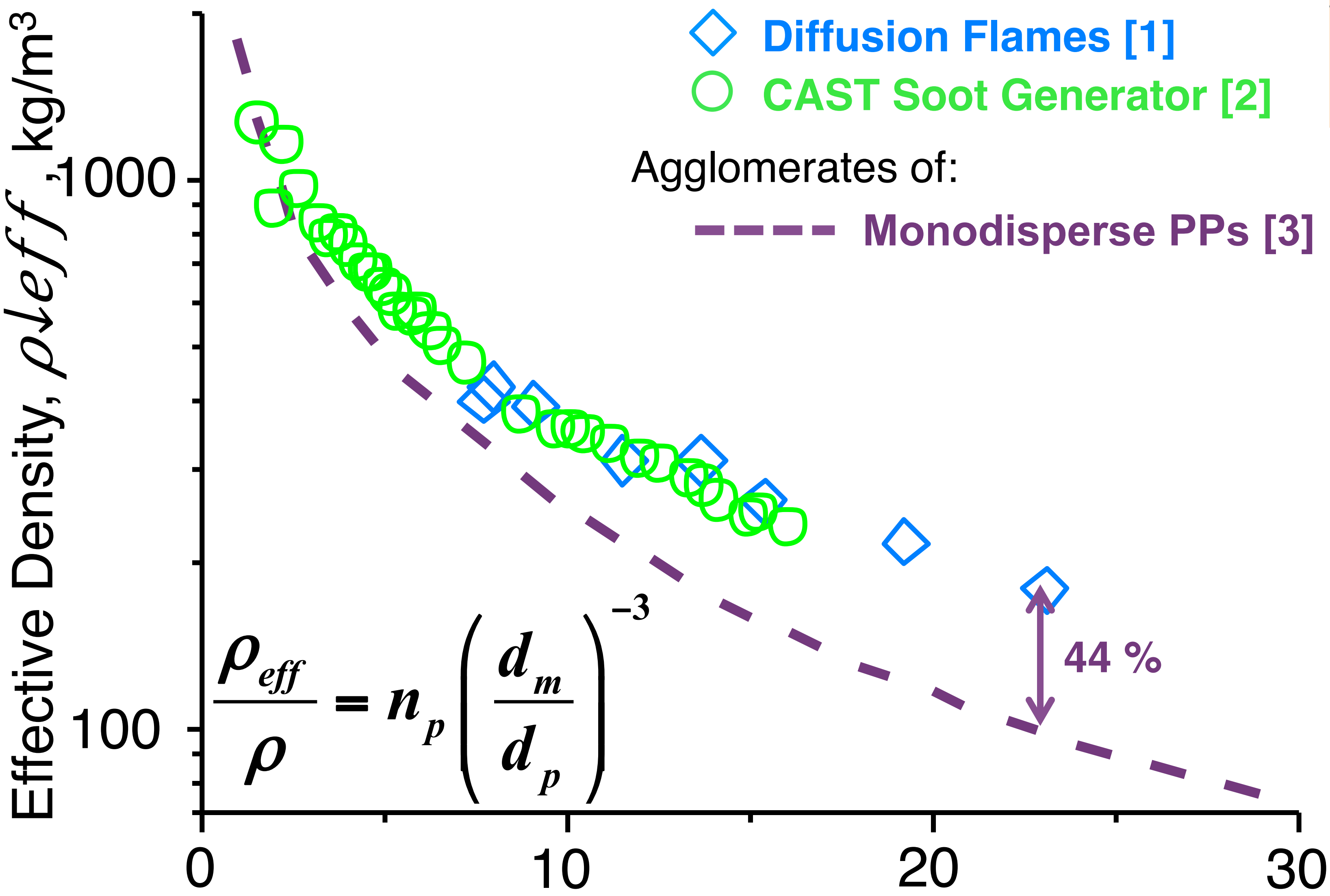
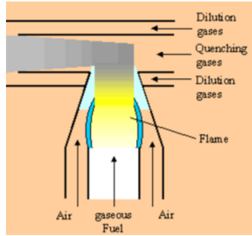
[2] Yon J, Bescond A, Ouf FX. (2015) *J. Aerosol Sci.* 87, 28

Soot Effective Density





$$\frac{\rho_{eff}}{\rho} = n_p \left(\frac{d_m}{d_p} \right)^{-3}$$

[1] Rissler J, Messing ME, Malik AI, Nilsson PT, Nordin EZ, Bohgard M, Sanati M, Pagels JH. (2013) *Aerosol Sci. Technol.* 47, 792.
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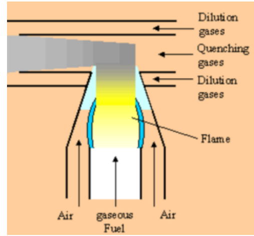

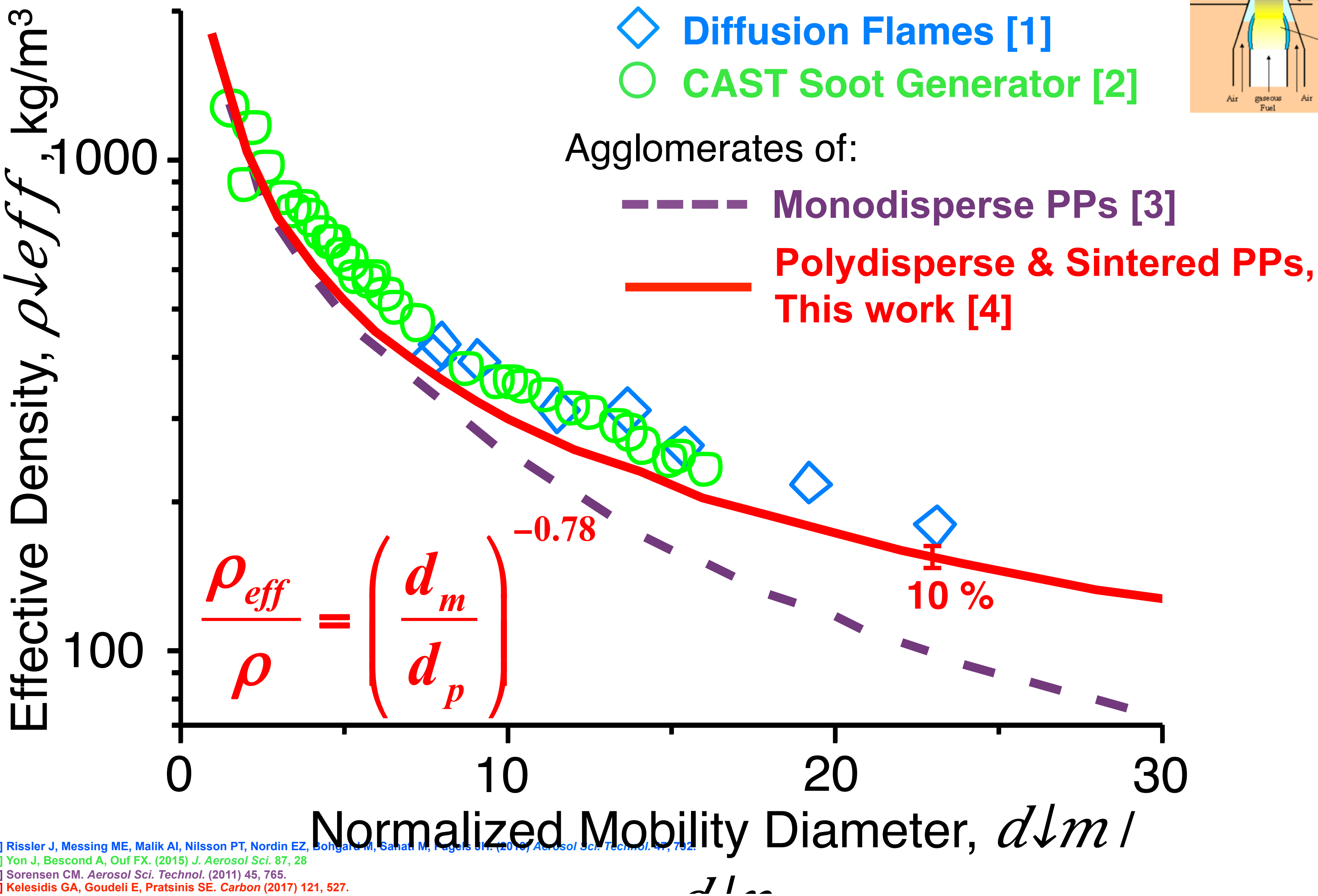

[1] Rissler J, Messing ME, Malik AI, Nilsson PT, Nordin EZ, Bohgard M, Sanati M, Pagels JH. (2013) *Aerosol Sci. Technol.* 47, 792.
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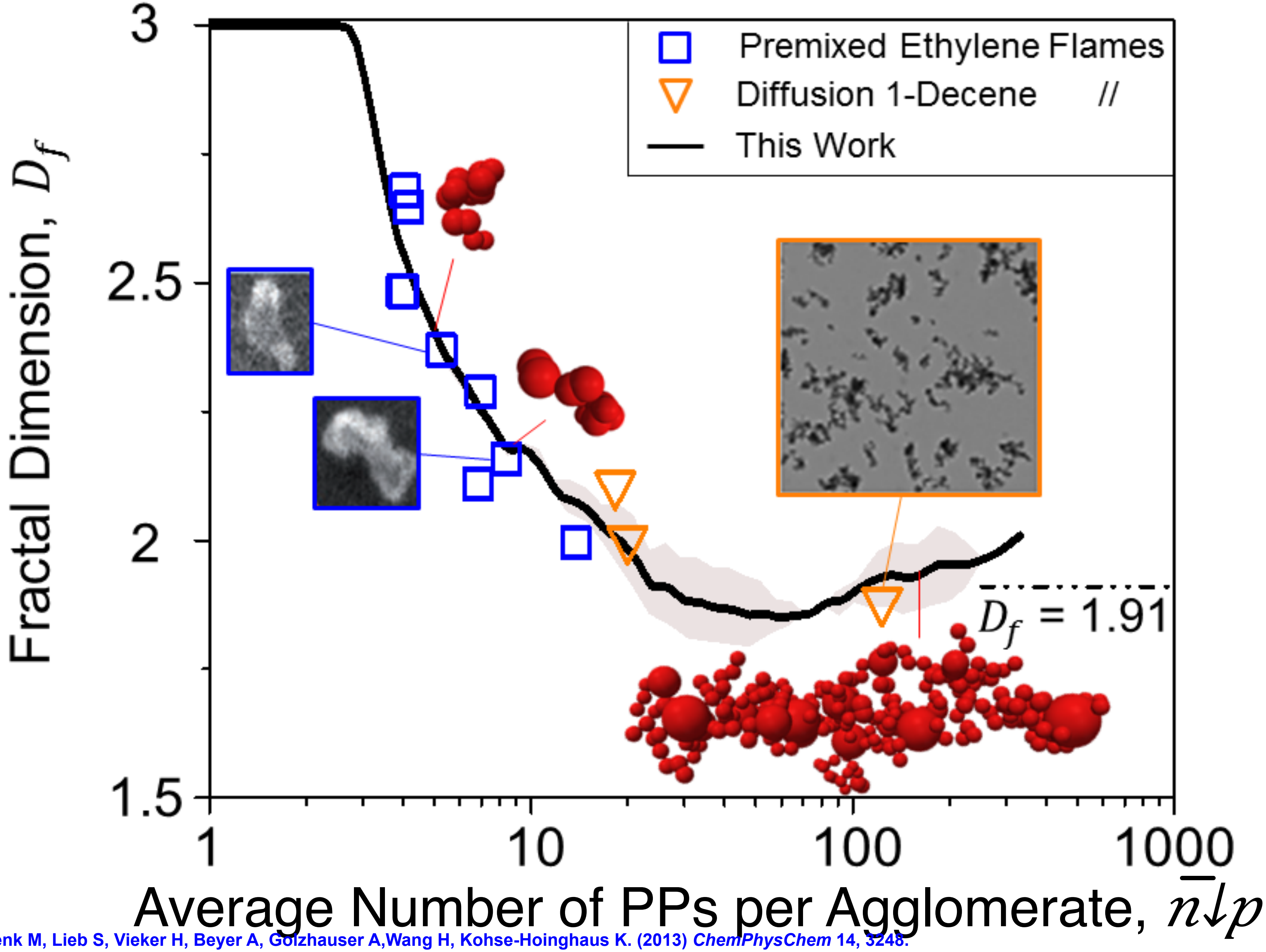
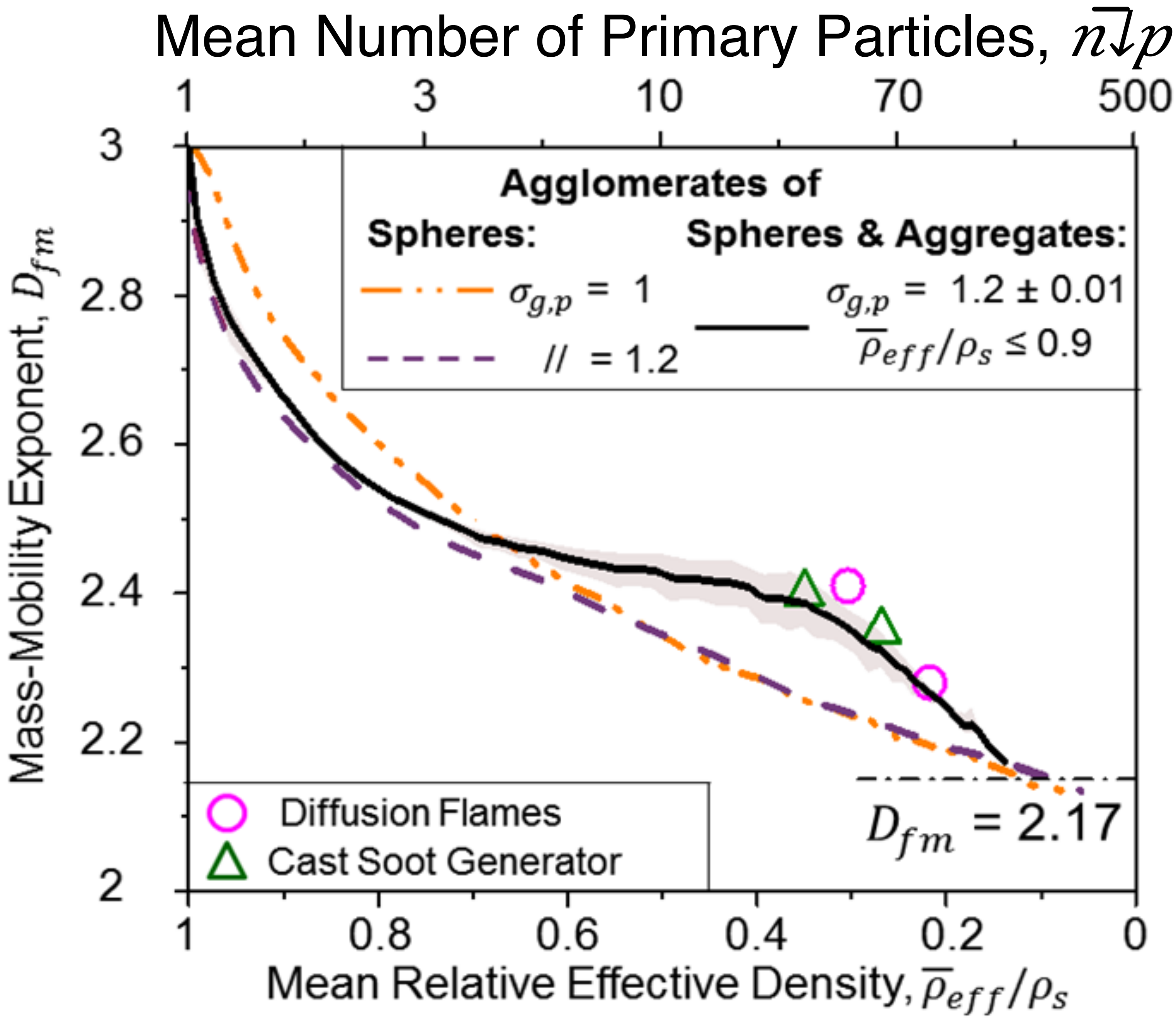
[3] Sorensen CM. *Aerosol Sci. Technol.* (2011) 45, 765.
[4] Kelesidis GA, Goudeli E, Pratsinis SE. *Carbon* (2017) 121, 527.

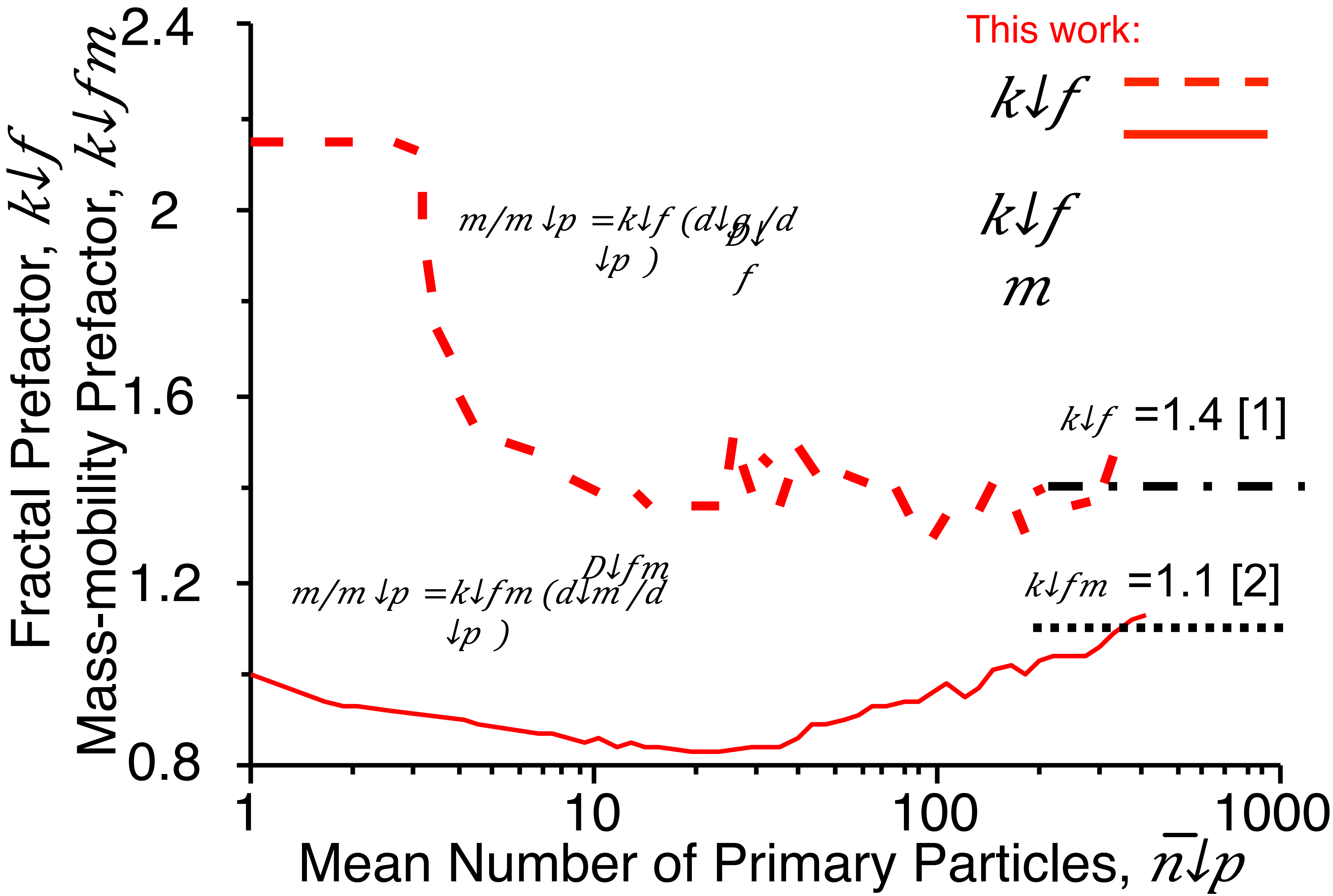
Evolution from Nascent to Mature Soot



Schenk M, Lieb S, Vieker H, Beyer A, Gölzhauser A,Wang H, Kohse-Hoinghaus K. (2013) *ChemPhysChem* 14, 3248.
Kholghy MR, Afarin Y, Sediako AD, Barba J, Lapuerta M, Chu C, Weingarten J, Borshanpour B, Chernov V, Thomson MJ. (2017) *Combust. Flame* 176, 567.



Rissler J, Messing ME, Malik AI, Nilsson PT, Nordin EZ, Bohgard M, Sanati M, PagelsJH. (2013) *Aerosol Sci. Technol.* 47, 792
Yon J, Bescond A, Ouf FX. (2015) *J. Aerosol Sci.* 87, 28



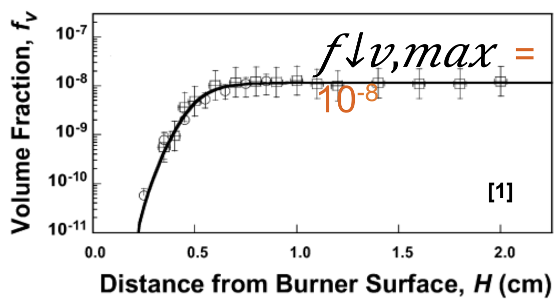
[1] Goudeli E, Eggersdorfer ML, Pratsinis SE. *Langmuir* (2015)
[2] Eggersdorfer ML, Pratsinis SE. *Aerosol Sci. Tech.* (2012)

Model
Description & Validation

Surface Growth Implementation

$$C_{soot}-H + H \leftrightarrow C_{soot}^{\bullet} + H_2$$
$$C_{soot}^{\bullet} + H \rightarrow C_{soot}-H$$
$$C_{soot}^{\bullet} + C_2H_2 \rightarrow C_{soot}-CAH + H$$

r_{HA}

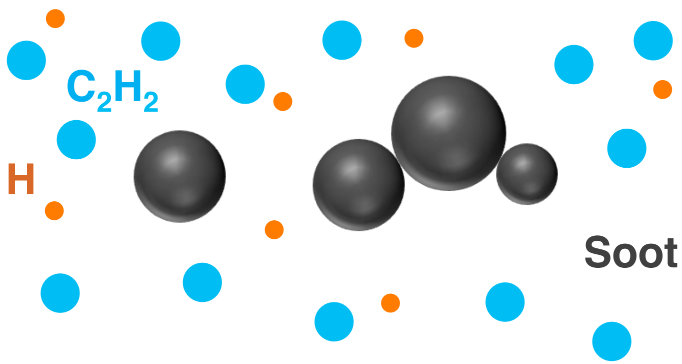


$f_{v,max} = 10^{-8}$

$x_{C2H2} = 0.02$

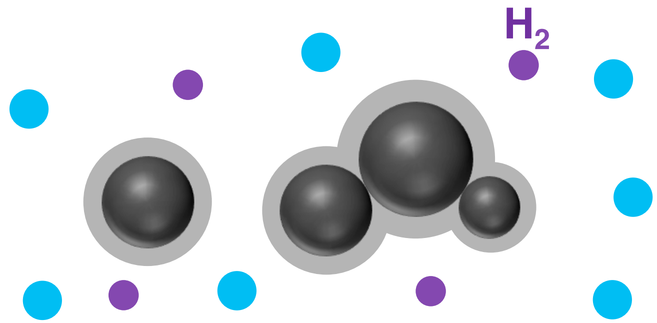
$x_{H2} = 0.1$ [1]

$x_{H} = 10^{-4}$ [2]



r_{HACA} [3]

β_{C2H2} [4]



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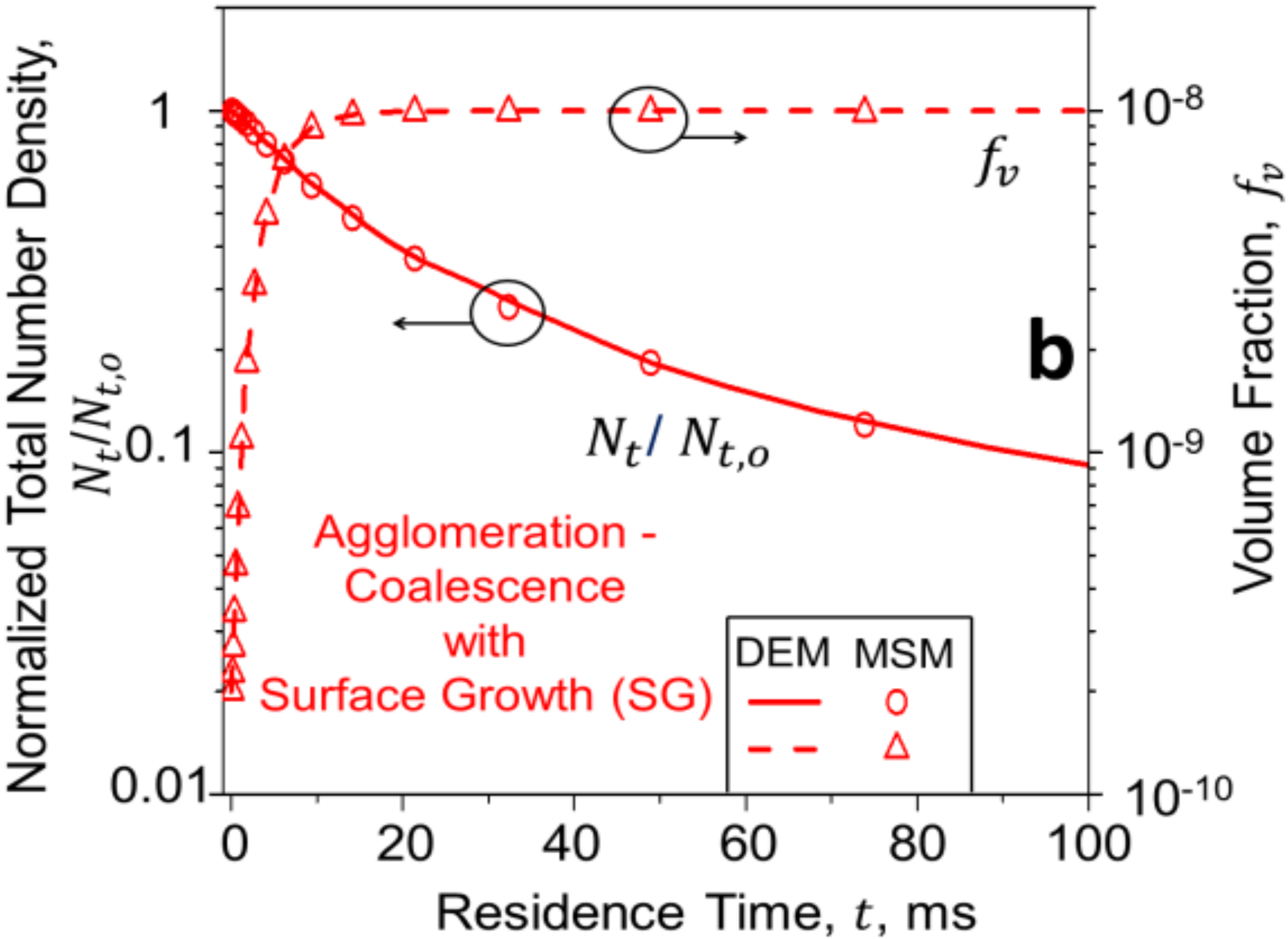
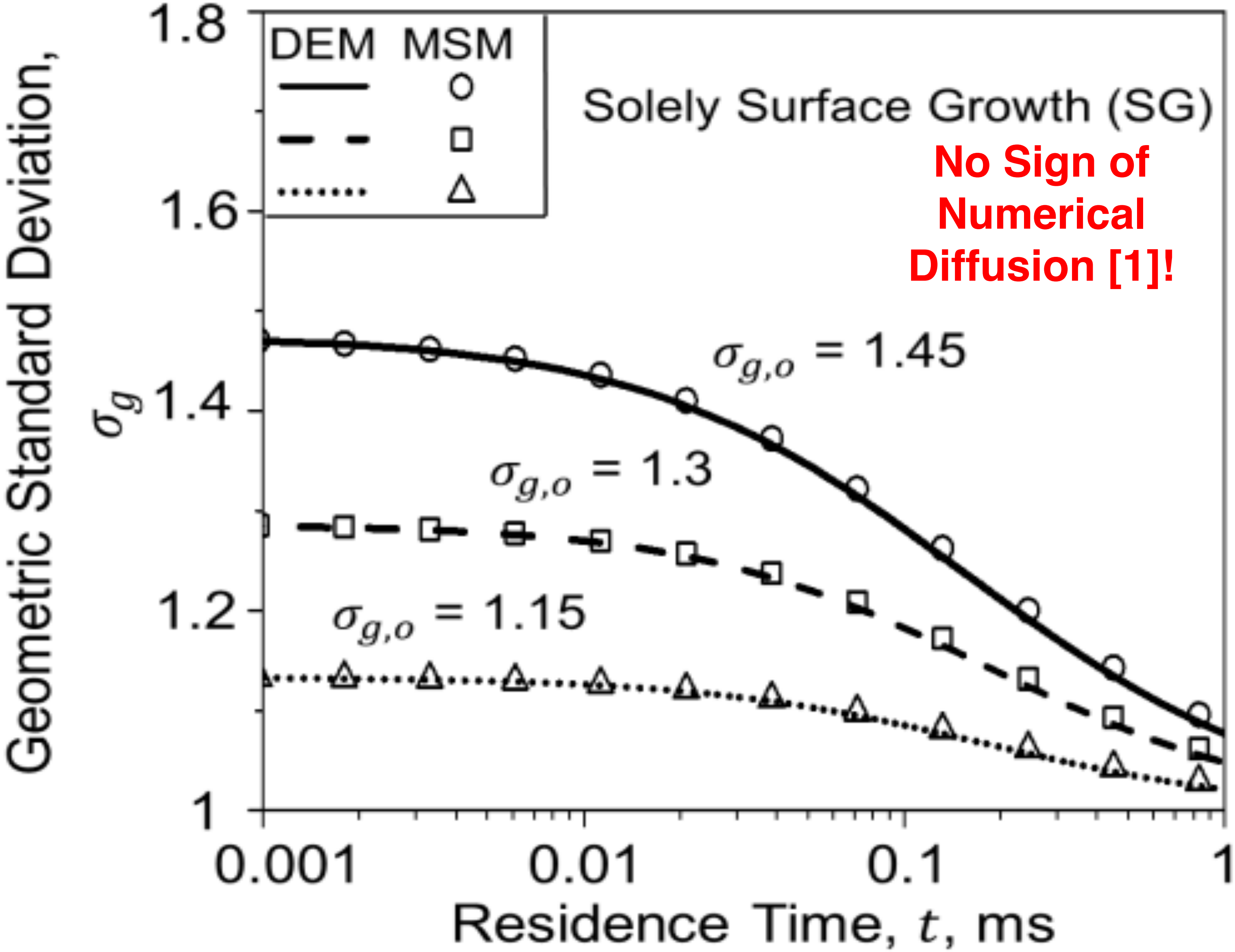
[1] Saggese C, Ferrario S, Camacho J, Cuoci A, Frassoldati A, Ranzi E, Wang H, Faravelli T. Wang H. (2015) *Combust. Flame* **162**, 3356.
[2] Abid AD, Heinz N, Tolmachoff ED, Phares DJ, Campbell CS, Wang H. (2008) *Combust. Flame* **154**, 775.
[3] Appel J, Bockhorn H, Frenklach M. (2000) *Combust. Flame* **121**, 122.
[4] Friedlander SK. (2000) Smoke, Dust, and Haze: Fundamentals of Aerosol Dynamics. Oxford University Press, New York.

Surface Growth Validation



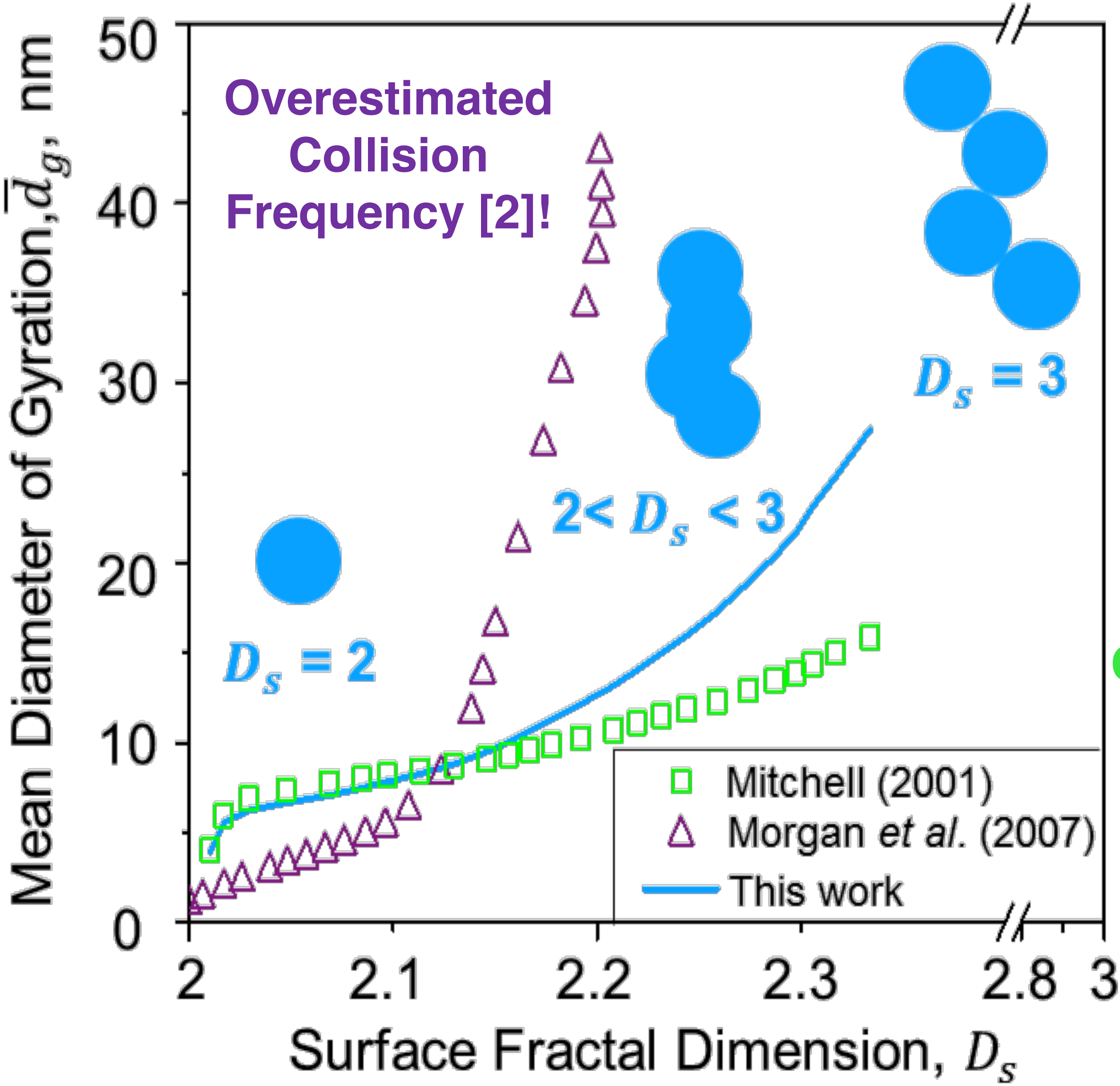
Surface Growth Validation



No Sign of Numerical Diffusion [1]!

[1] Warren DR, Seinfeld JH. (1985) *J. Colloid Interface Sci.* **105**, 136.

Benchmarking with Previous Studies



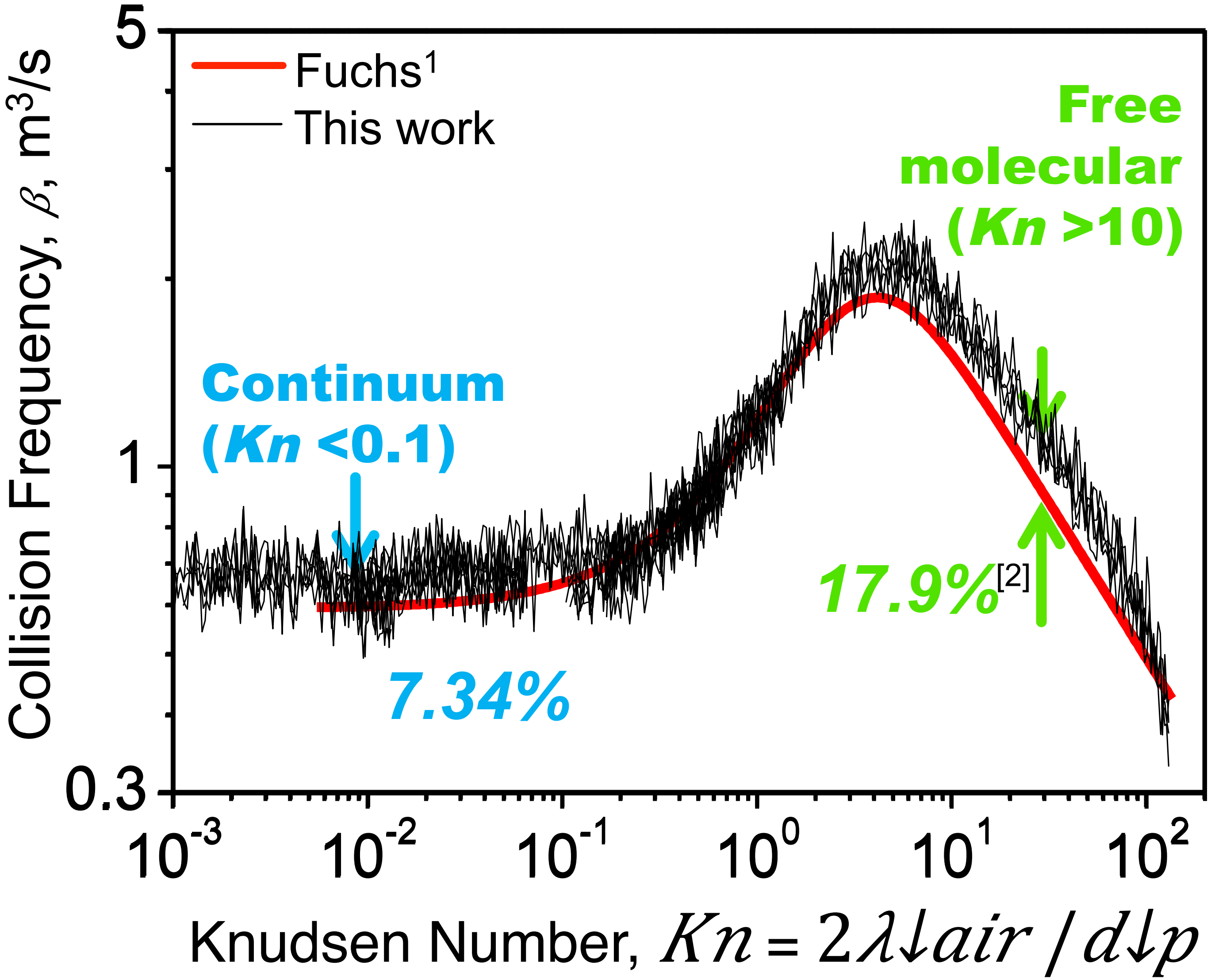
$$\frac{a}{a_{p,o}} = \left(\frac{v}{v_{p,o}}\right)^{D_s/3}$$

Only Particle - Cluster Collisions [1]!

[1] Mitchell P, PhD thesis, University of California, Berkeley, U.S.A., 2001.

[2] Morgan N, Kraft M, Balthasar M, Wong D, Frenklach M, Mitchell P. (2007) *Proc. Combust. Inst.* **31**, 693.

Coagulation Validation



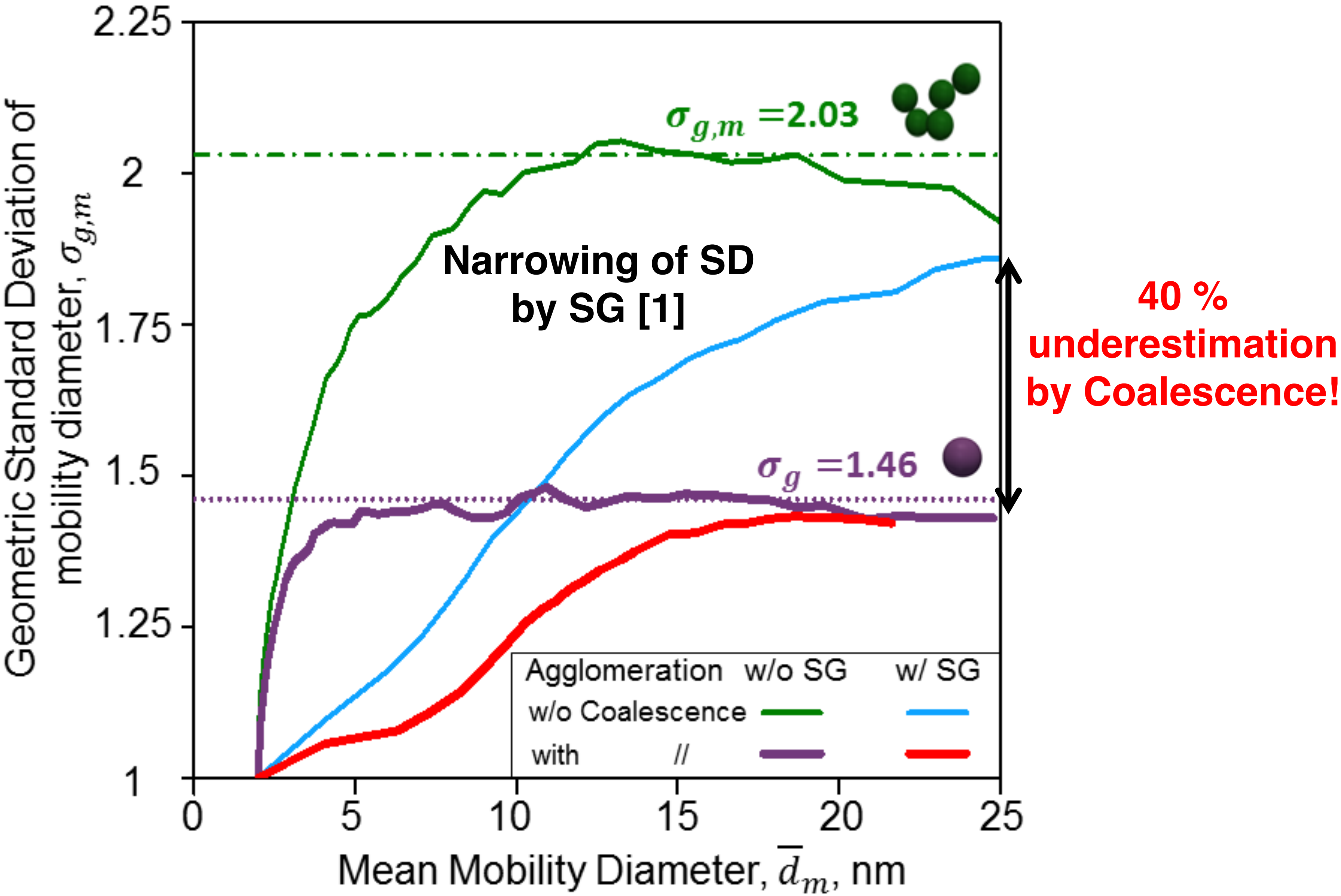
$$\beta = 2\frac{\frac{1}{N_2} - \frac{1}{N_1}}{t_2 - t_1}$$

Enhancement due to *polydispersity from the rapid attainment of SPSD*

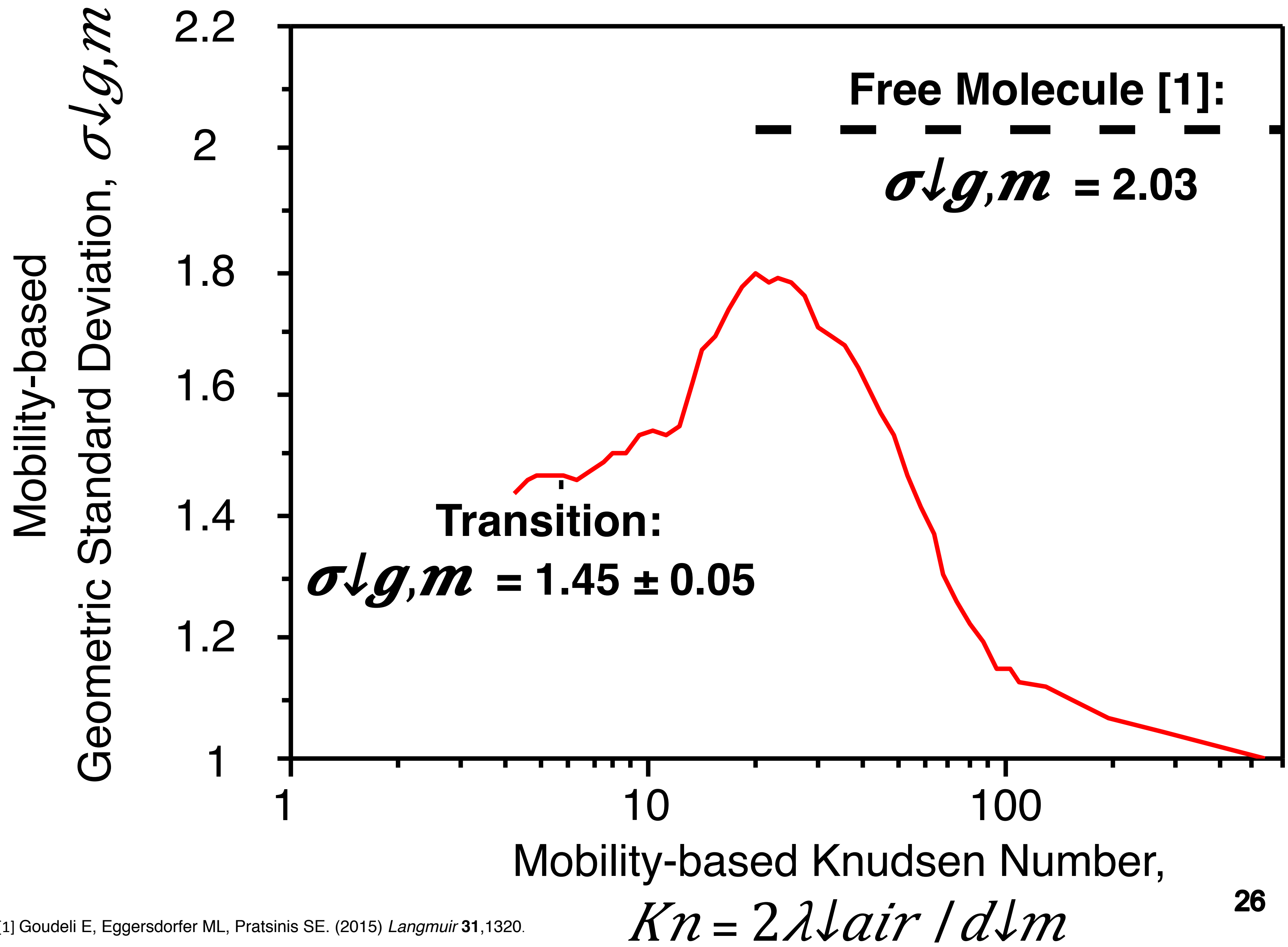
1. Fuchs NA. (1964). Mechanics of Aerosols. Macmillan, New York.
2. Buesser B, Heine MC, Pratsinis SE. (2009). *J. Aerosol Sci.*, **40**, 89–100.

Evolution of Soot Mobility Size and Mass Distributions

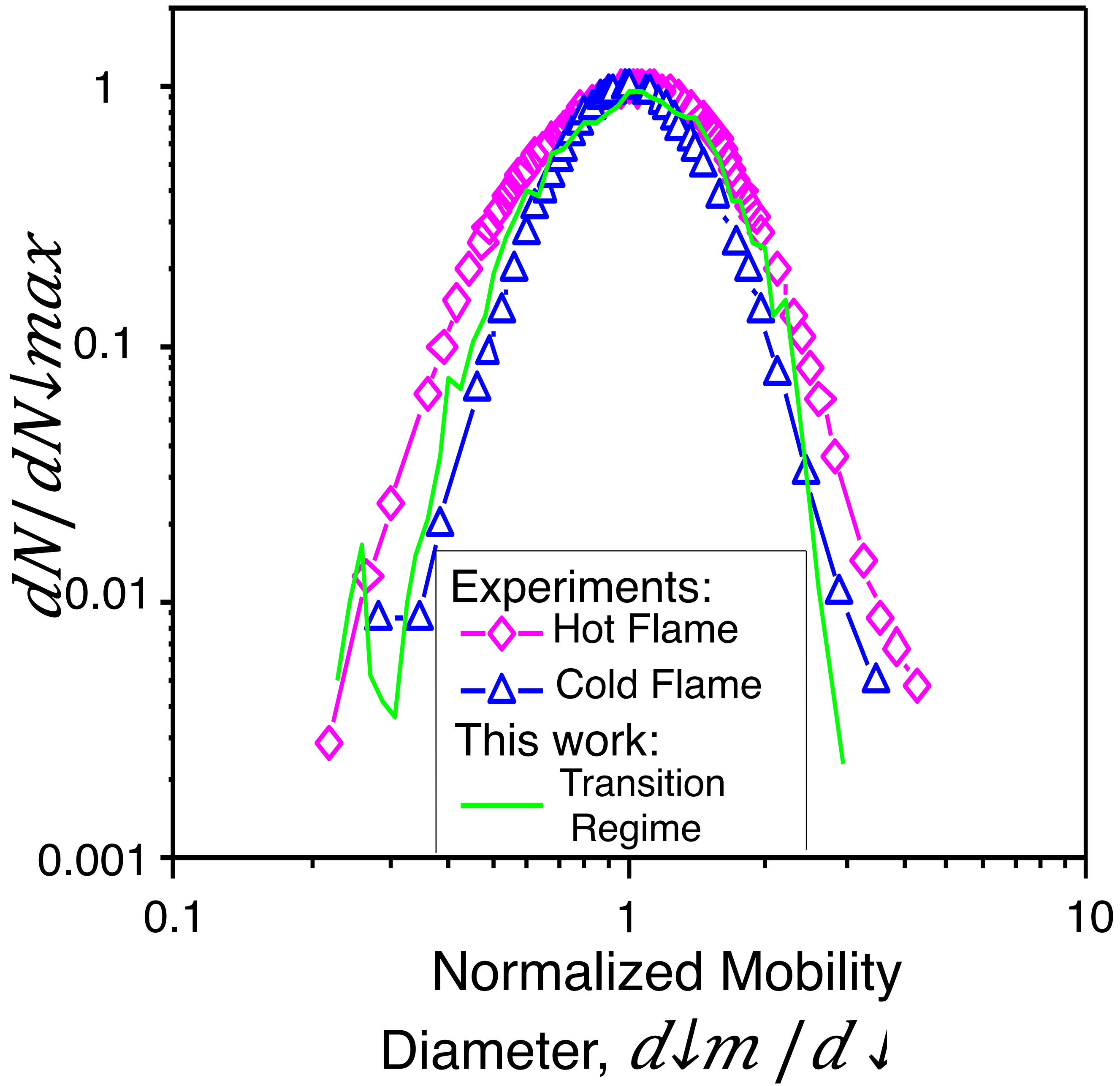
Evolution of Geometric Standard Deviation



[1] Spicer PT, Chaoul O, Tsantilis S, Pratsinis SE. (2002) *J. Aerosol Sci.* **33**, 17.
[2] Landgrebe JD, Pratsinis SE. (1989) *Ind. Eng. Chem. Res.* **28**, 1474.
[3] Goudeli E, Eggersdorfer ML, Pratsinis SE. (2015) *Langmuir* **31**,1320.

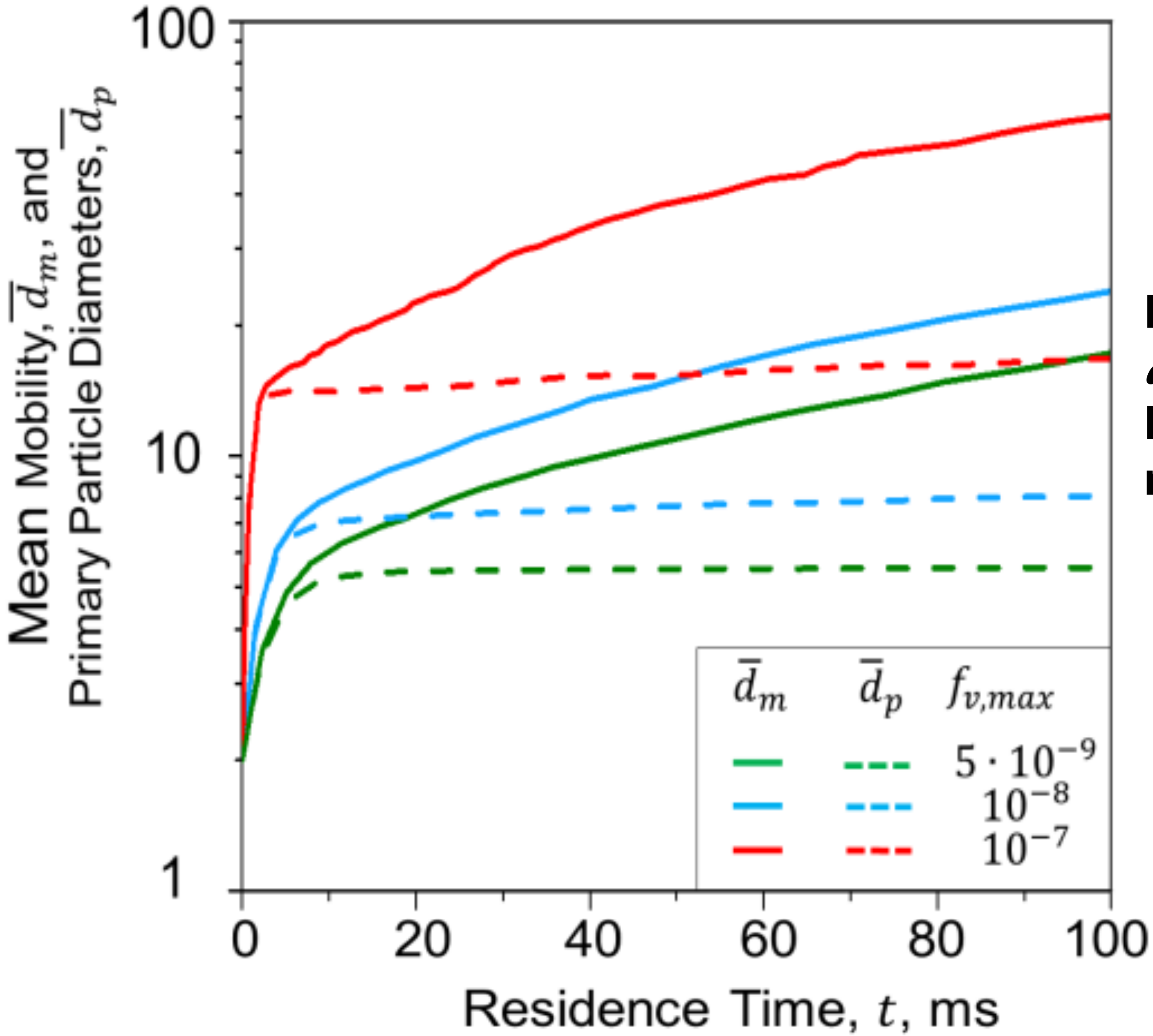


[1] Goudeli E, Eggersdorfer ML, Pratsinis SE. (2015) *Langmuir* **31**,1320.


1
0.1
0.01
0.001
0.1
1
10
dN/dN_{max}
Experiments:
Hot Flame
Cold Flame
This work:
Transition Regime
Normalized Mobility Diameter, d_m / d

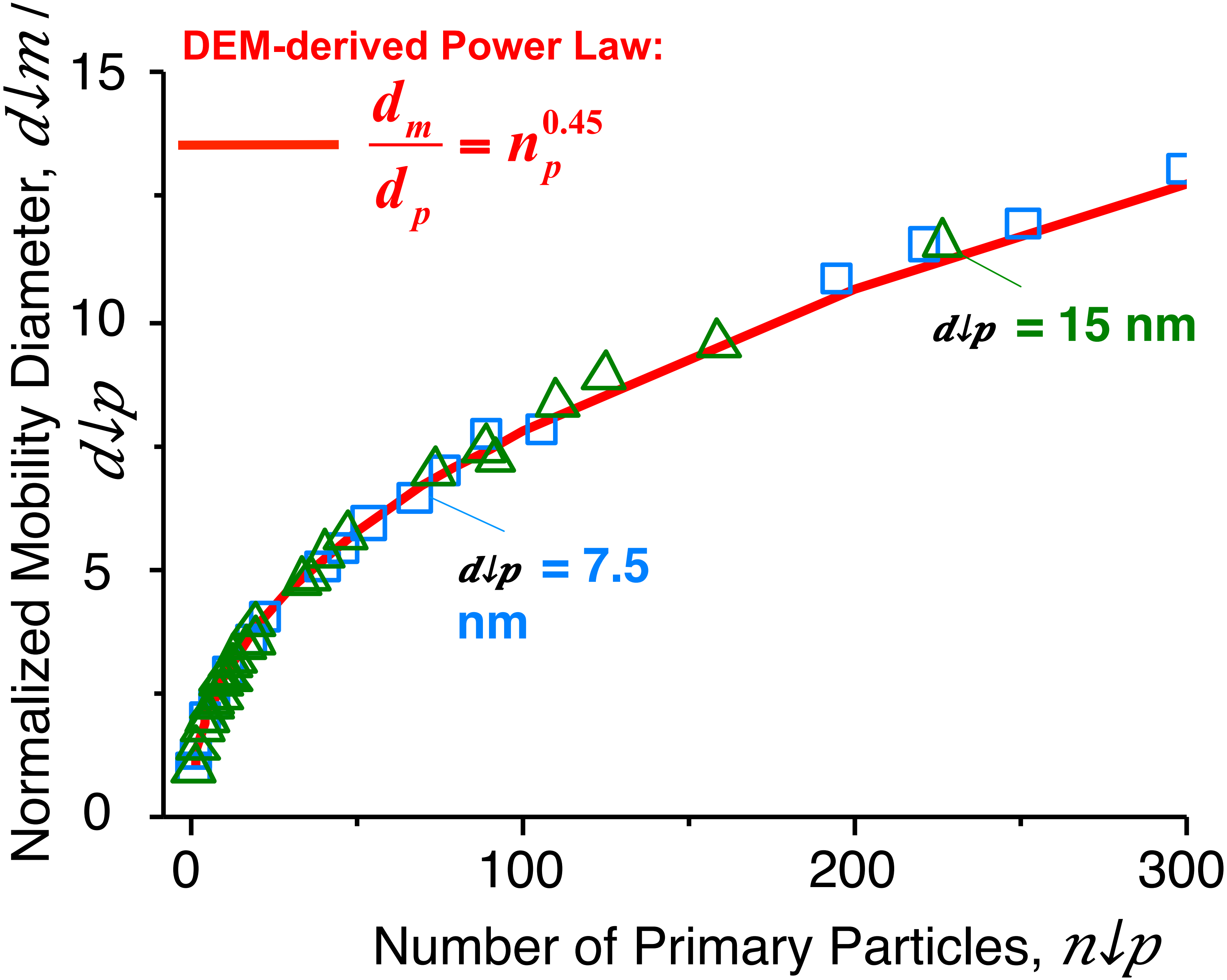
Sensitivity Analysis on
Flame Synthesis Parameters

$f_{v,max}$

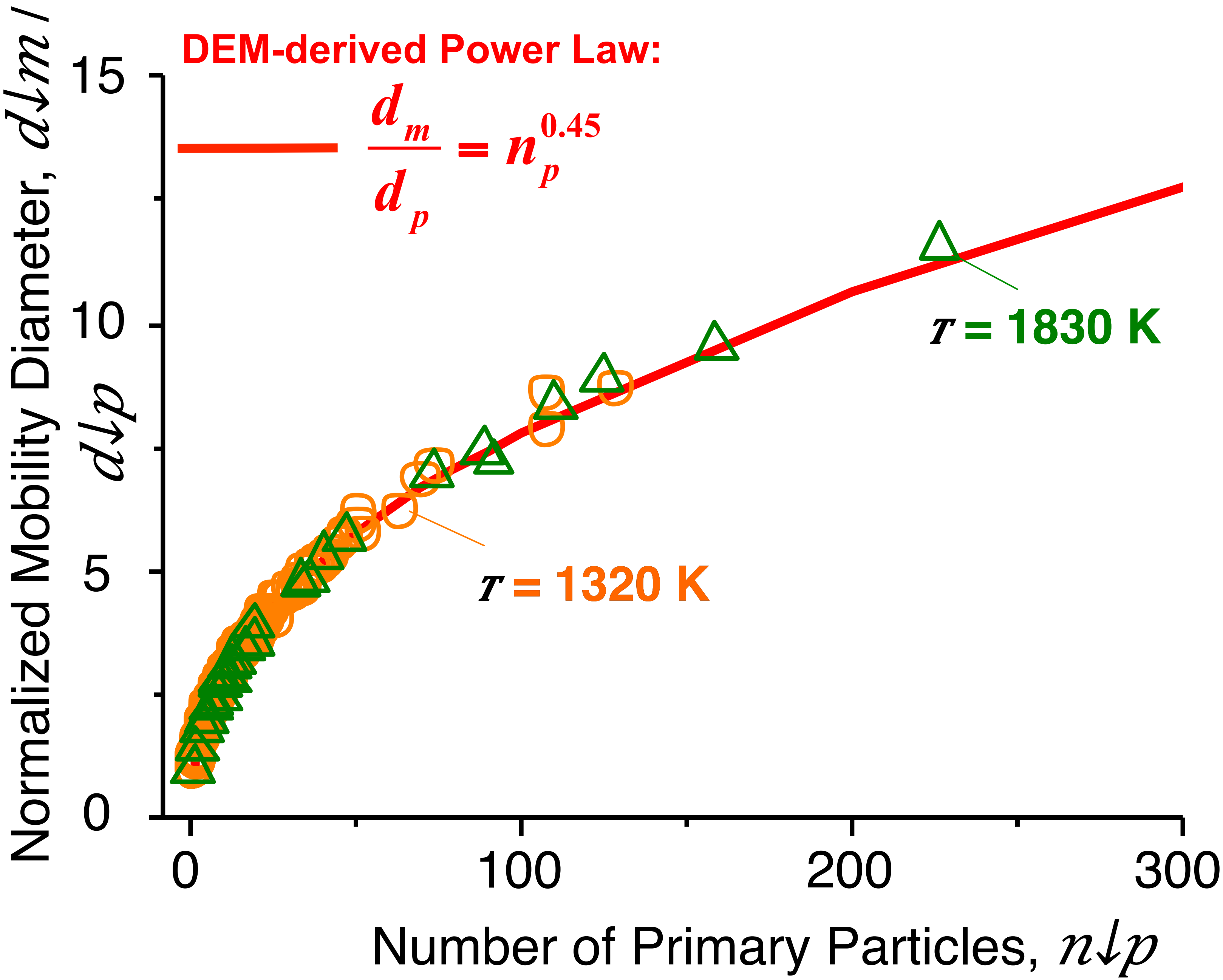


Larger $f_{v,nax}$ and d_p attained by higher equivalence ratios

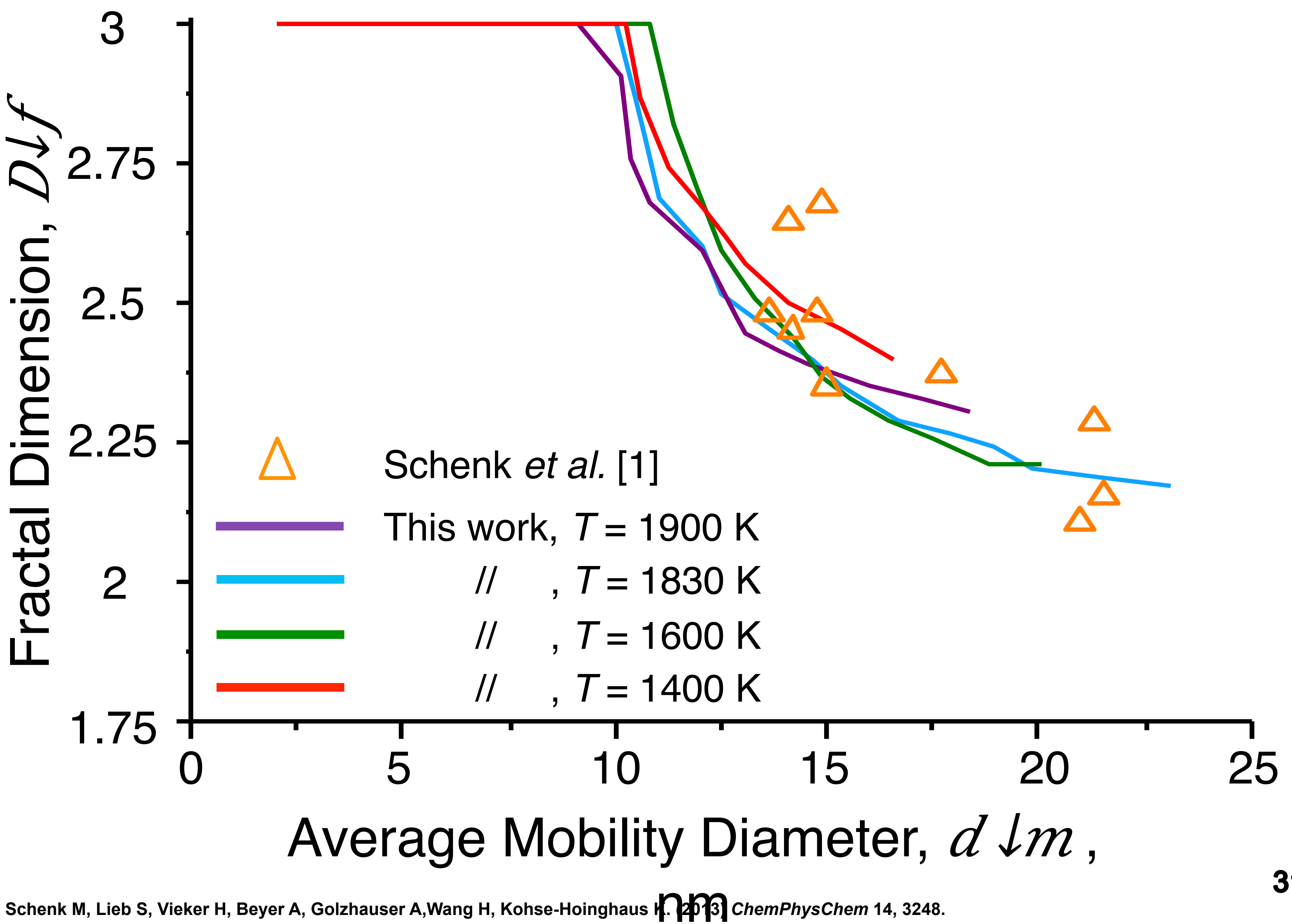
Effect of Primary Particle Diameter



Temperature Effect

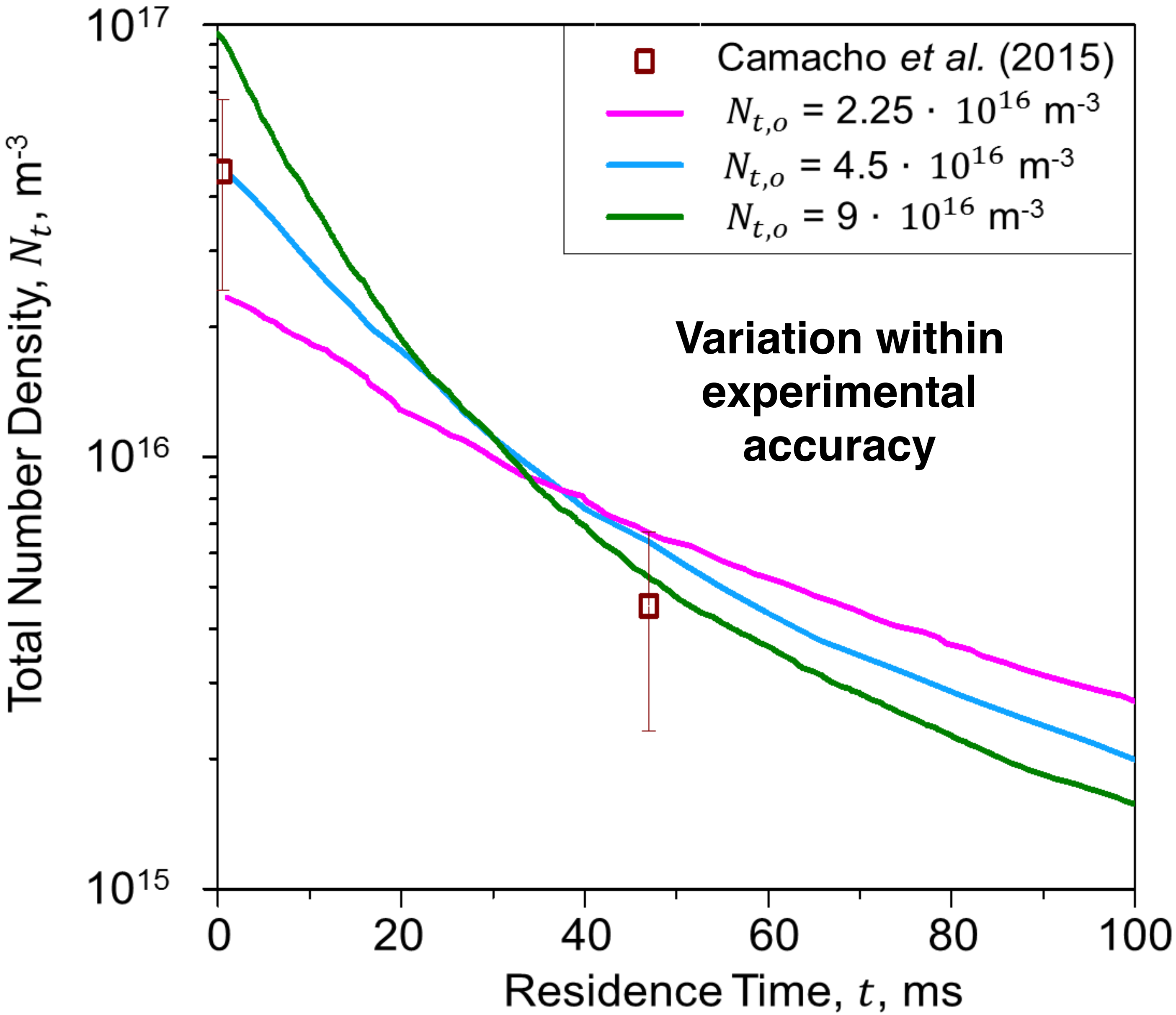


Temperature Effect



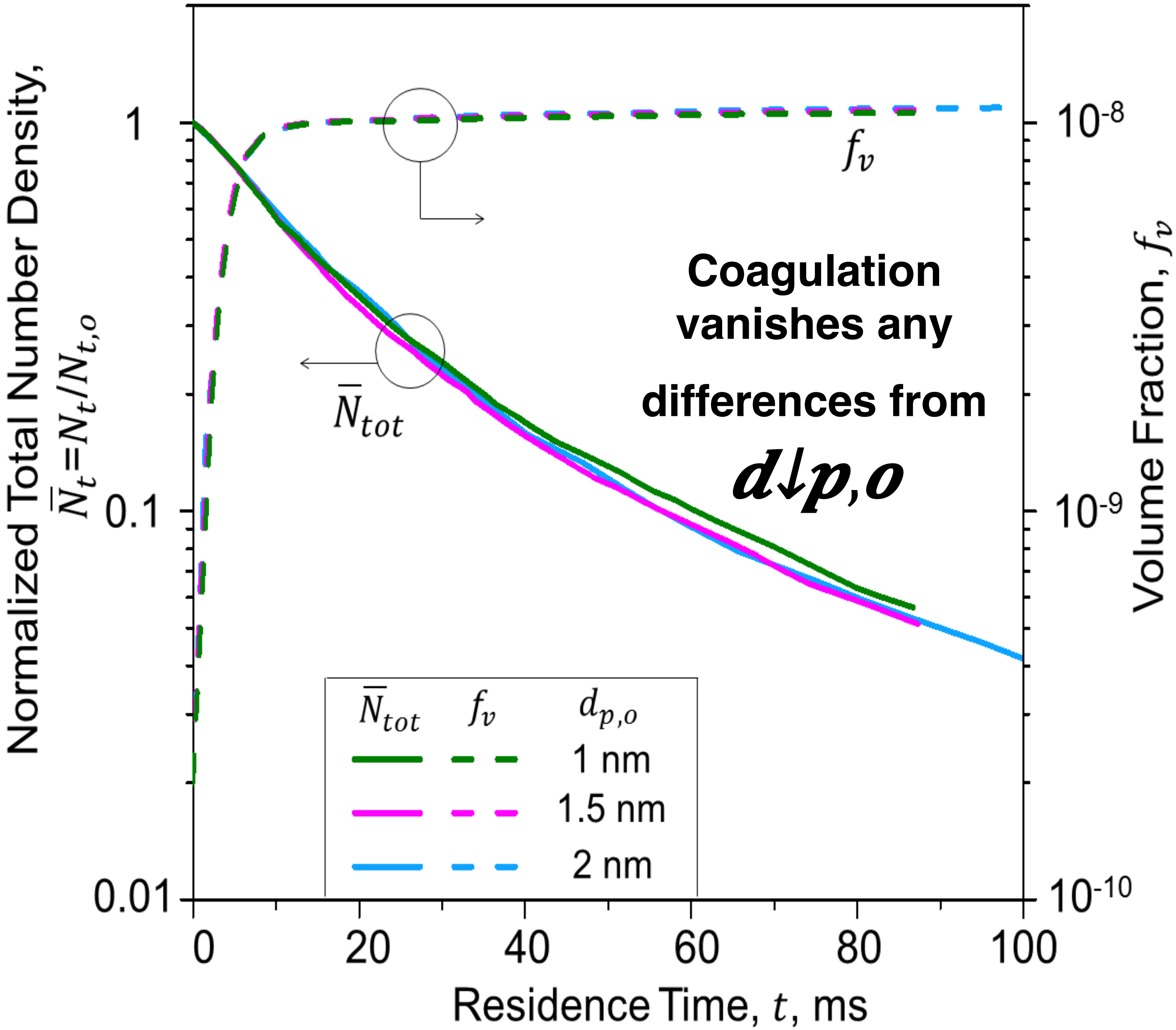
[1] Schenk M, Lieb S, Vieker H, Beyer A, Golzhauser A,Wang H, Kohse-Hoinghaus K. (2013) *ChemPhysChem* 14, 3248.

Effect of Initial Concentration, *N↓t,o*



[1] 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.

Effect of Nuclei Diameter, $d_{p,o}$



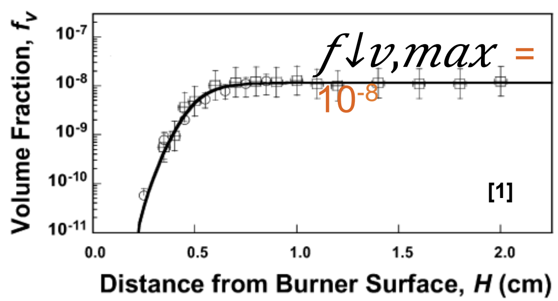
Surface Growth Implementation

$C_{soot}\text{-}H + H \leftrightarrow C_{soot}^{\bullet} + H_2$

$C_{soot}^{\bullet} + H \rightarrow C_{soot}\text{-}H$

$C_{soot}^{\bullet} + C_2H_2 \rightarrow C_{soot}\text{-}CAH + H$

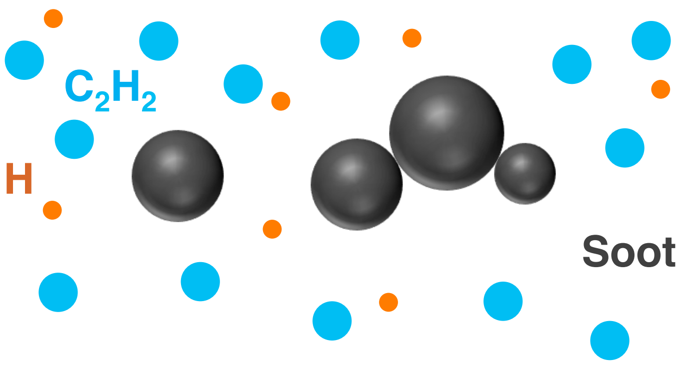
r_{HA}



$x_{C2H2} = 0.02$

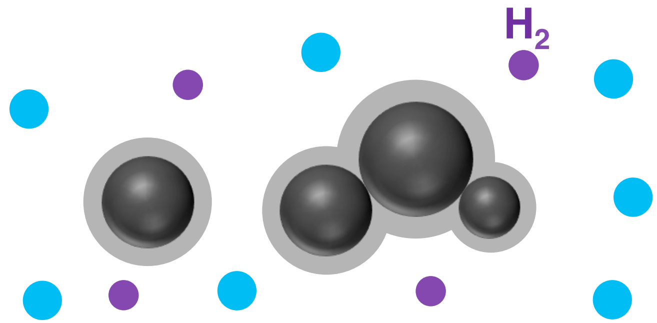
$x_{H2} = 0.1$ [1]

$x_H = 10^{-4}$ [2]



r_{HACA} [3]

β_{C2H2} [4]

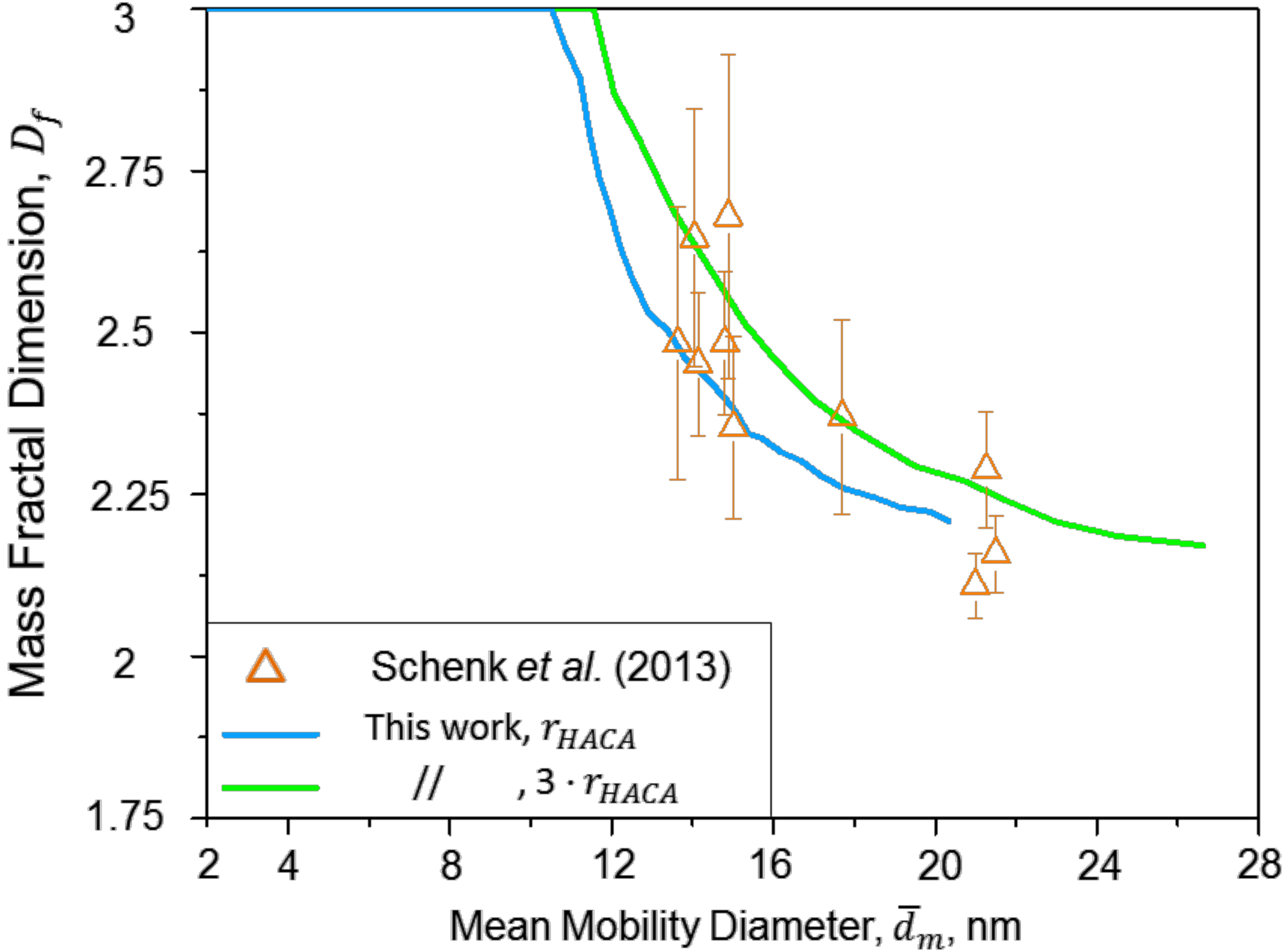


Mass Balance
for each C_2H_2 reaction:

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

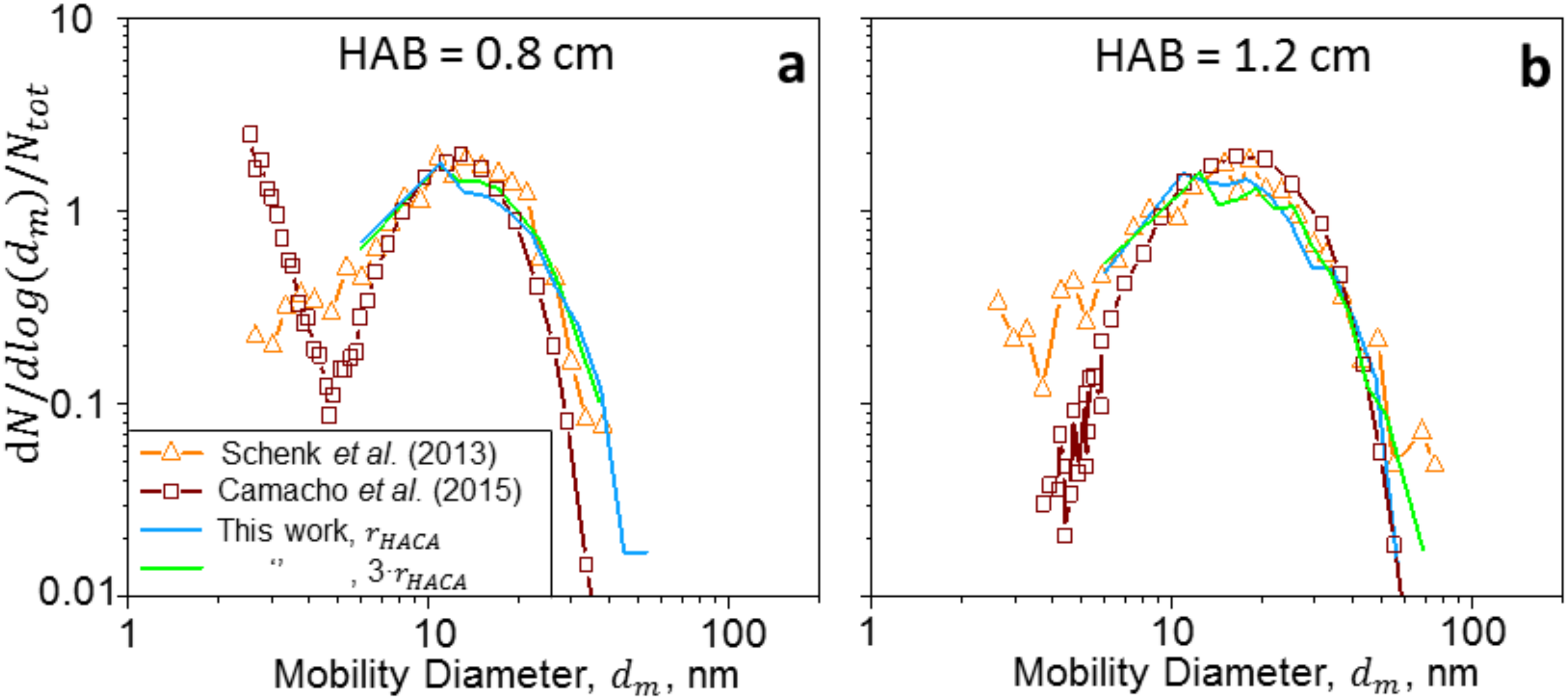
[1] Saggese C, Ferrario S, Camacho J, Cuoci A, Frassoldati A, Ranzi E, Wang H, Faravelli T. Wang H. (2015) *Combust. Flame* **162**, 3356.
[2] Abid AD, Heinz N, Tolmachoff ED, Phares DJ, Campbell CS, Wang H. (2008) *Combust. Flame* **154**, 775.
[3] Appel J, Bockhorn H, Frenklach M. (2000) *Combust. Flame* **121**, 122.
[4] Friedlander SK. (2000) Smoke, Dust, and Haze: Fundamentals of Aerosol Dynamics. Oxford University Press, New York.

Effect of Reaction Rate, $r\downarrow HACA$



[1] Schenk M, Lieb S, Vieker H, Beyer A, Golzhauser A,Wang H, Kohse-Hoinghaus K. (2013) *PhysChemPhys* **14**, 3248.

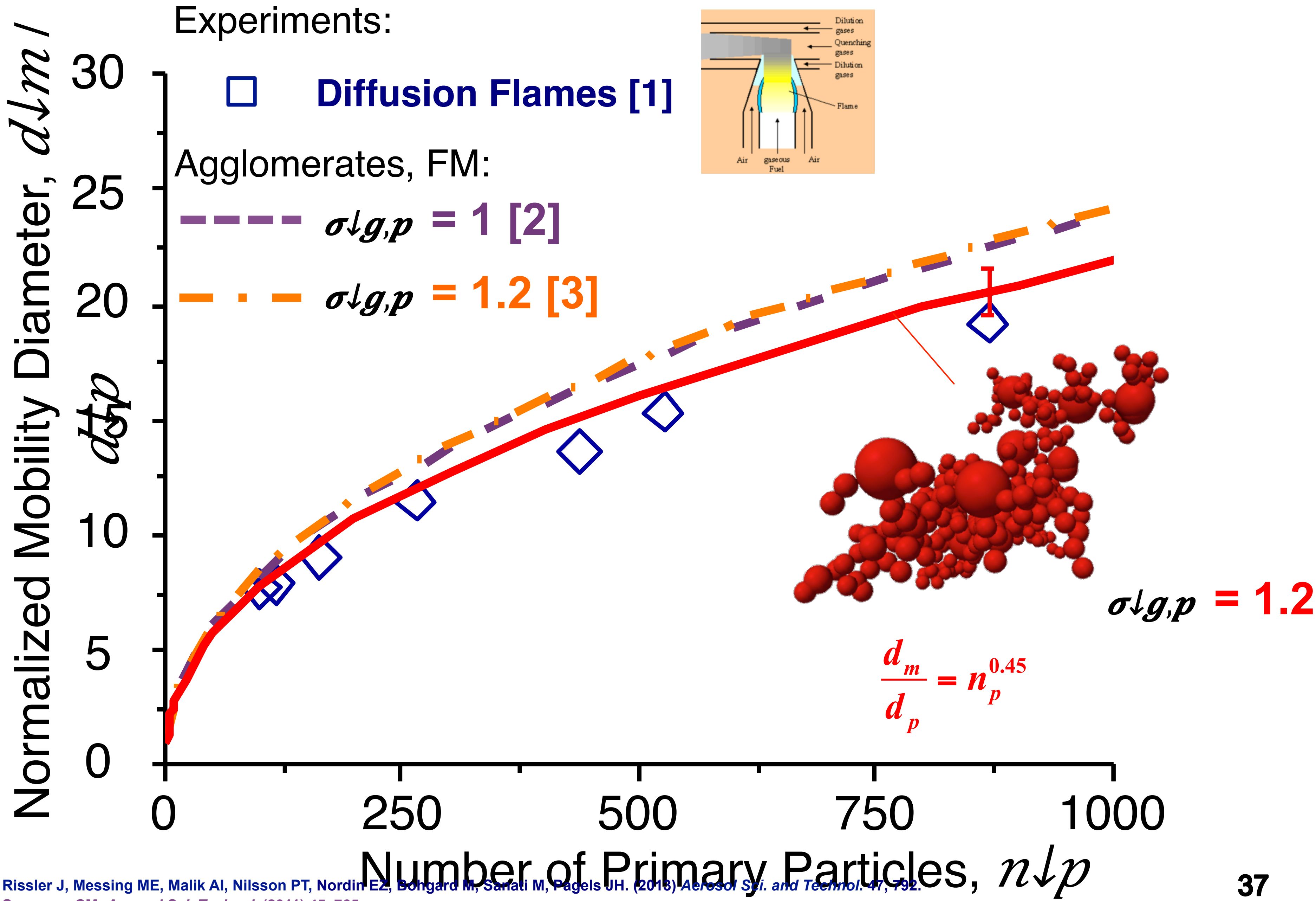
Effect of Reaction Rate, r_{HACA}



[1] Schenk M, Lieb S, Vieker H, Beyer A, Golzhauser A,Wang H, Kohse-Hoinghaus K. (2013) *PhysChemPhys* **14**, 3248.

[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.

Free Molecular (FM) Regime Models



[1] Rissler J, Messing ME, Malik AI, Nilsson PT, Nordin EZ, Bohgard M, Sanati M, Pagels JH. (2013) *Aerosol Sci. and Technol.* 47, 792.
[2] Sorensen CM. *Aerosol Sci. Technol.* (2011) 45, 765.
[3] Dastanpour R, Rogak S. *Aerosol Sci. Tech.* (2016) 92, 22.

ETH zürich

Morphology and Optical Properties of Flame-made Nanoparticles

Georgios A. Kelesidis

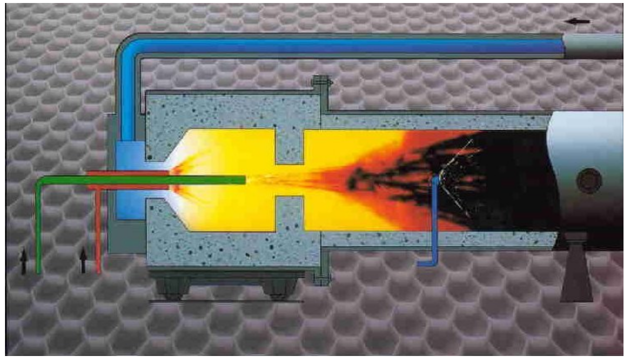
Particle Technology Laboratory, ETH Zürich, Switzerland

PTL Particle Technology Laboratory

Carbon Black: A $10 B Industry

Lamp Black Process [1]
China, 2000 BC

Furnace Process

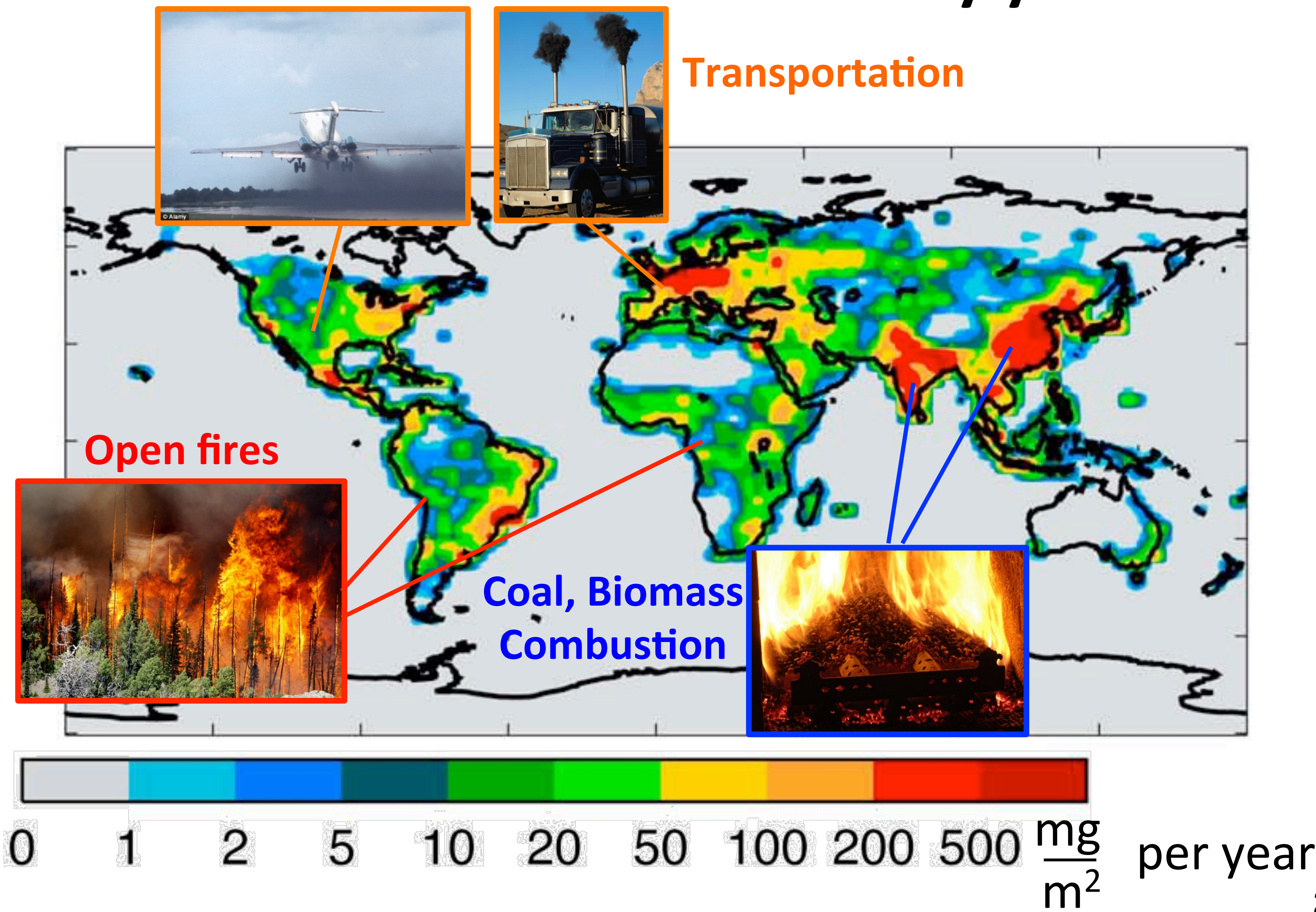


11 Mt/year in 2012 [2]

[1] Ulrich, G.D. Chem Eng News 1984, 62, 22.

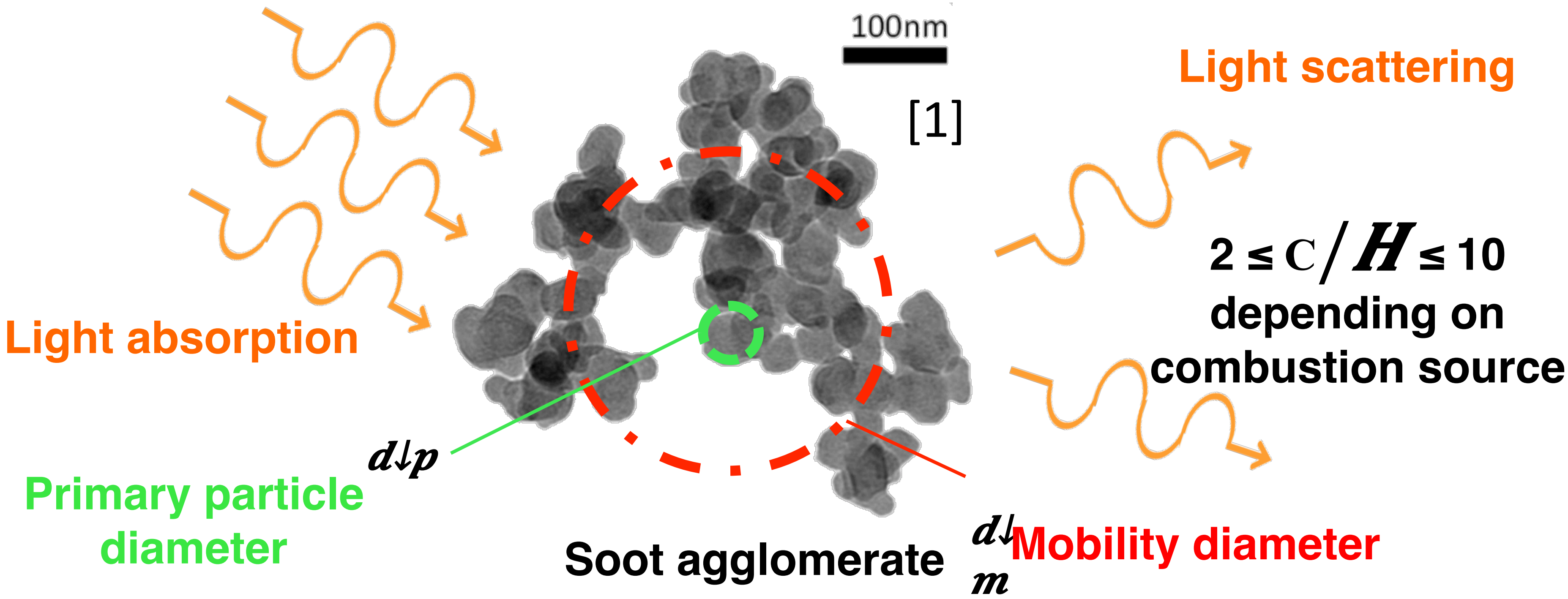
[2] International Carbon Black Association, Carbon Black User's Guide, 2012.

8 Mt of soot emissions every year!



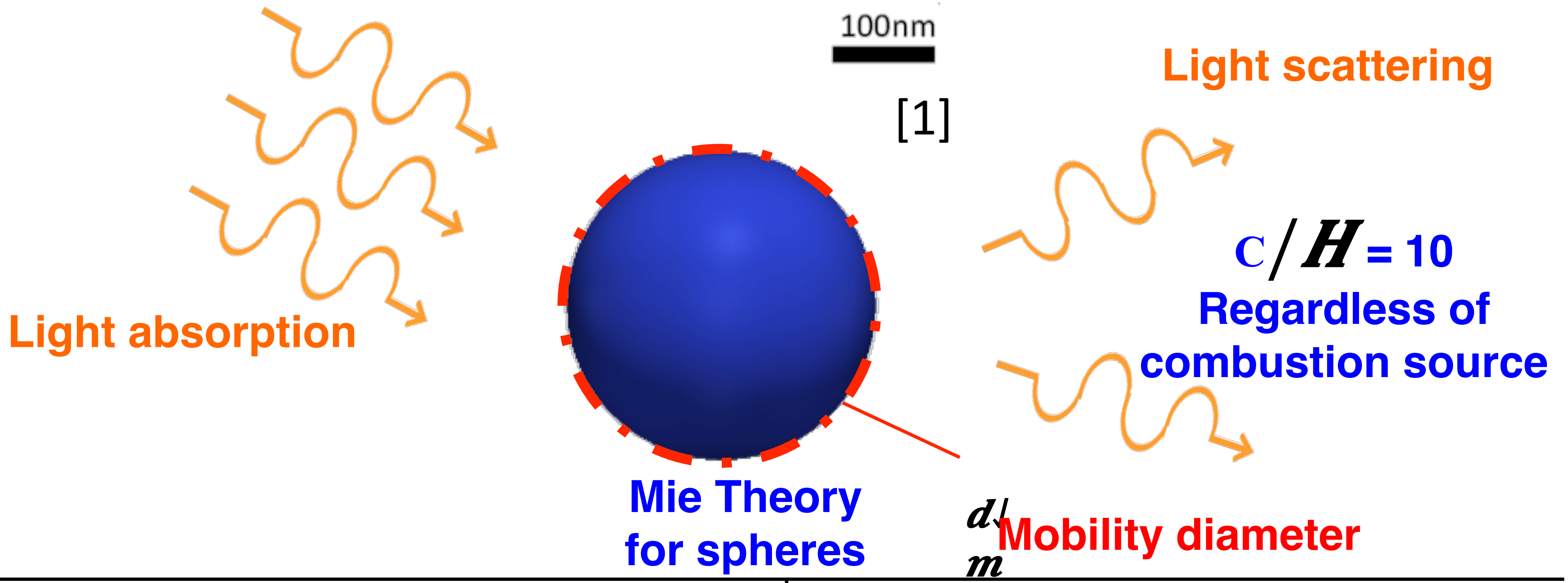
Bond, T. C.; Doherty, S. J.; Fahey, D., et al. J Geophys Res 2013, 118, 5380.

Soot Morphology & Optical Properties



[1] Lapuerta, M.; Barba, J.; Sediako, A. D.; Kholghy, M. R.; Thomson, M. J. J Aerosol Sci 2017, 111, 65.

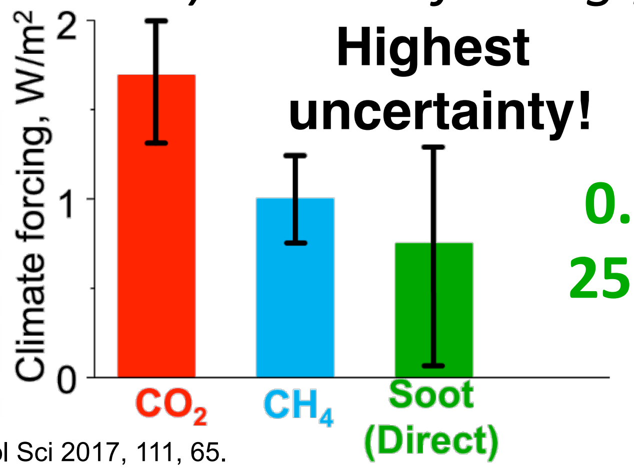
Soot Morphology & Optical Properties



i) Optical Diagnostics, Fire detectors:

UK:
1 billion £/year
due to false
alarms [2]!

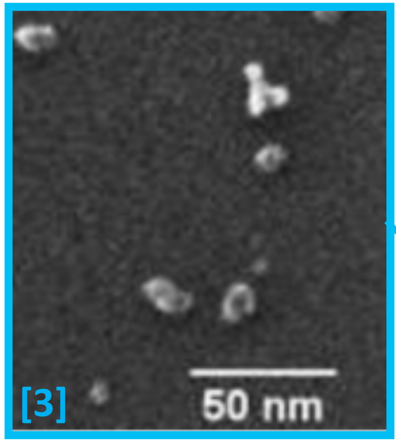
ii) Climate forcing [3]:



0. 71 W/m²
25 % of total
forcing

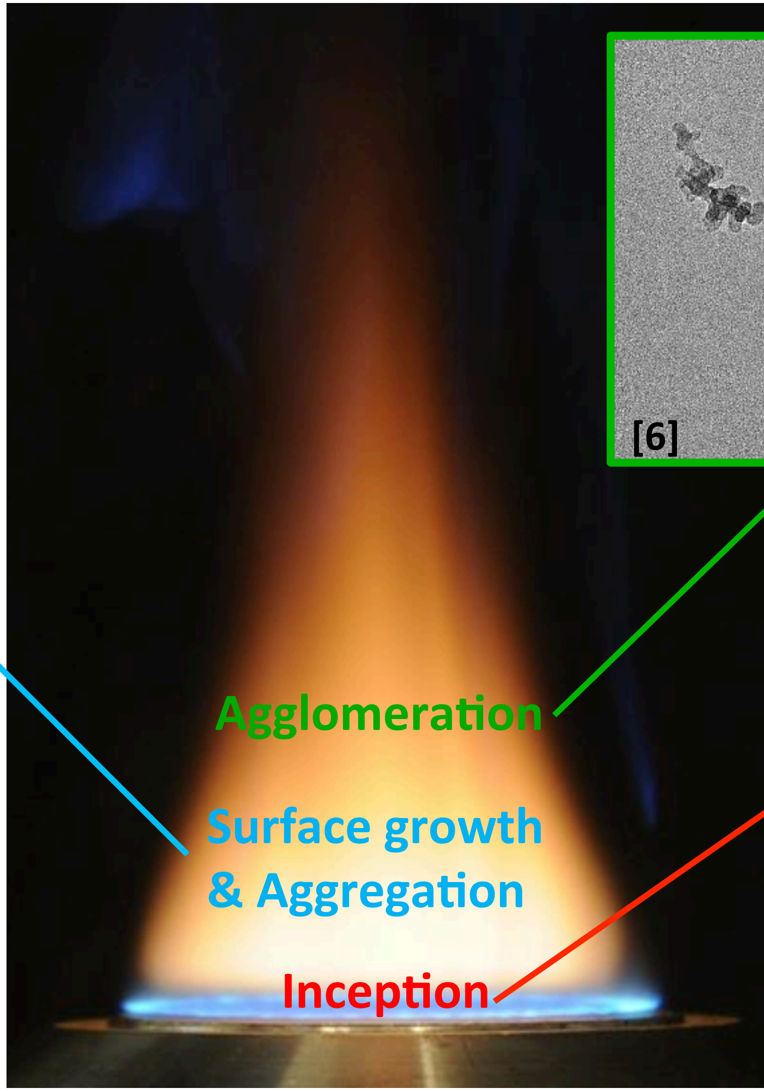
[1] Lapuerta, M.; Barba, J.; Sediako, A. D.; Kholghy, M. R.; Thomson, M. J. J Aerosol Sci 2017, 111, 65.
[2] Chagger, R.; Smith, D. The causes of false alarms in buildings, 2014, bre.co.uk.
[3] Bond, T. C.; Doherty, S. J.; Fahey, D., et al. J Geophys Res 2013, 118, 5380.

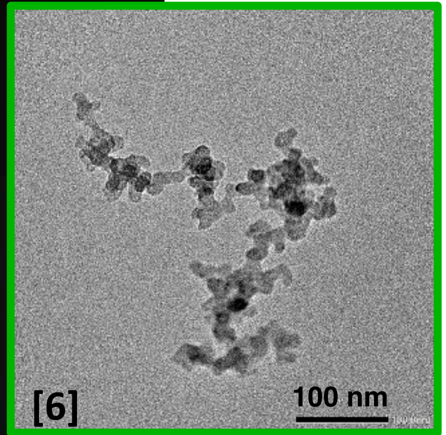
Soot formation dynamics



Nascent soot:

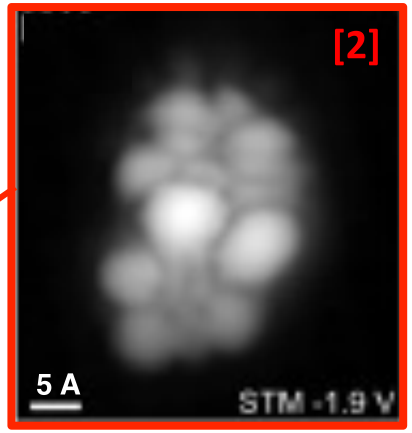
3 nm < d_m < 30 nm
2 < C/H < 10
Slightly absorb visible and IR [4]





Mature soot:

d_m > 30 nm
C/H > 10
Strong light absorber and scatterer [5]



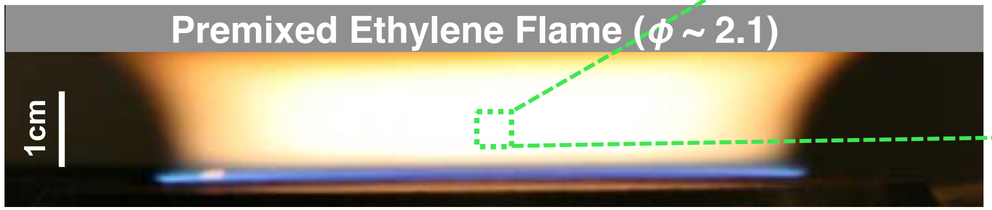
Incipient soot:

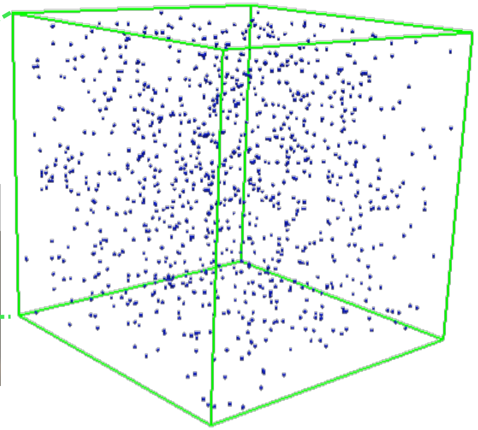
d_m < 3 nm
C/H < 2
Transparent to visible and IR [1]

[1] D'Anna, A.; Rolando, A.; Allouis, C.; Minutolo, P.; D'Alessio, A. Proc Combust Inst 2005, 30, 1449.
[2] Schultz, F.; Commodo, M.; Kaiser, K.; De Falco, G.; Minutolo, P.; Meyer, G.; D'Anna, A.; Gross, L. Proc Combust Inst, 2019, 37, 885-892.
[3] Schenk, M.; Lieb, S.; Vieker, H.; Beyer, A.; Golzhauser, A.; Wang, H.; Kohse-Hoinghaus, K. ChemPhysChem 2013, 14, 3248.
[4] Bejaoui, S.; Lemaire, R.; Desgroux, P.; Therssen, E. Appl Phys B 2014, 116, 313.
[5] Michelsen, H.A.; Schrader, P.E.; Goulay, F. Carbon 2010, 48, 2175.
[6] Kelesidis, G.A.; Kholghy, M.R.; Zurcher, J.; Robertz, J.; Allemann, M.; Duric, A.; Pratsinis, S.E. Powder Technol 2019, in press.

Soot Dynamics by Discrete Element Modeling (DEM)

i) Initial configuration inception has largely ended.





T = 1830 K

$d_{m,o}$ = 2 nm

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

[1,2]

[1] Abid, A. D.; Heinz, N.; Tolmachoff, E.D.; Phares, D.J.; Campbell, C.S.; Wang, H. Combust Flame 2008, 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. Combust Flame 2015, 162, 3810.

[3] Goudeli, E.; Eggersdorfer, M. L.; Pratsinis, S. E. Langmuir 2015, 31,1320.

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

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

[6] Kelesidis, G. A.; Goudeli, E.; Pratsinis, S. E. Proc Combust Inst 2017 36, 29.

Soot Dynamics by Discrete Element Modeling (DEM)

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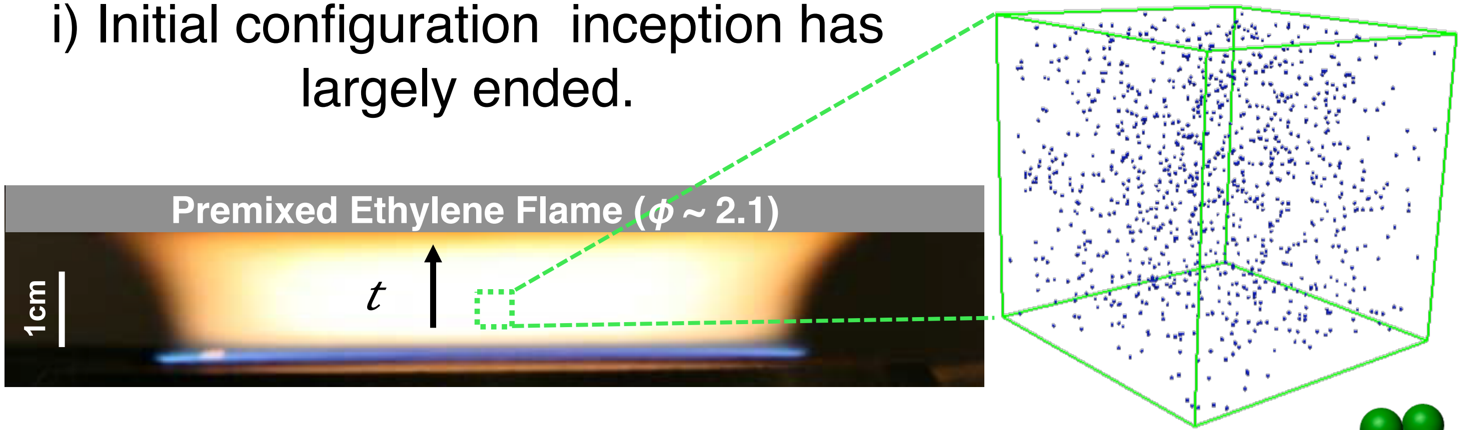


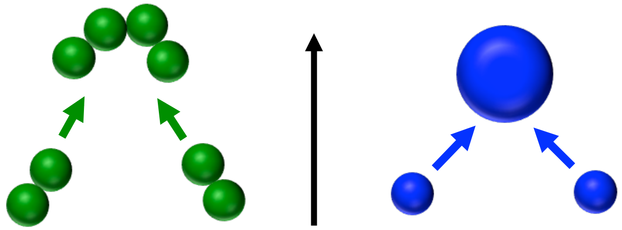
T = 1830 K

$d_{m,o}$ = 2 nm

$N_{tot,o}$ = $4.5\cdot10^{16}$ m

[1,2]

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



[1] Abid, A. D.; Heinz, N.; Tolmachoff, E.D.; Phares, D.J.; Campbell, C.S.; Wang, H. Combust Flame 2008, 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. Combust Flame 2015, 162, 3810.

[3] Goudeli, E.; Eggersdorfer, M. L.; Pratsinis, S. E. Langmuir 2015, 31,1320.

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

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

[6] Kelesidis, G. A.; Goudeli, E.; Pratsinis, S. E. Proc Combust Inst 2017 36, 29.

Soot Dynamics by Discrete Element Modeling (DEM)

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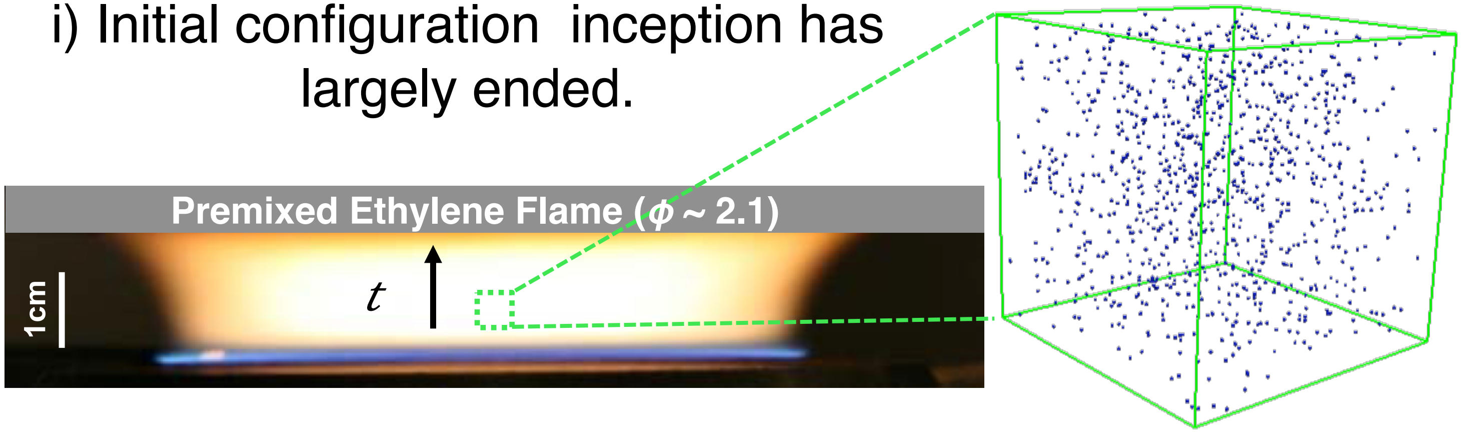


T = 1830 K

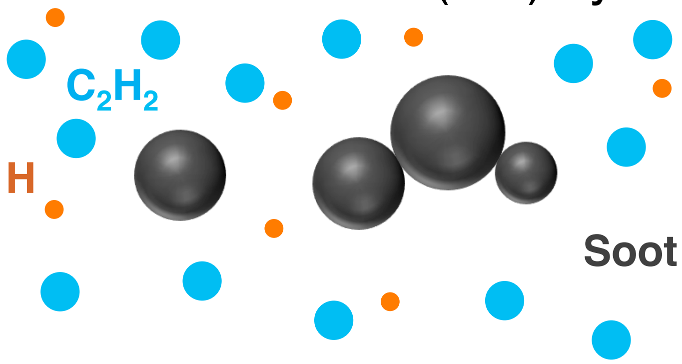
$d_{m,o}$ = 2 nm

$N_{tot,o}$ = 4.5·10^{16} m

[1,2]

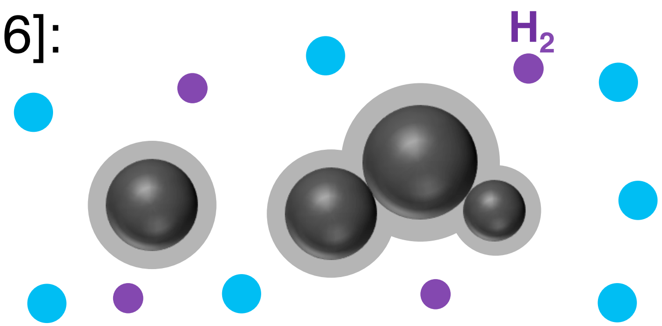
ii) Discrete Element Modeling (DEM) of **Particle Motion** and **Coagulation** [3]

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



r_{HACA} [4]

β_{C2H2} [6]



Mass Balance for each C_2H_2 reaction:

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

[1] Abid, A. D.; Heinz, N.; Tolmachoff, E.D.; Phares, D.J.; Campbell, C.S.; Wang, H. Combust Flame 2008, 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. Combust Flame 2015, 162, 3810.

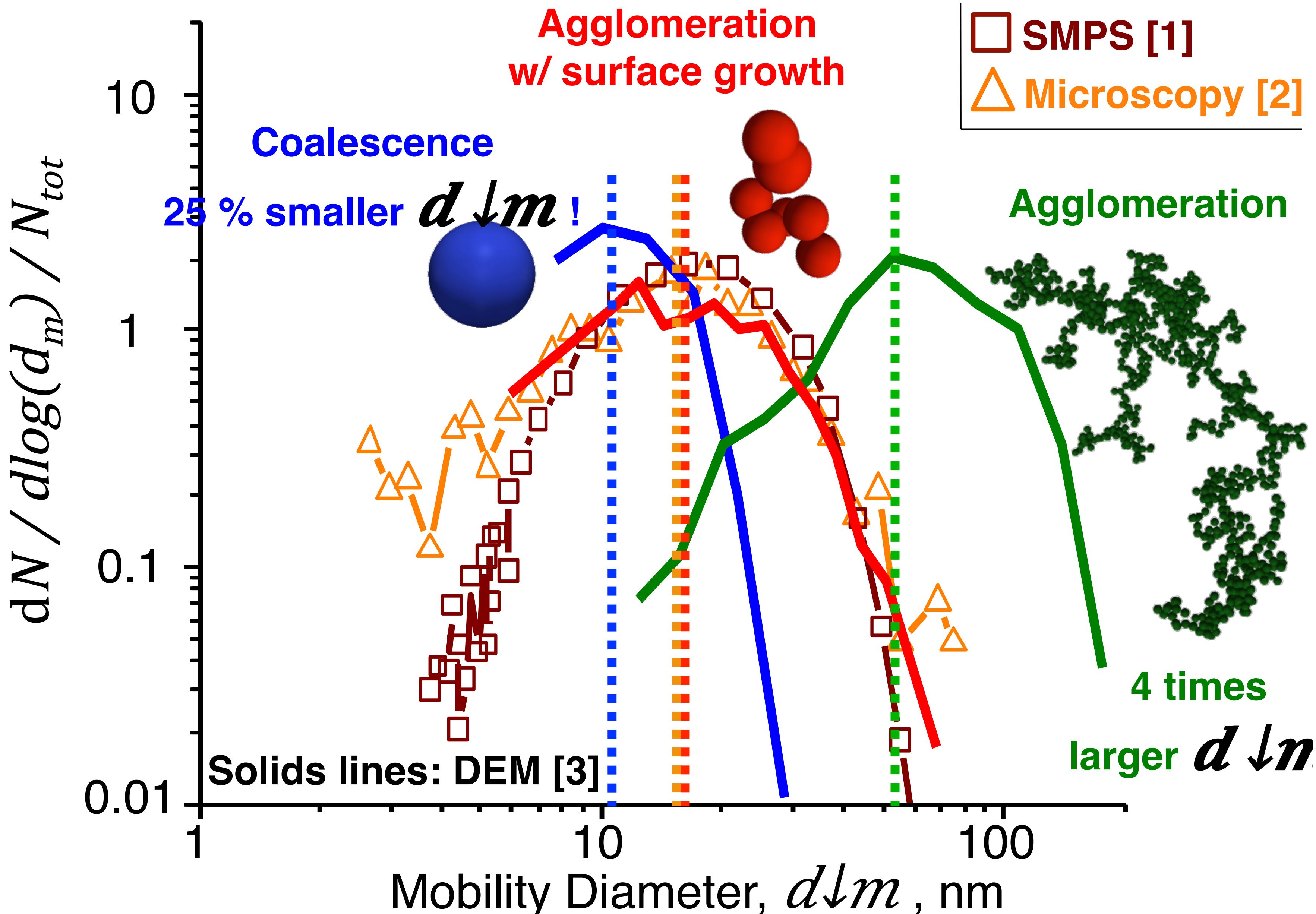
[3] Goudeli, E.; Eggersdorfer, M. L.; Pratsinis, S. E. Langmuir 2015, 31,1320.

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

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

[6] Kelesidis, G. A.; Goudeli, E.; Pratsinis, S. E. Proc Combust Inst 2017 36, 29.

Nascent Soot Size Distribution, HAB = 1.2 cm

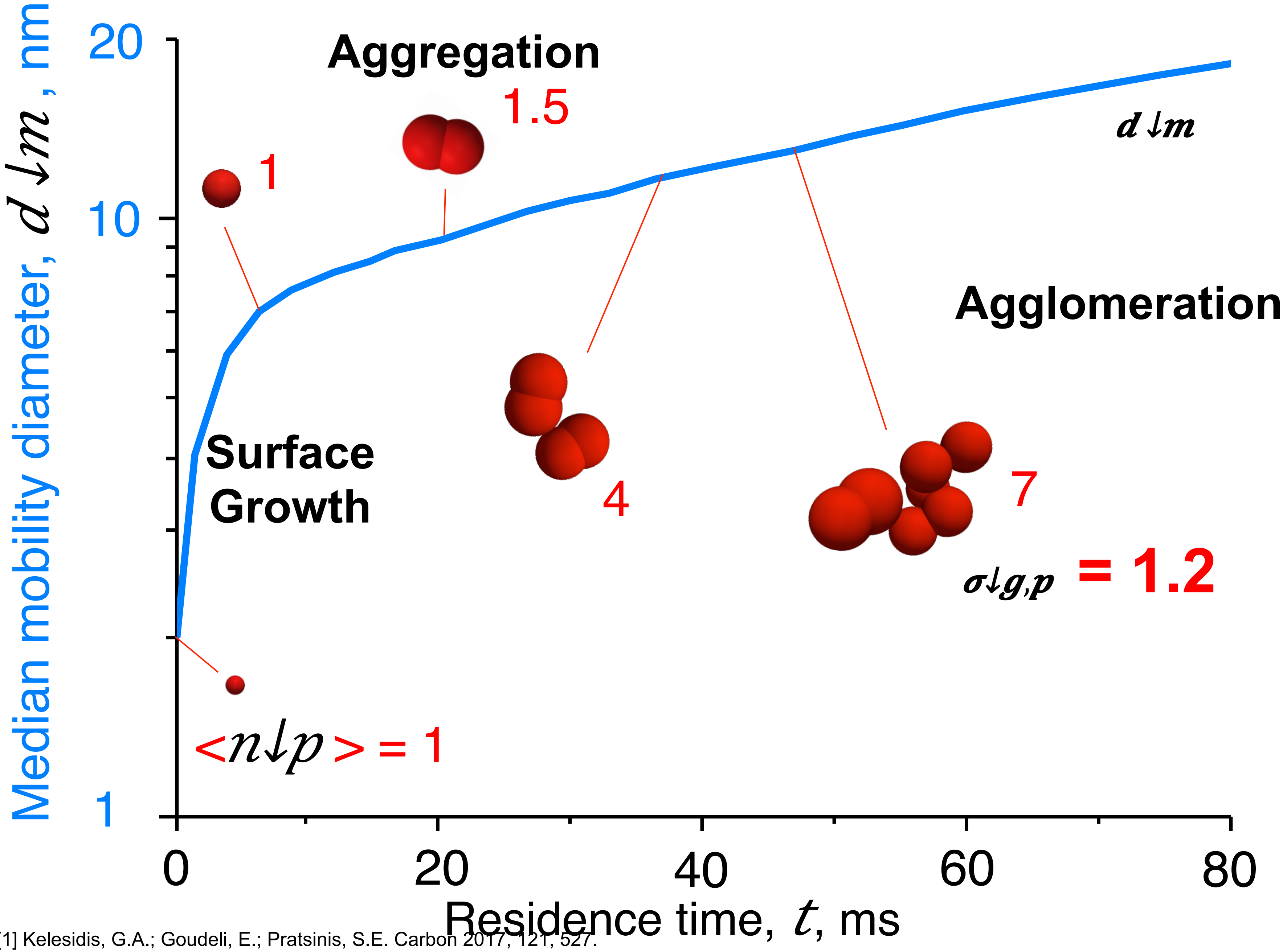


[1] Camacho ,J.; Liu, C.; Gu, C.; Lin, H.; Huang, Z.; Tang, Q.; You, X.; Saggese, C.; Li, Y.; Jung, H.; Deng, L.; Wlokas, I.; Wang, H. Combust Flame 2015, 162, 3810.

[2] Schenk, M.; Lieb, S.; Vieker, H.; Beyer, A.; Golzhauser, A,; Wang, H.; Kohse-Hoinghaus, K. ChemPhysChem 2013, 14, 3248.

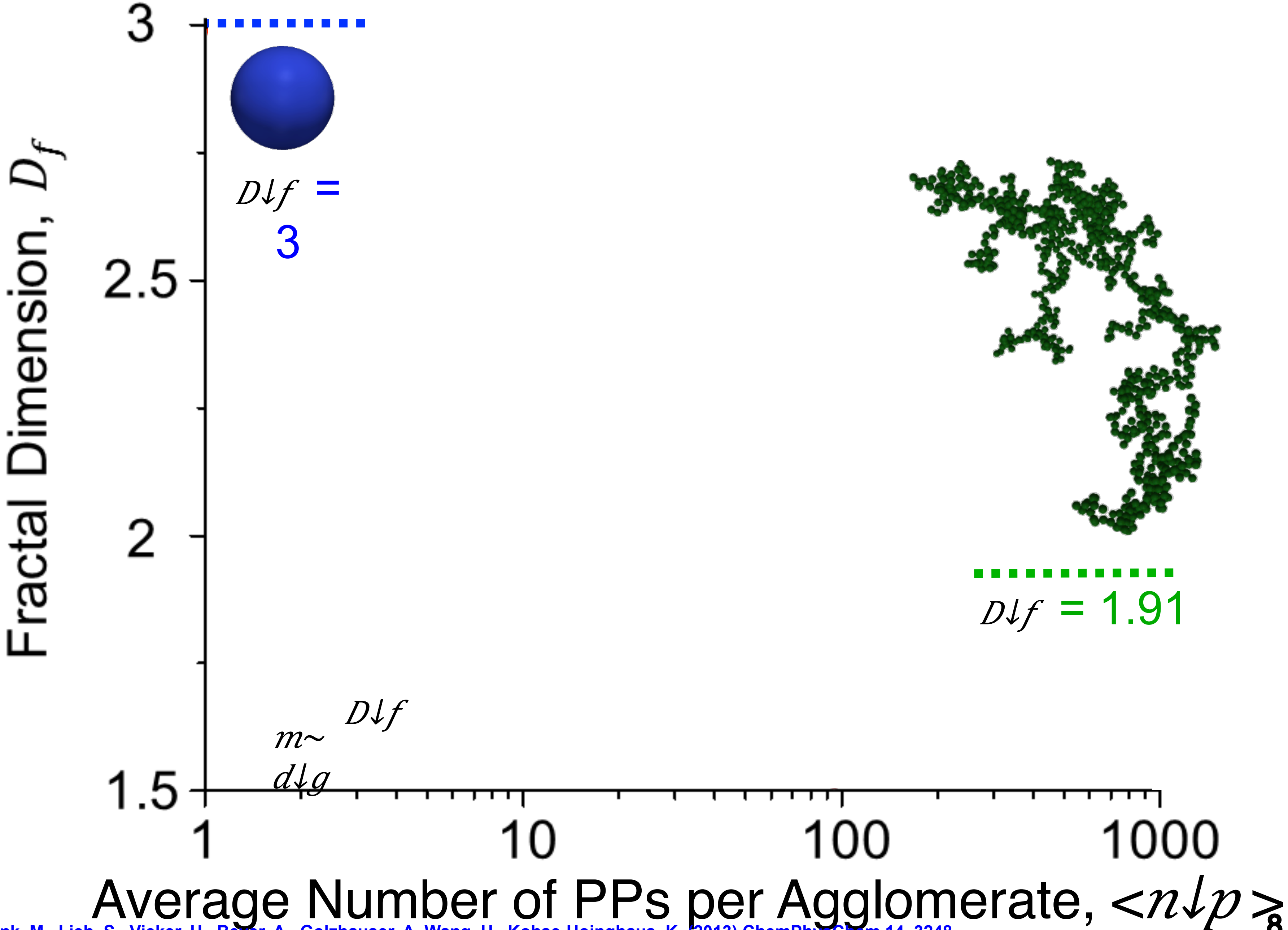
[3] Kelesidis, G. A.; Goudeli, E.; Pratsinis, S. E. Proc Combust Inst 2017, 36, 28.

Residence Time Soot Dynamics by DEM [1]



[1] Kelesidis, G.A.; Goudeli, E.; Pratsinis, S.E. Carbon 2017, 121, 527.

Evolution from Nascent to Mature Soot



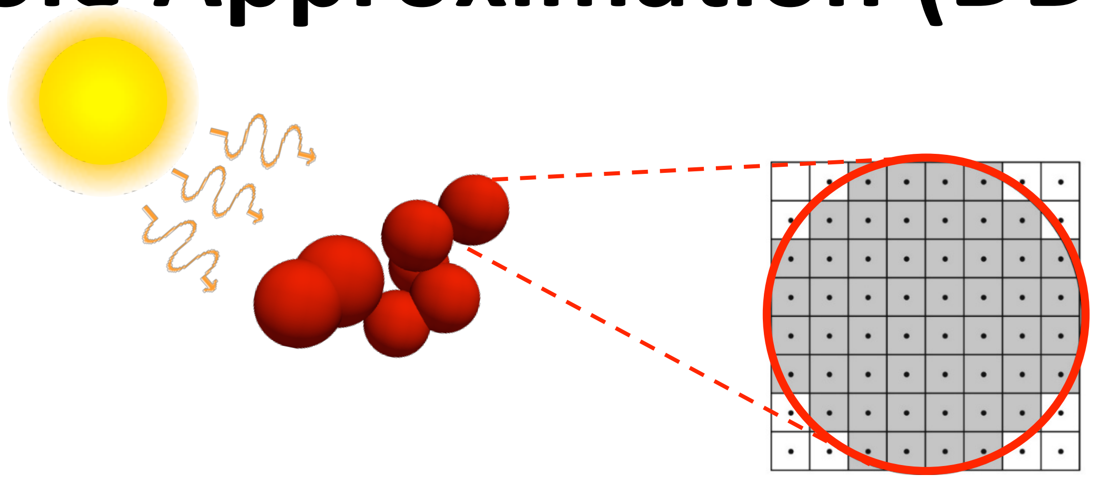
Schenk, M., Lieb, S., Vieker, H., Beyer, A., Golzhauser, A.,Wang, H., Kohse-Hoinghaus, K. (2013) ChemPhysChem 14, 3248.

Kholghy, M.R., Afarin, Y., Sediako, A.D., Barba, J., Lapuerta, M., Chu, C., Weingarten, J., Borshanpour, B., Chernov, V., Thomson, M.J. (2017) Combust. Flame 176, 567.

Discrete Dipole Approximation (DDA)

Input:

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

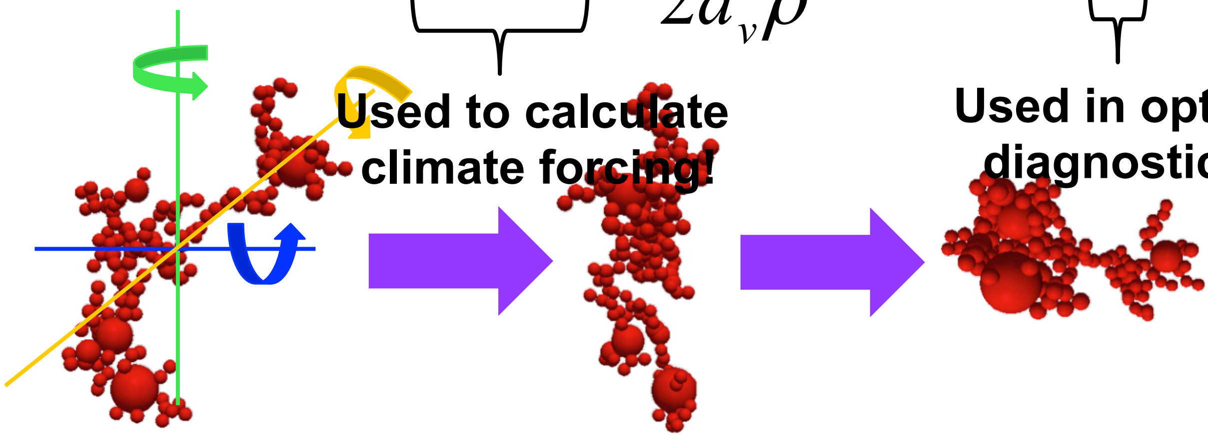


$$MAC = \frac{3Q_{abs}}{2d_v\rho}$$

Used to calculate climate forcing!

$$C = \frac{\lambda^2}{4\pi^2}\left(S_{11} - S_{12}\right)$$

Used in optical diagnostics!



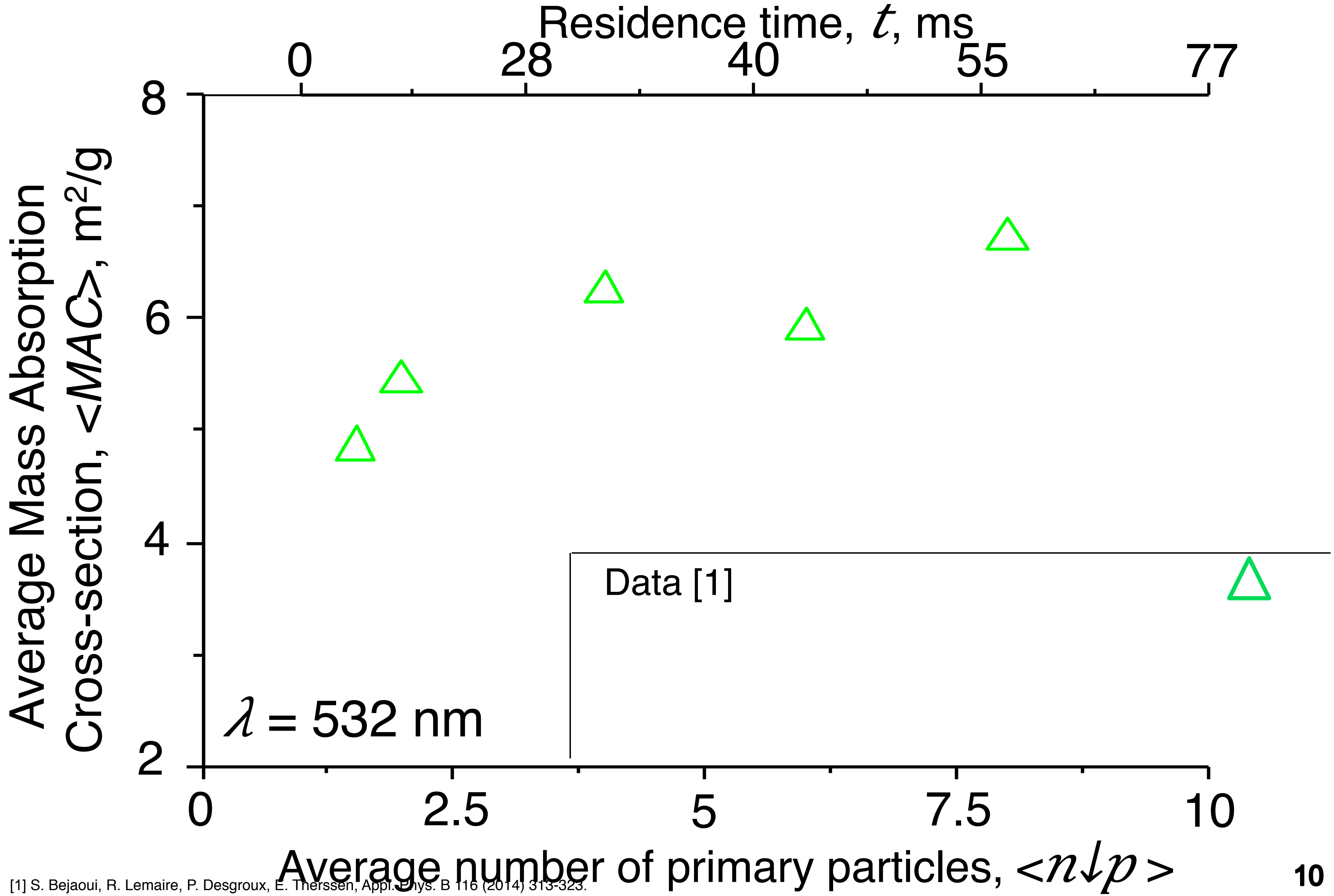
Averaging of *MAC* and *C*:
- over 100 agglomerates per time step.
- over 343 orientations.

✓ Good statistics.

✓ Computational efficiency.

Kelesidis, G.A.; Pratsinis, S.E. Proc Combust Inst 2019, 37, 1177.

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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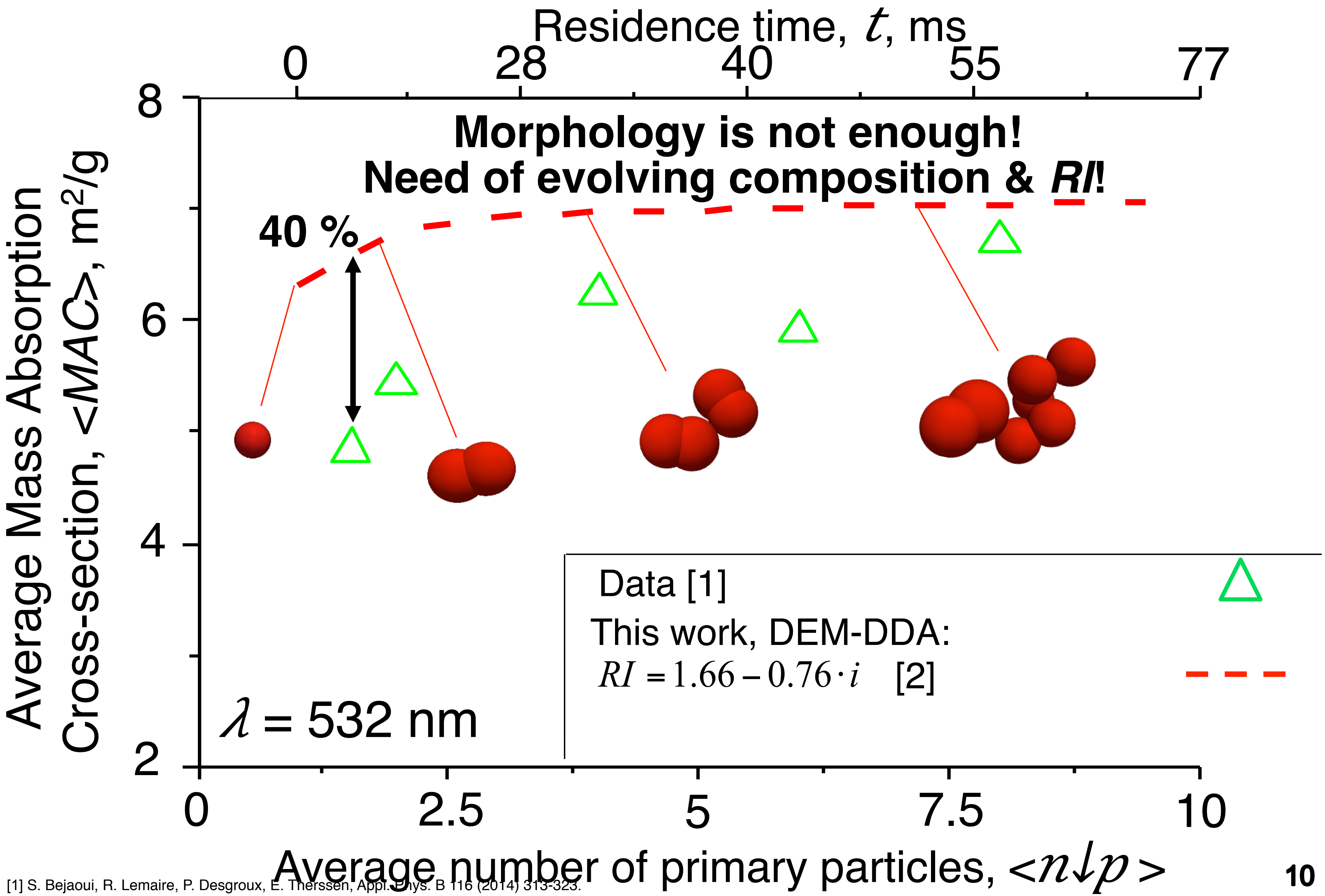
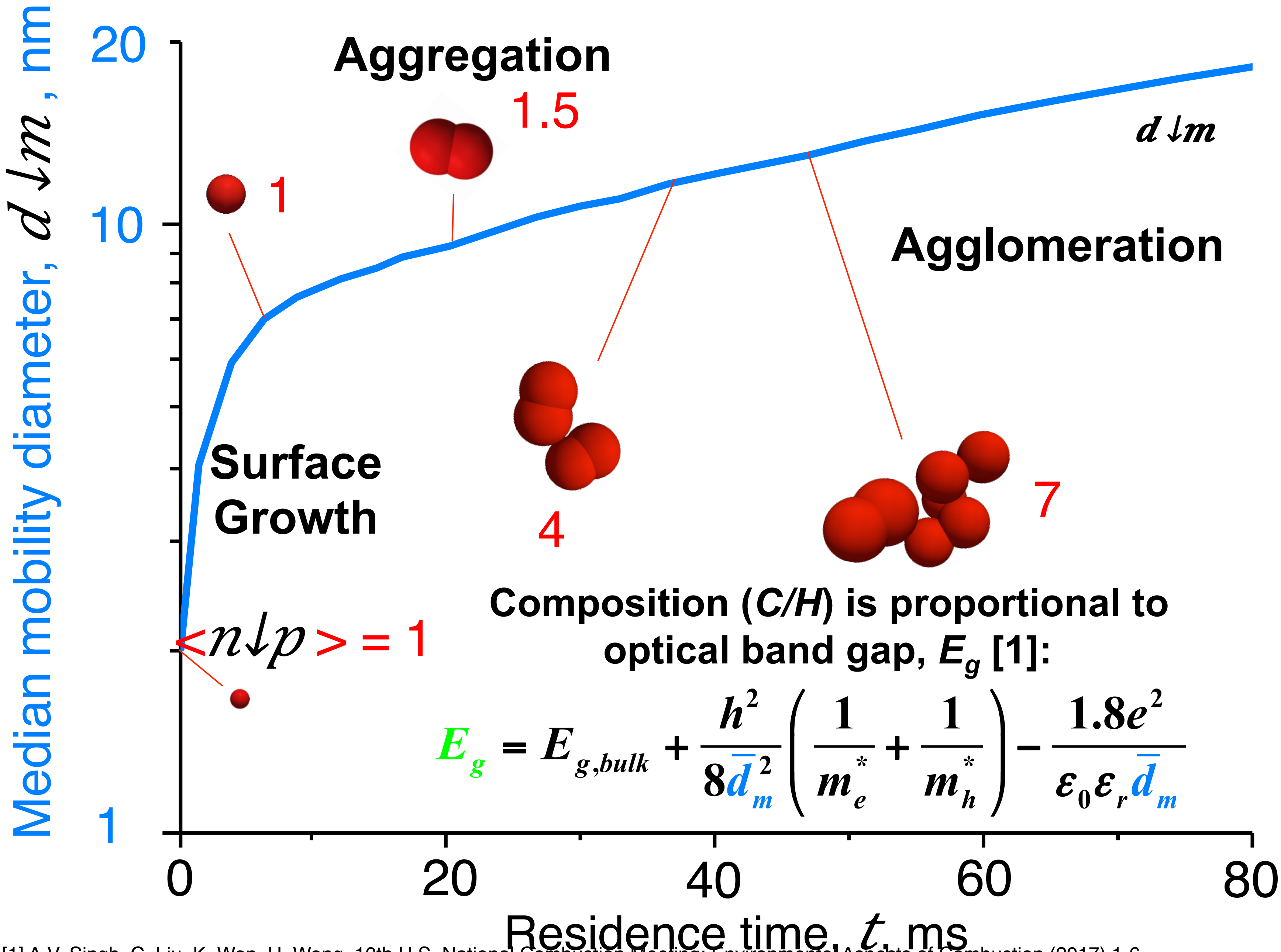


[1] S. Bejaoui, R. Lemaire, P. Desgroux, E. Therssen, Appl. Phys. B 116 (2014) 313-323.
[2] J. Yon, A. Bescond, F. Liu, J. Quant. Spectrosc. Radiat. Transf. 162 (2015) 197-206.

Evolution of soot composition

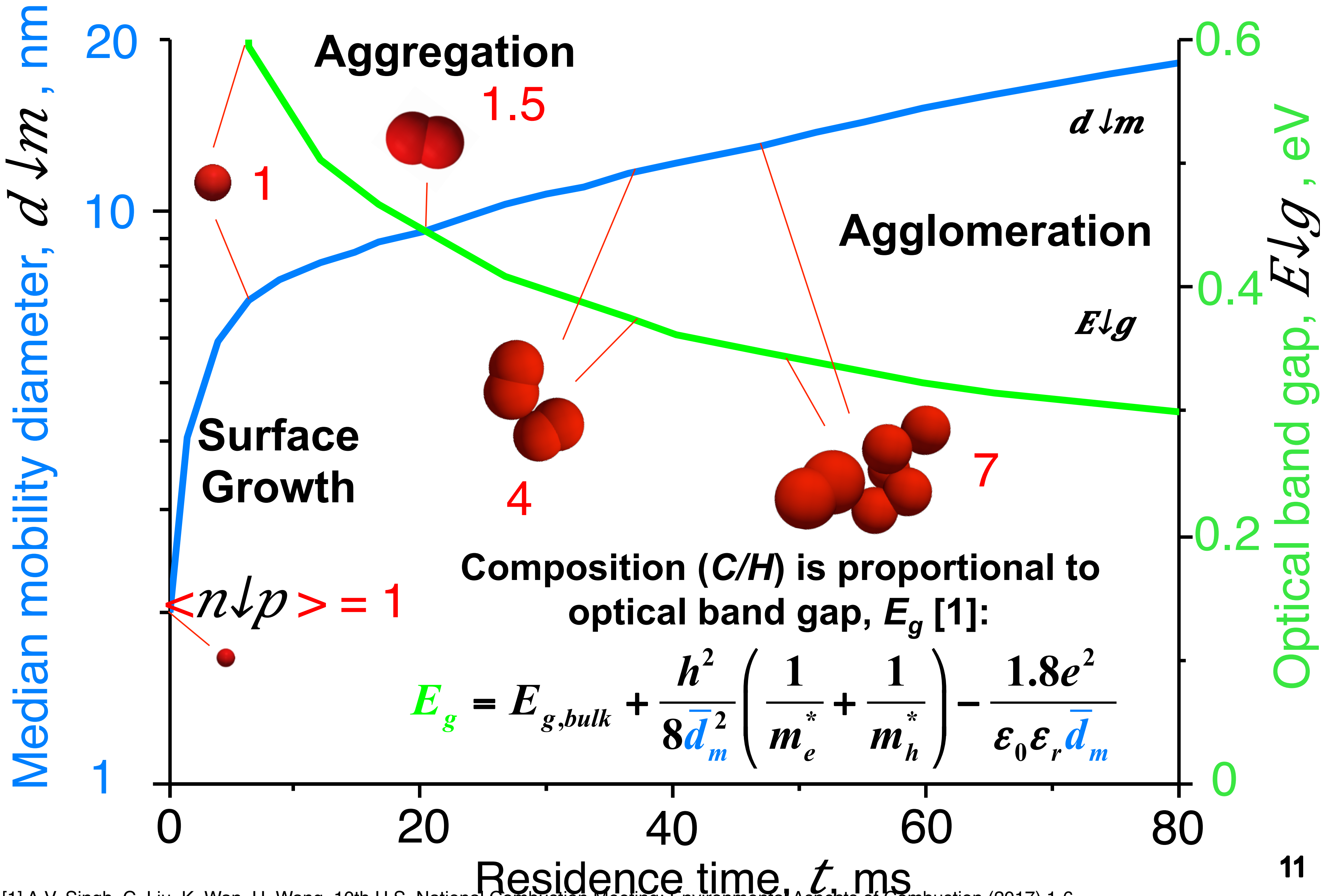


Composition (*C/H*) is proportional to optical band gap, E_g [1]:

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

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

Evolution of soot composition



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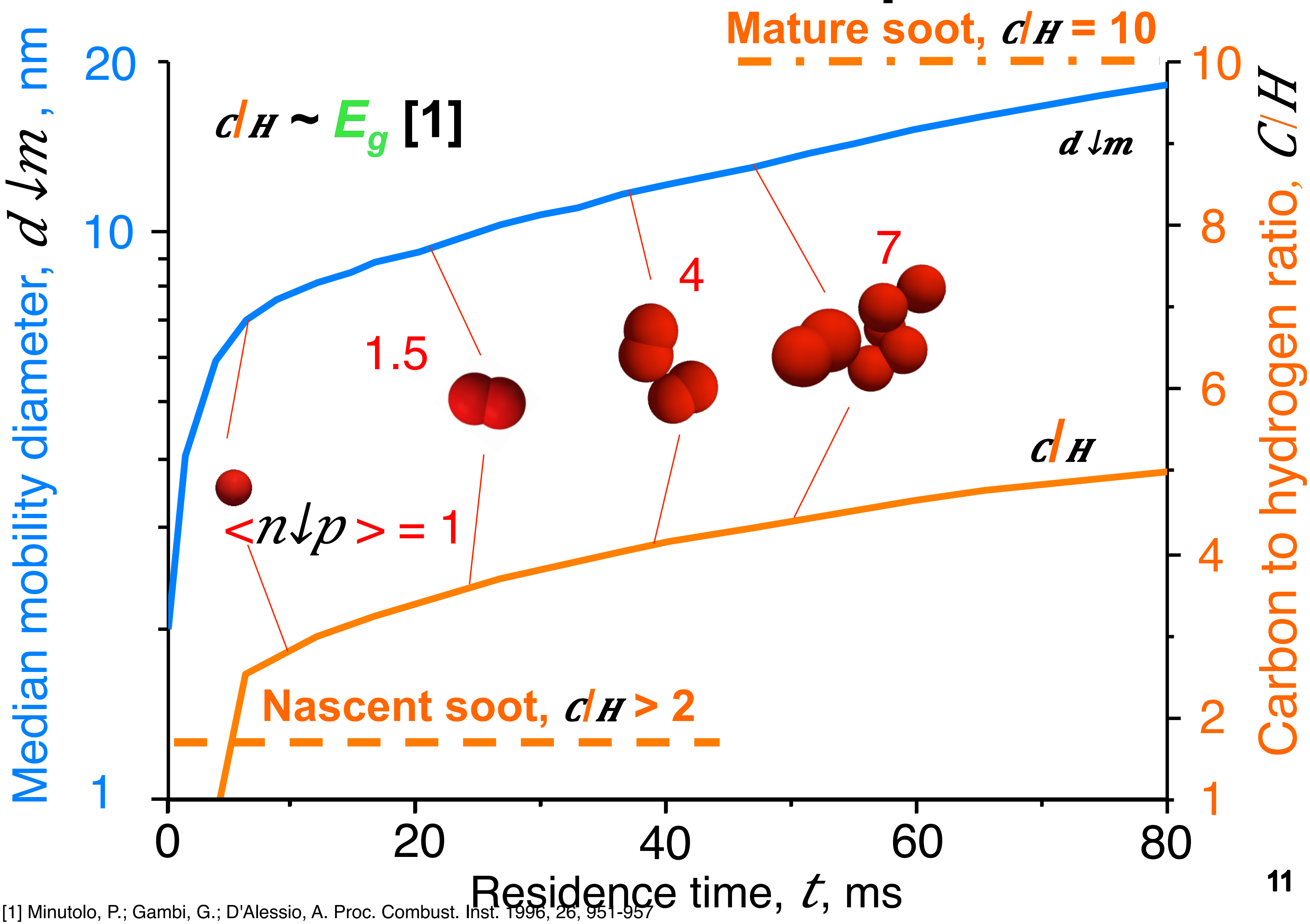
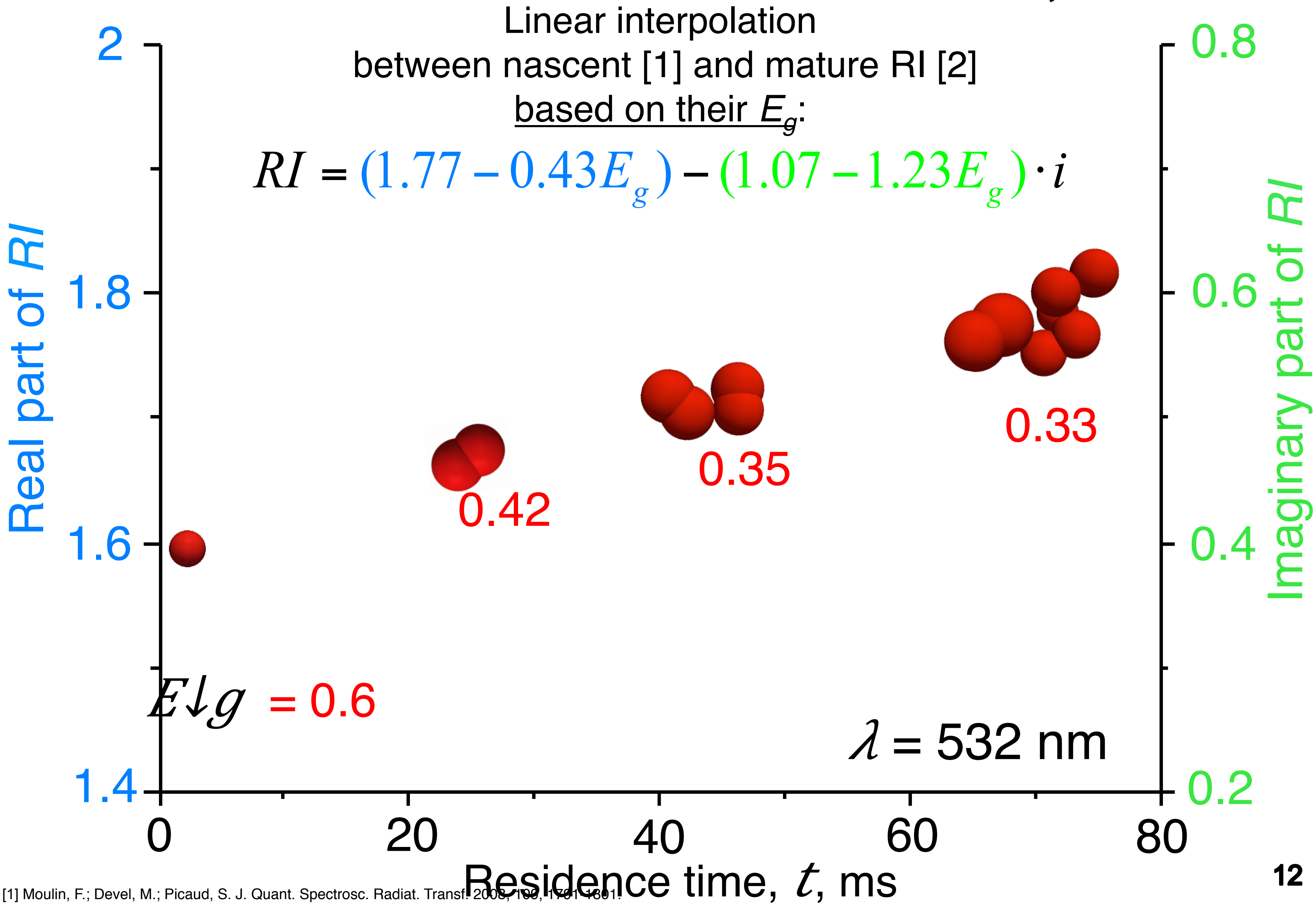


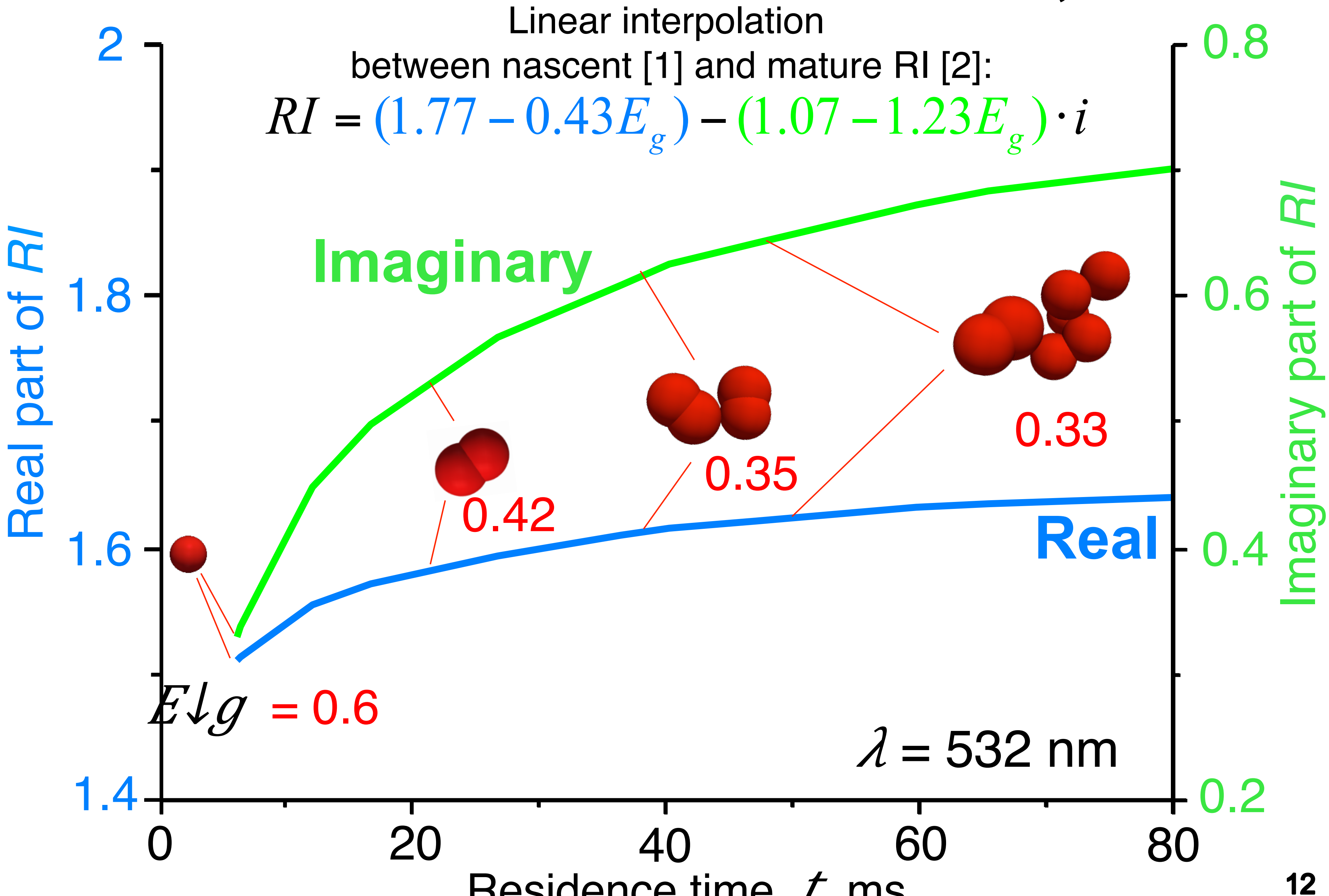
[1] Minutolo, P.; Gambi, G.; D'Alessio, A. Proc. Combust. Inst. 1996, 26, 951-957

Evolution of refractive index, *RI*



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

Evolution of refractive index, *RI*



[1] Moulin, F.; Devel, M.; Picaud, S. J. Quant. Spectrosc. Radiat. Transf. 2008, 109, 1791-1801.
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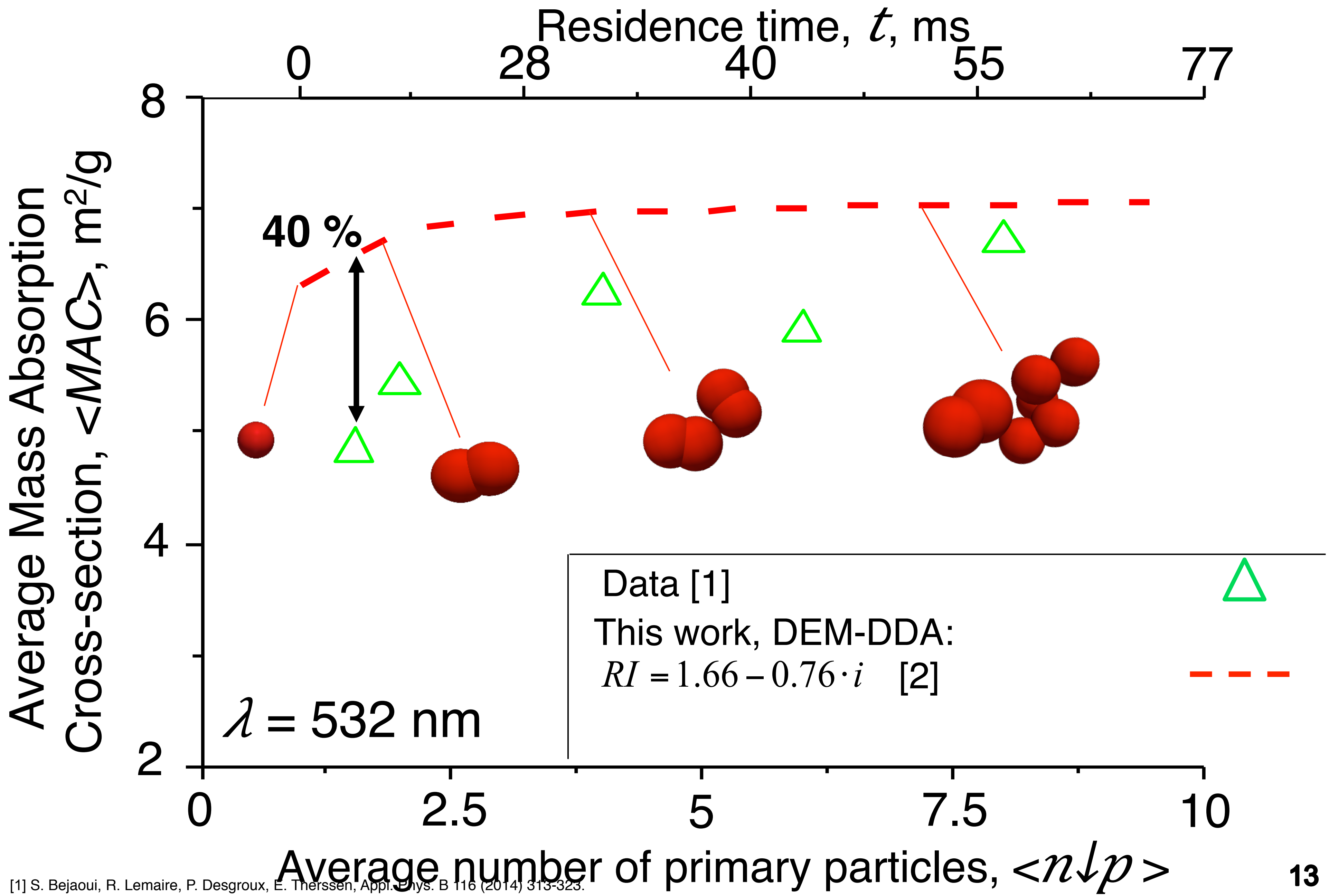
From nascent to mature soot *MAC*



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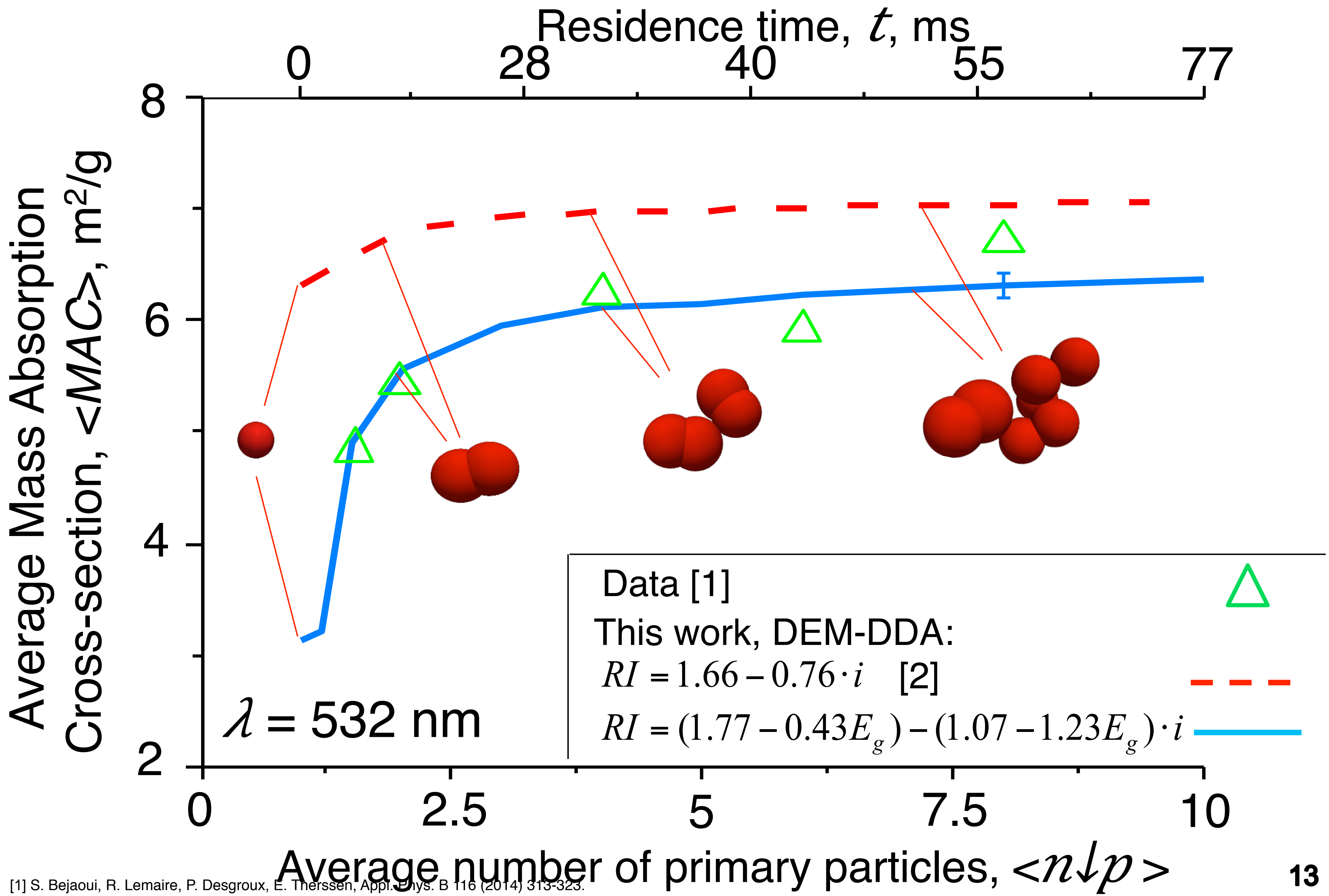
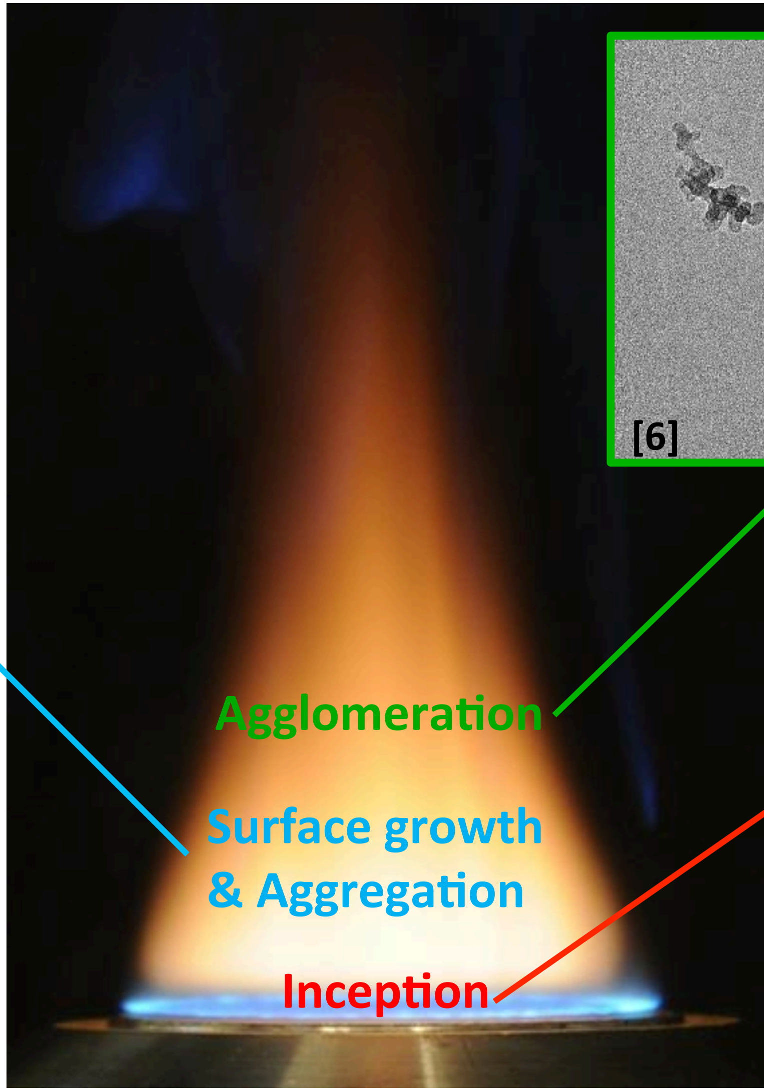
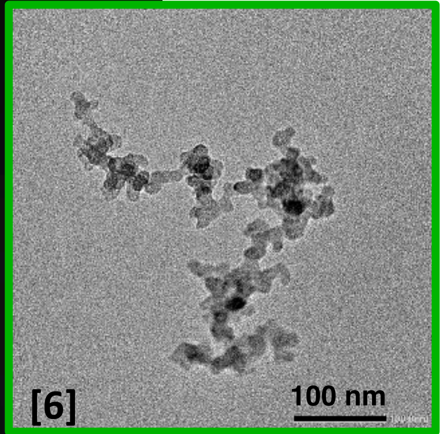


[1] S. Bejaoui, R. Lemaire, P. Desgroux, E. Therssen, Appl. Phys. B 116 (2014) 313-323.

[2] J. Yon, A. Bescond, F. Liu, J. Quant. Spectrosc. Radiat. Transf. 162 (2015) 197-206.

Soot formation dynamics



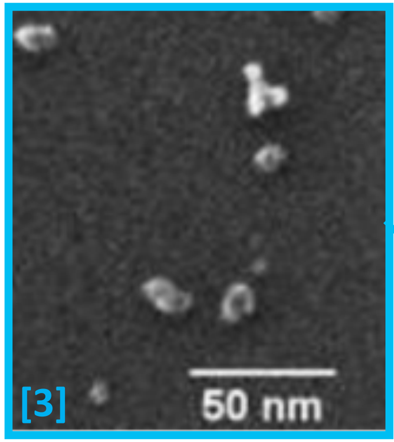


Mature soot:

$d_m > 30$ nm

$C/H > 10$

Strong light absorber and scatterer [5]

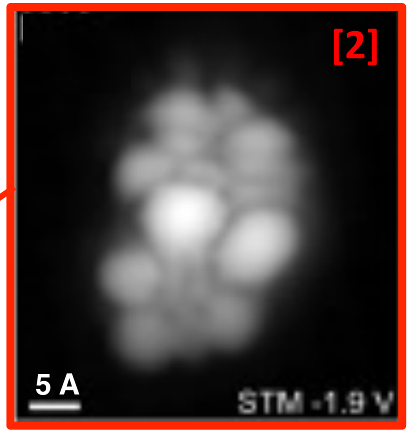


Nascent soot:

3 nm $< d_m <$ 30 nm

$2 < C/H < 10$

Slightly absorb visible and IR [4]



Incipient soot:

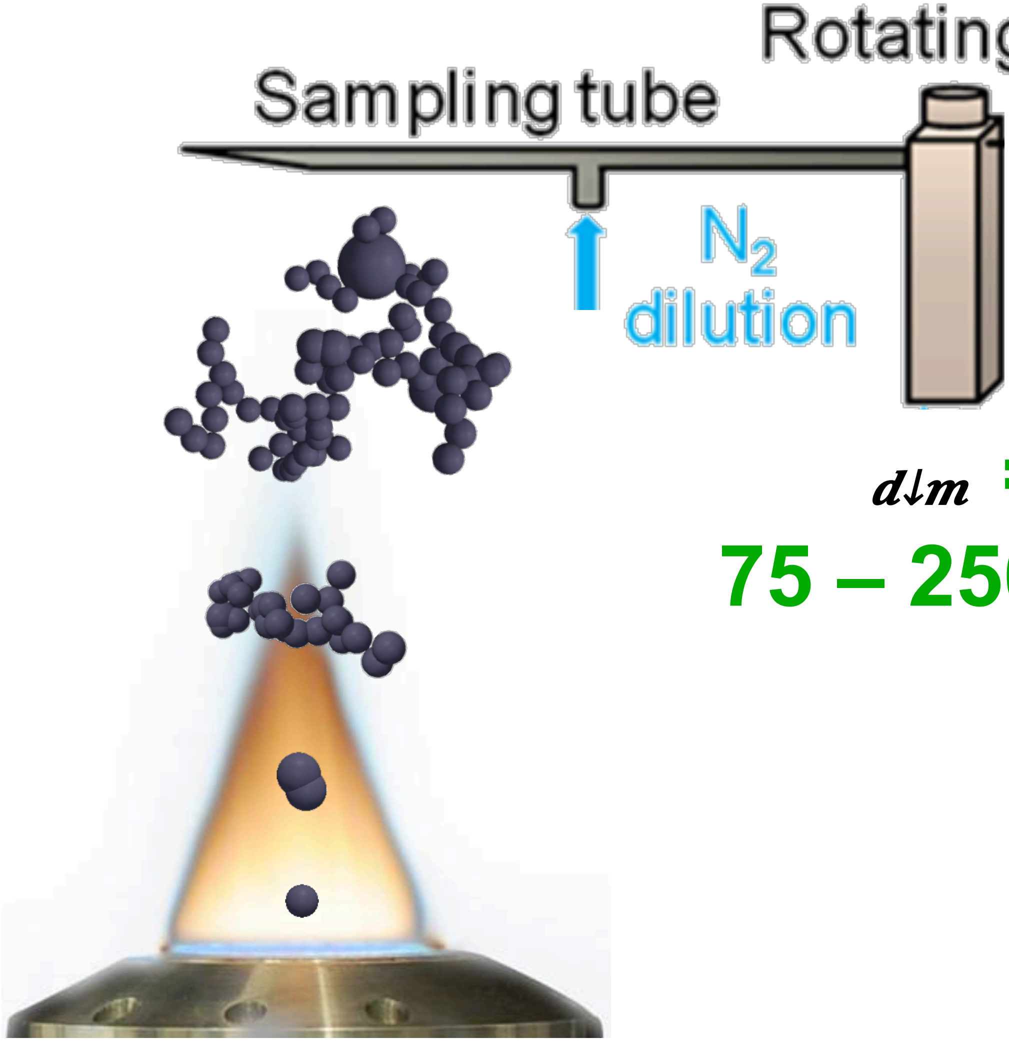
$d_m < 3$ nm

$C/H < 2$

Transparent to visible and IR [1]

[1] D'Anna, A.; Rolando, A.; Allouis, C.; Minutolo, P.; D'Alessio, A. Proc Combust Inst 2005, 30, 1449.
[2] Schultz, F.; Commodo, M.; Kaiser, K.; De Falco, G.; Minutolo, P.; Meyer, G.; D'Anna, A.; Gross, L. Proc Combust Inst, 2019, 37, 885-892.
[3] Schenk, M.; Lieb, S.; Vieker, H.; Beyer, A.; Golzhauser, A.; Wang, H.; Kohse-Hoinghaus, K. ChemPhysChem 2013, 14, 3248.
[4] Bejaoui, S.; Lemaire, R.; Desgroux, P.; Therssen, E. Appl Phys B 2014, 116, 313.
[5] Michelsen, H.A.; Schrader, P.E.; Goulay, F. Carbon 2010, 48, 2175.
[6] Kelesidis, G.A.; Kholghy, M.R.; Zurcher, J.; Robertz, J.; Allemann, M.; Duric, A.; Pratsinis, S.E. Powder Technol 2019, in press.

Experimental Set-Up

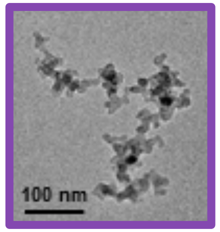


Premixed ethylene flame (φ ~ 2.15)

d_m =

75 – 250 nm

m



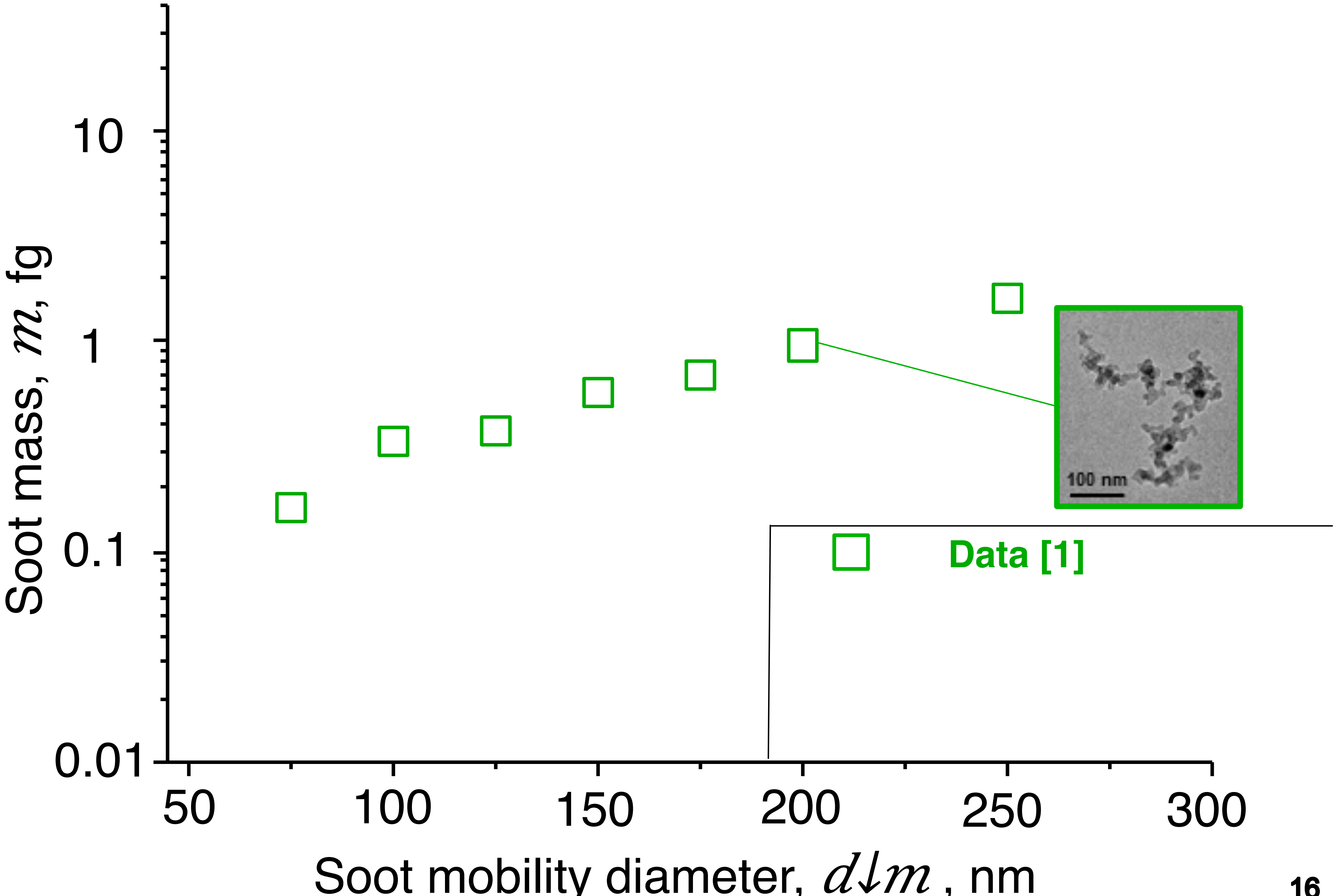
c

SIEMENS

λ = 405 nm

Kelesidis, G.A.; Kholghy, M.R.; Zurcher, J.; Robertz, J.; Allemann, M.; Duric, A.; Pratsinis, S.E. Powder Technol 2019, doi.org/10.1016/j.powtec.2019.02.003.

Mature soot morphology



[1] Kelesidis, G.A.; Kholghy, M.R.; Zurcher, J.; Robertz, J.; Allemann, M.; Duric, A.; Pratsinis, S.E. Powder Technol 2019, doi.org/10.1016/j.powtec.2019.02.003.

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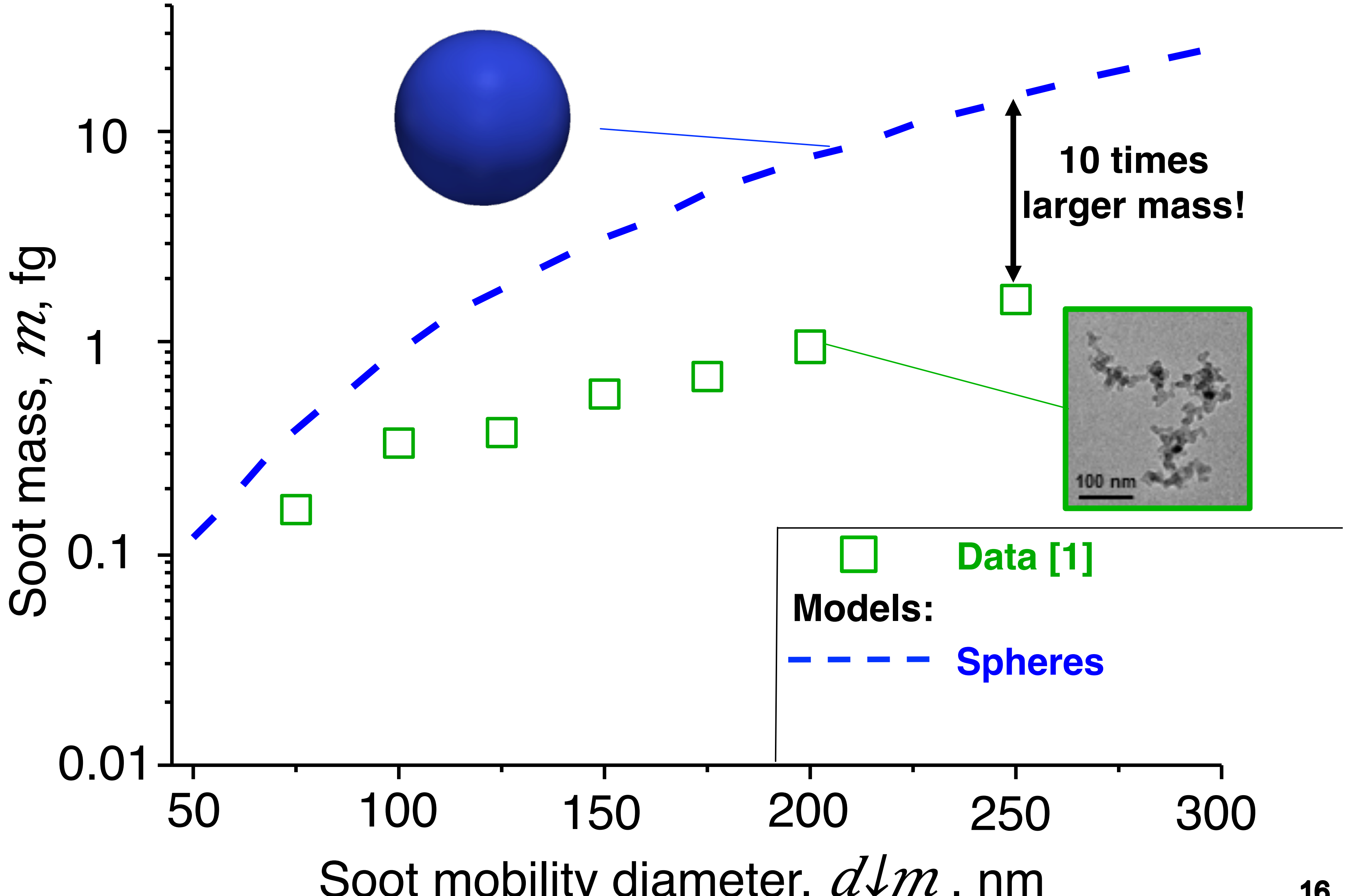

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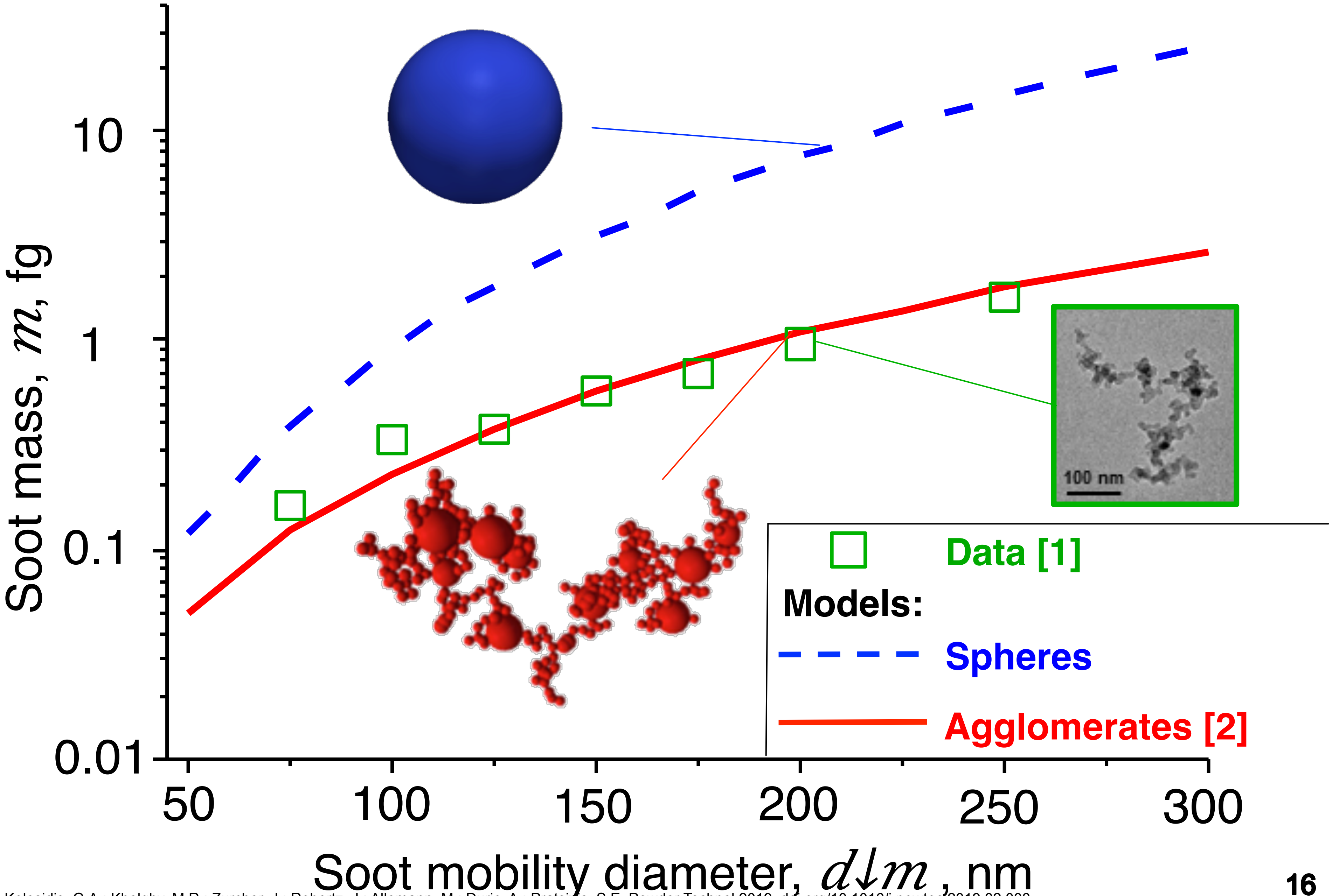
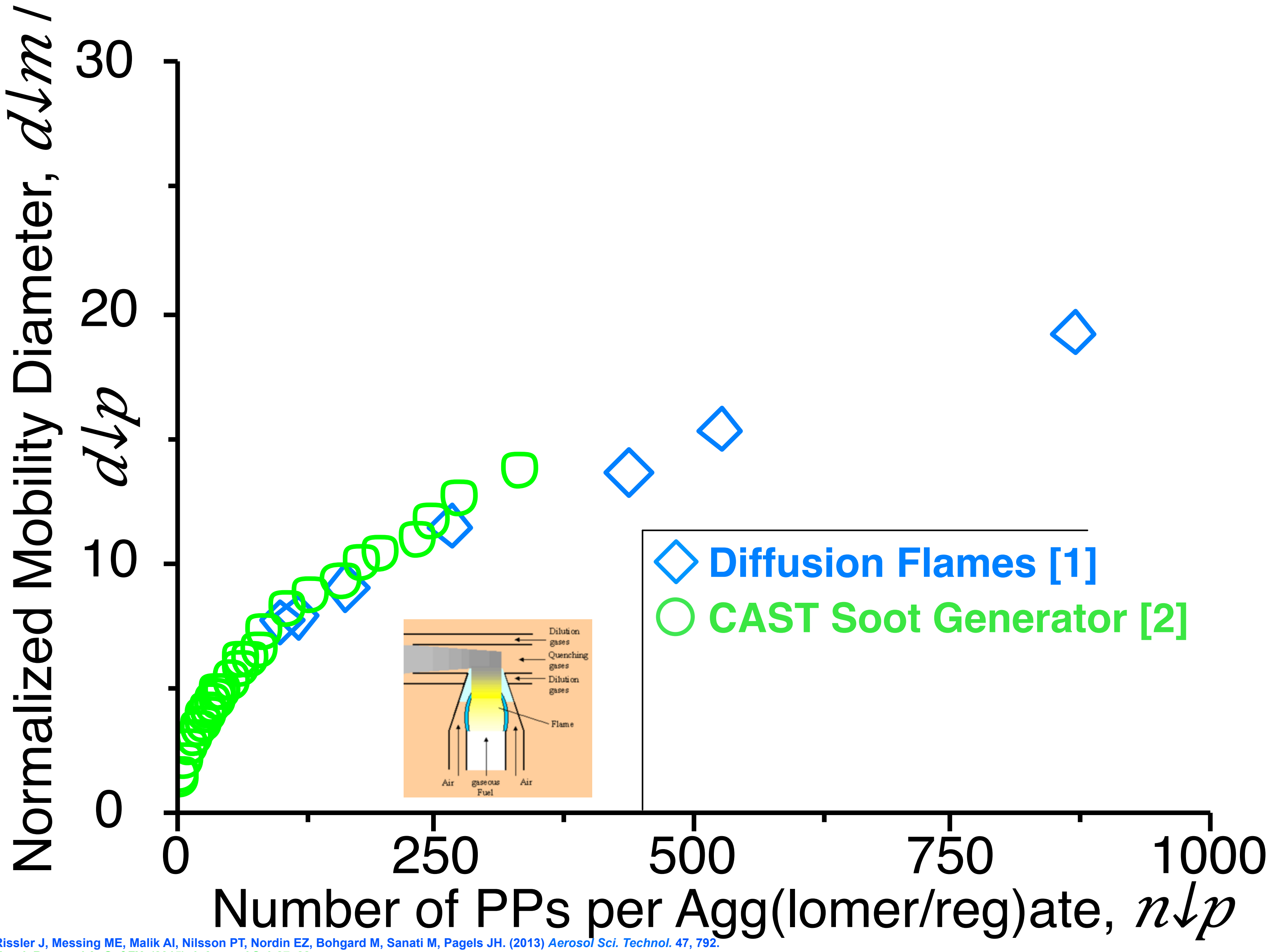


[1] Kelesidis, G.A.; Kholghy, M.R.; Zurcher, J.; Robertz, J.; Allemann, M.; Duric, A.; Pratsinis, S.E. Powder Technol 2019, doi.org/10.1016/j.powtec.2019.02.003.
[2] Kelesidis, G.A.; Goudeli, E.; Pratsinis, S.E. Carbon 2017, 121, 527.

Comparison to other sources:



[1] Rissler J, Messing ME, Malik AI, Nilsson PT, Nordin EZ, Bohgard M, Sanati M, Pagels JH. (2013) *Aerosol Sci. Technol.* 47, 792.
[2] Yon J, Bescond A, Ouf FX. (2015) *J. Aerosol Sci.* 87, 28.

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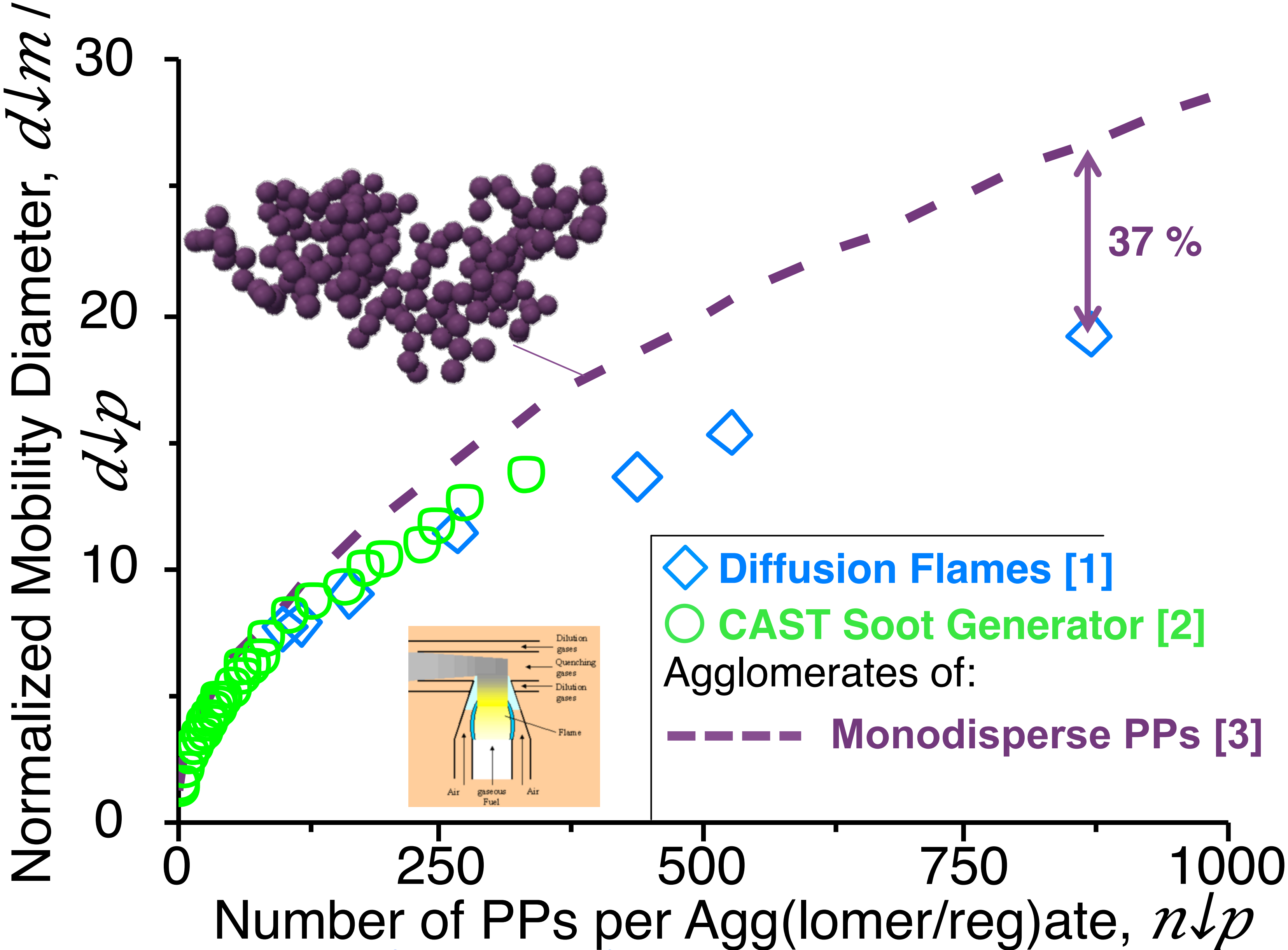

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[2] Yon J, Bescond A, Ouf FX. (2015) *J. Aerosol Sci.* 87, 28.
[3] Sorensen CM. *Aerosol Sci. Technol.* (2011) 45, 765.

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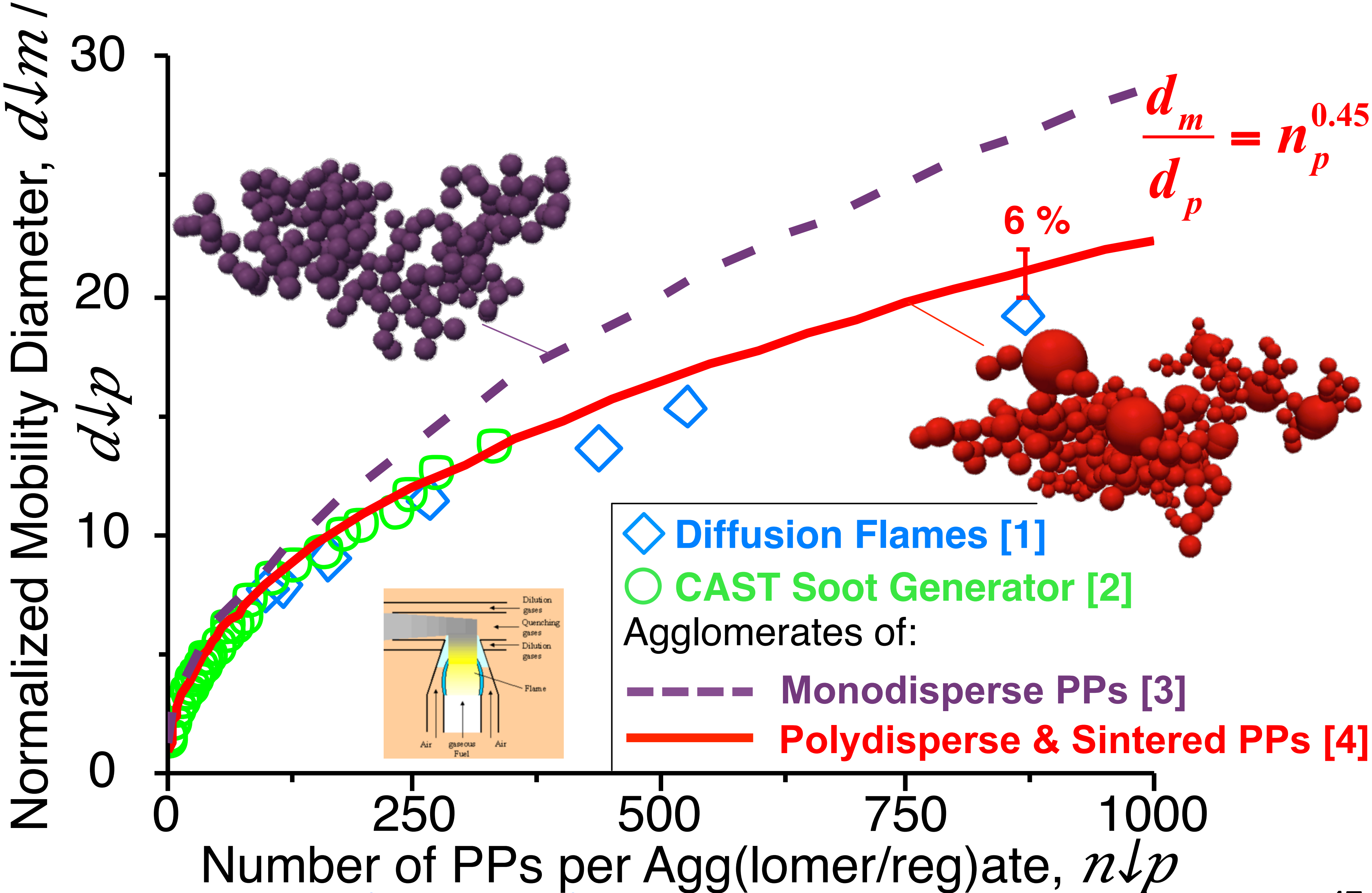

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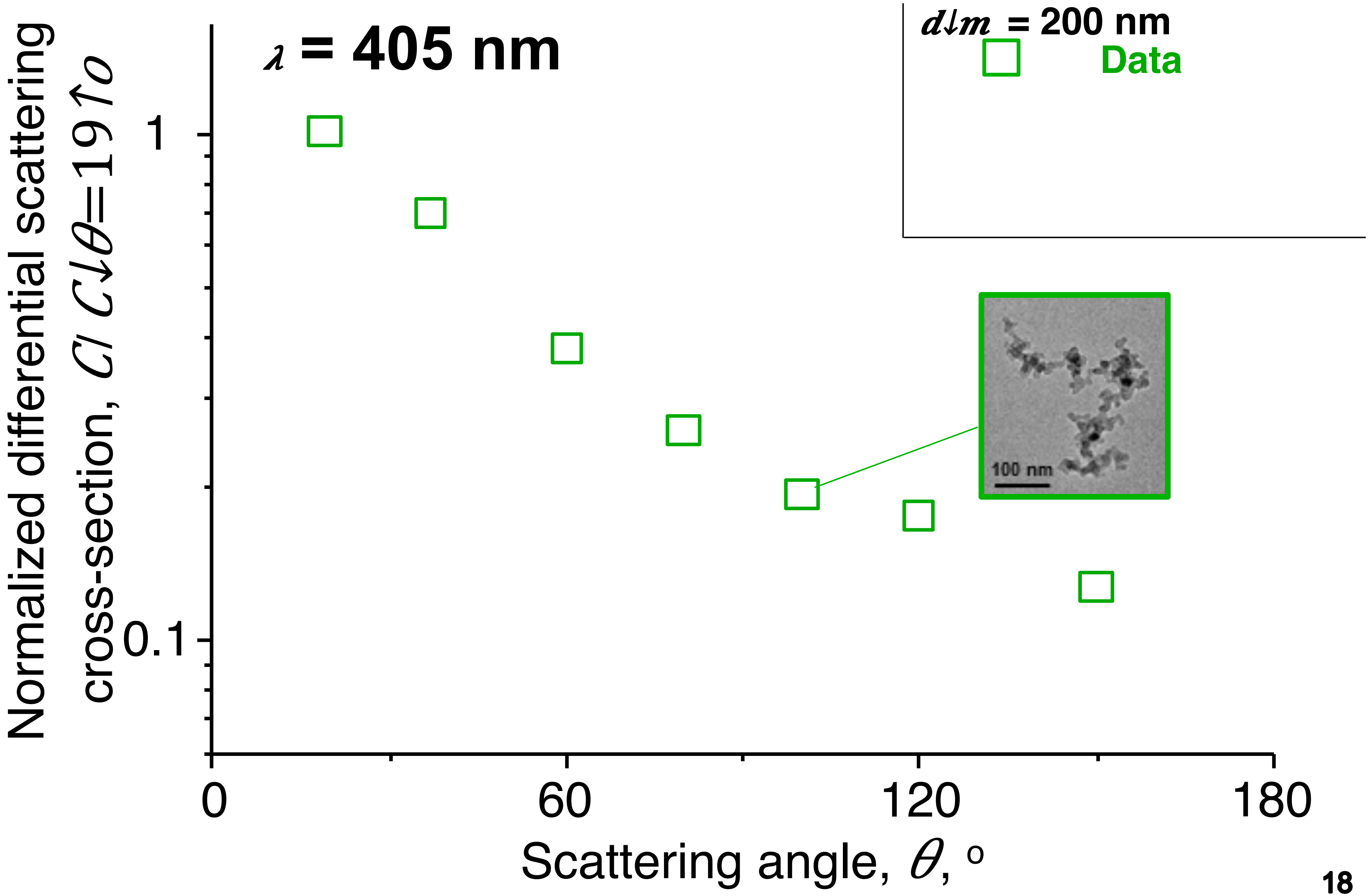
[4] Kelesidis GA, Goudeli E, Pratsinis SE. *Carbon* (2017) 121, 527.

Soot light scattering



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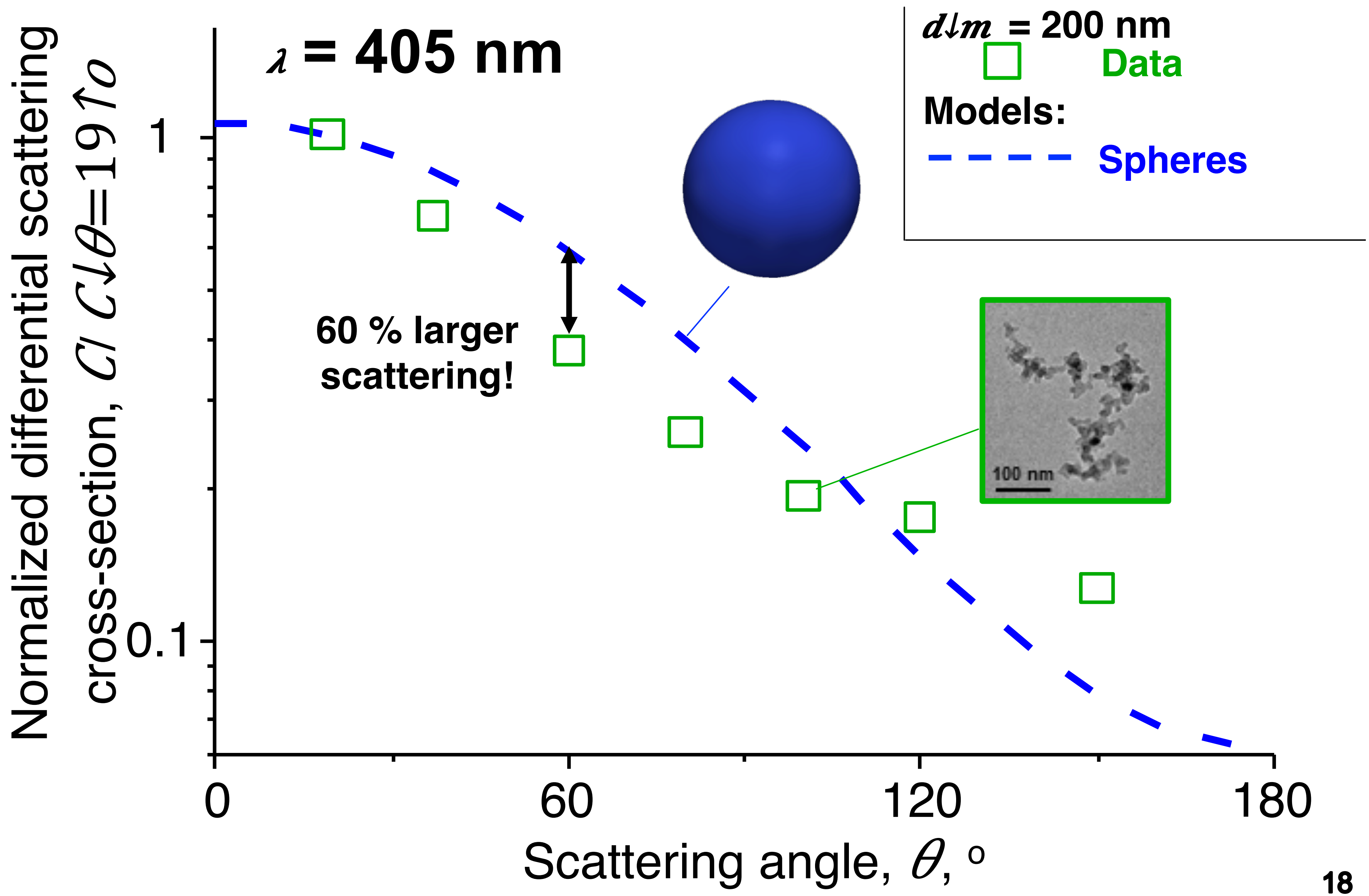

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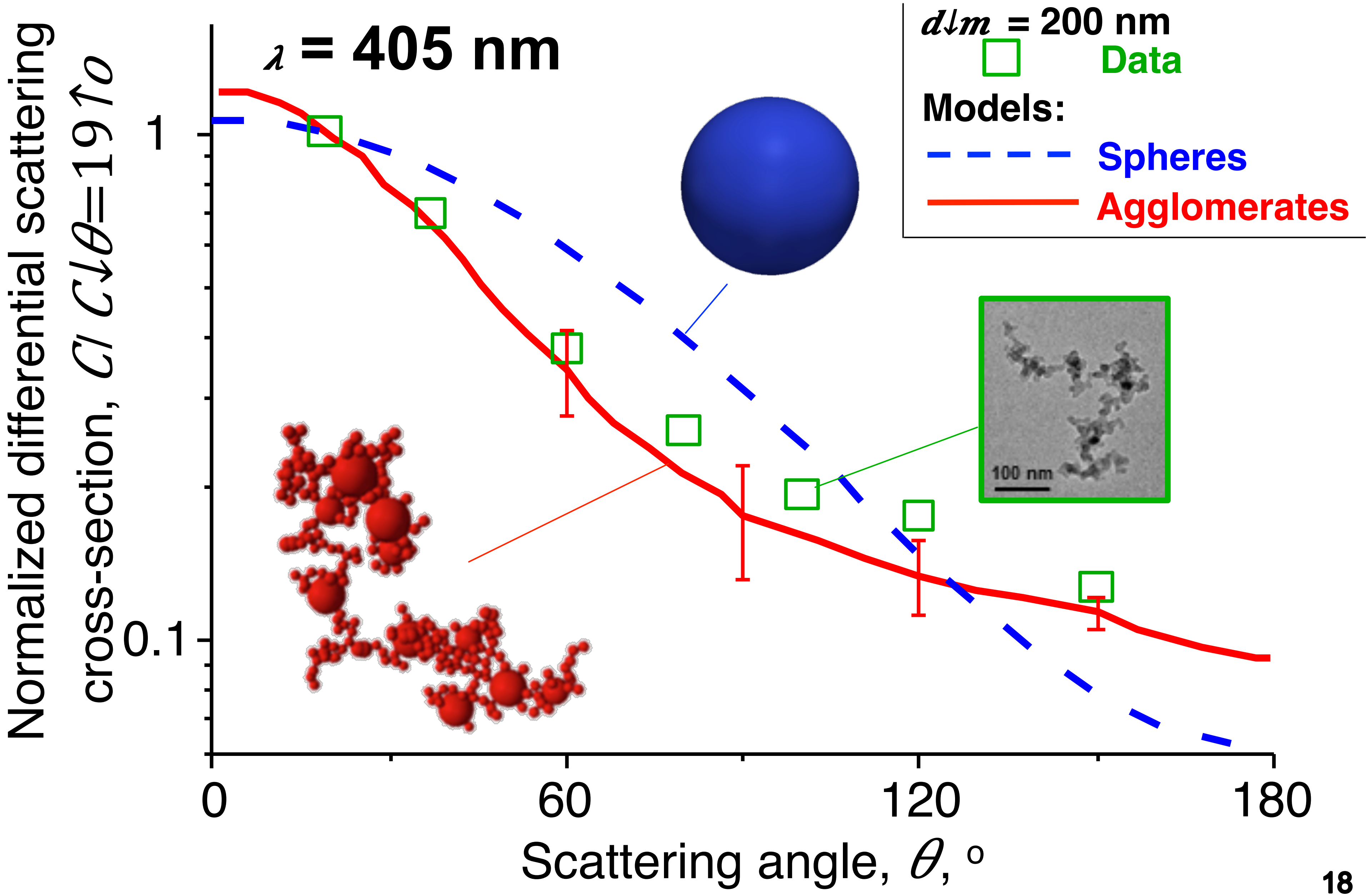

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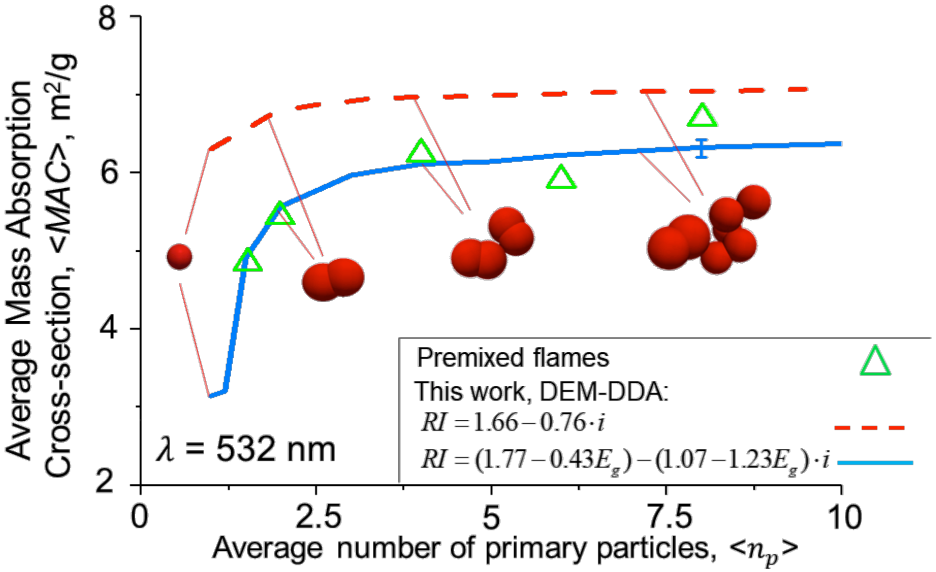
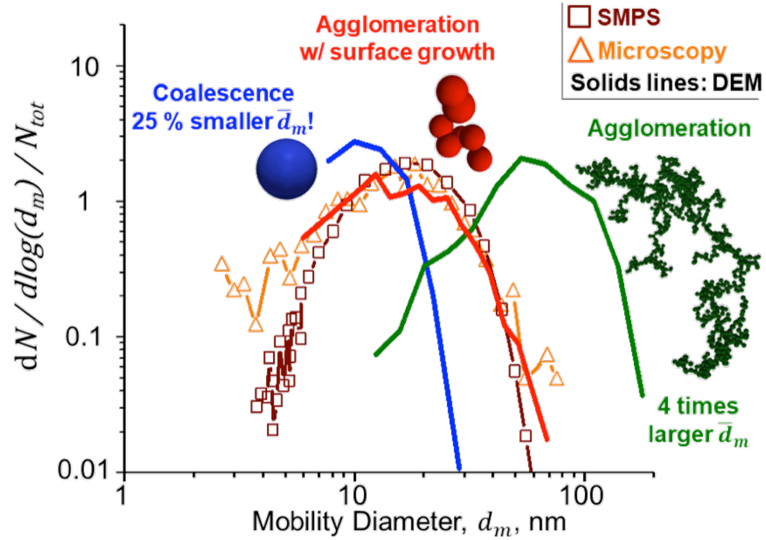
Conclusions

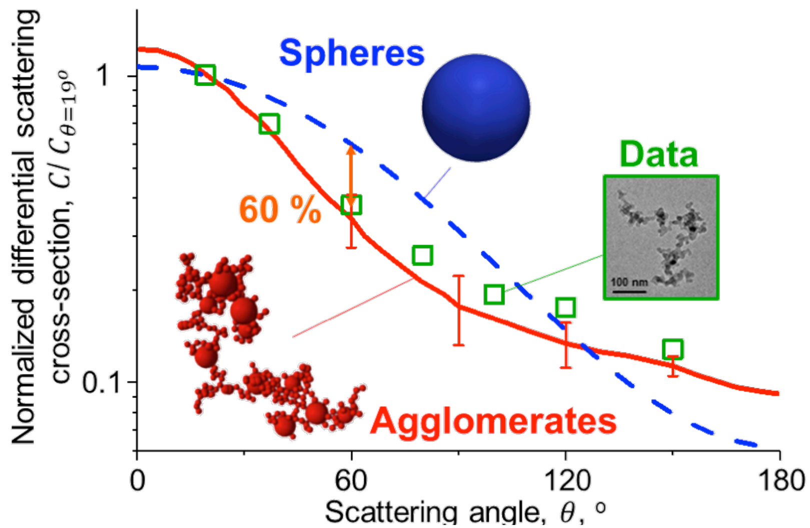
- Realistic pathway of soot formation by surface growth and agglomeration.



- **DEM-DDA can be used for improved optical diagnostics and climate impact calculations!**

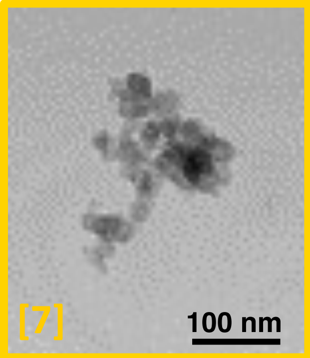


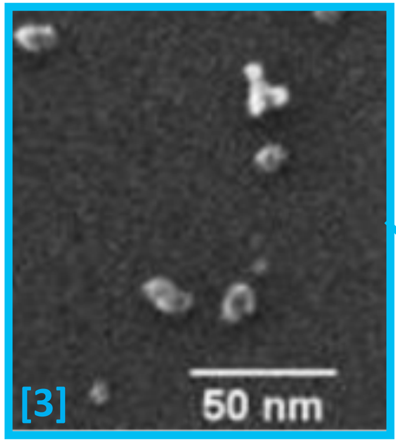
- Structure AND Composition are essential for soot optical properties!



Outlook

Soot formation dynamics





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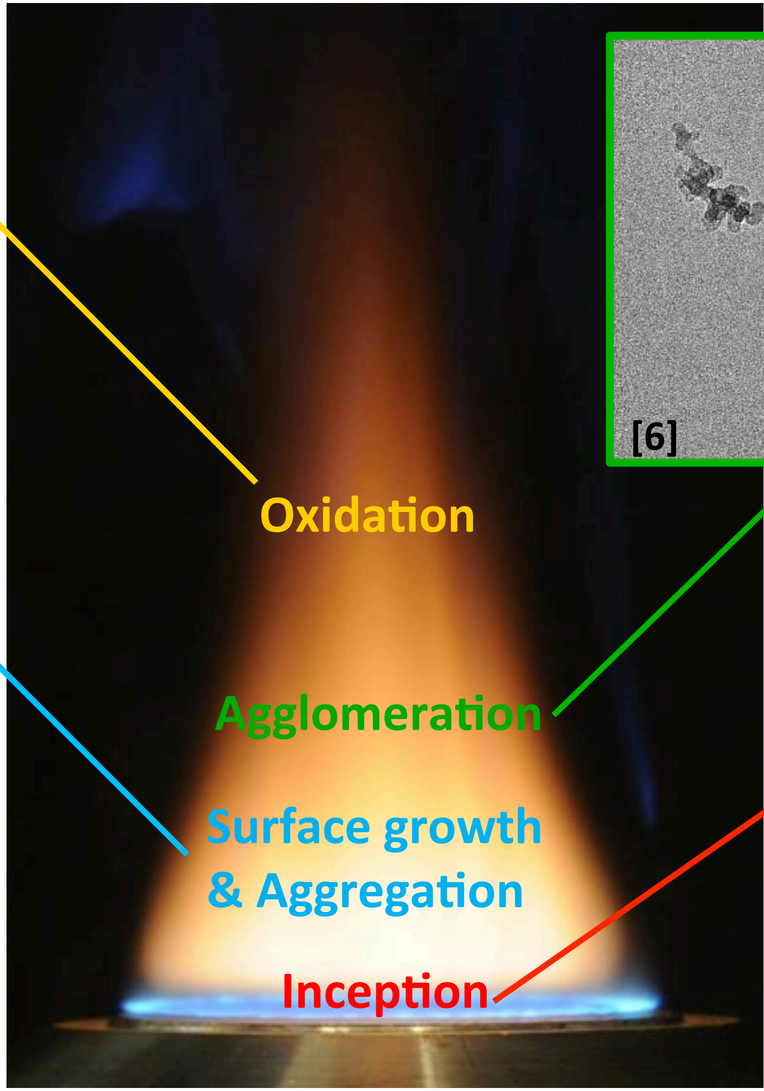
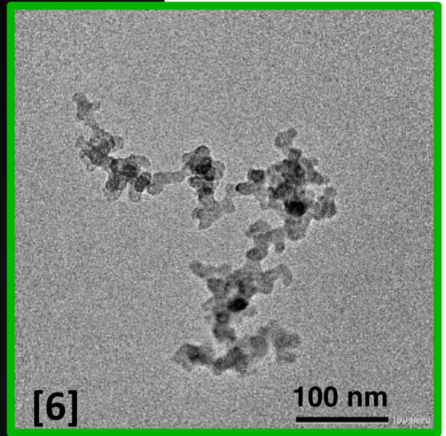
Slightly absorb visible and IR [4]





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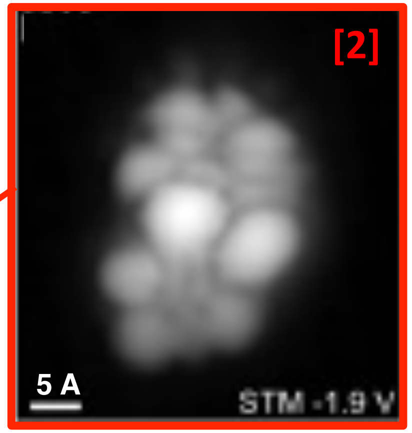

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[3] Schenk, M.; Lieb, S.; Vieker, H.; Beyer, A.; Golzhauser, A.; Wang, H.; Kohse-Hoinghaus, K. ChemPhysChem 2013, 14, 3248.
[4] Bejaoui, S.; Lemaire, R.; Desgroux, P.; Therssen, E. Appl Phys B 2014, 116, 313.
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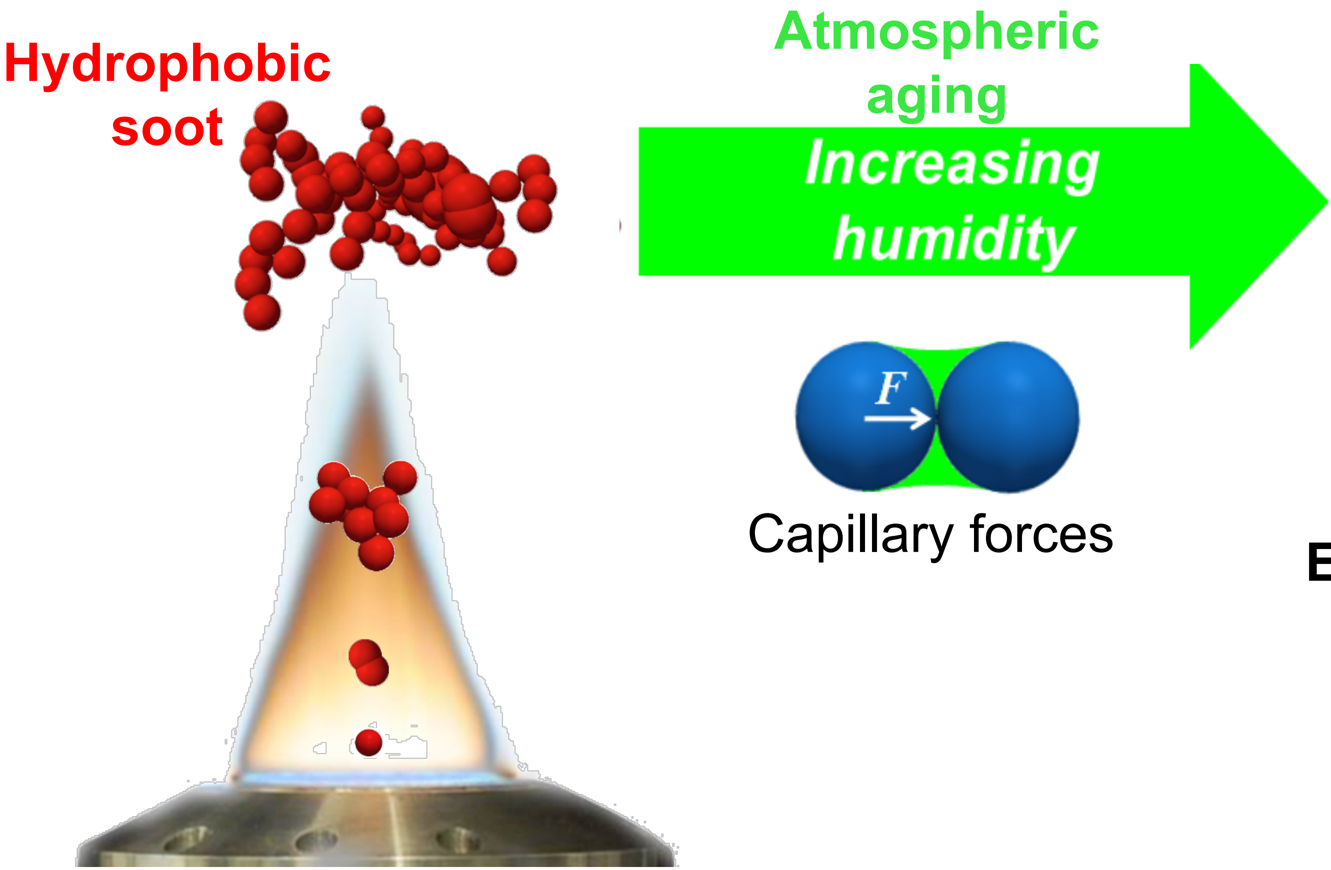
[7] Jung, H.J.; Kittelson, D.B.; Zachariah, M.R. Combust Flame 2004, 136, 445.

Atmospheric aging of nanoparticles

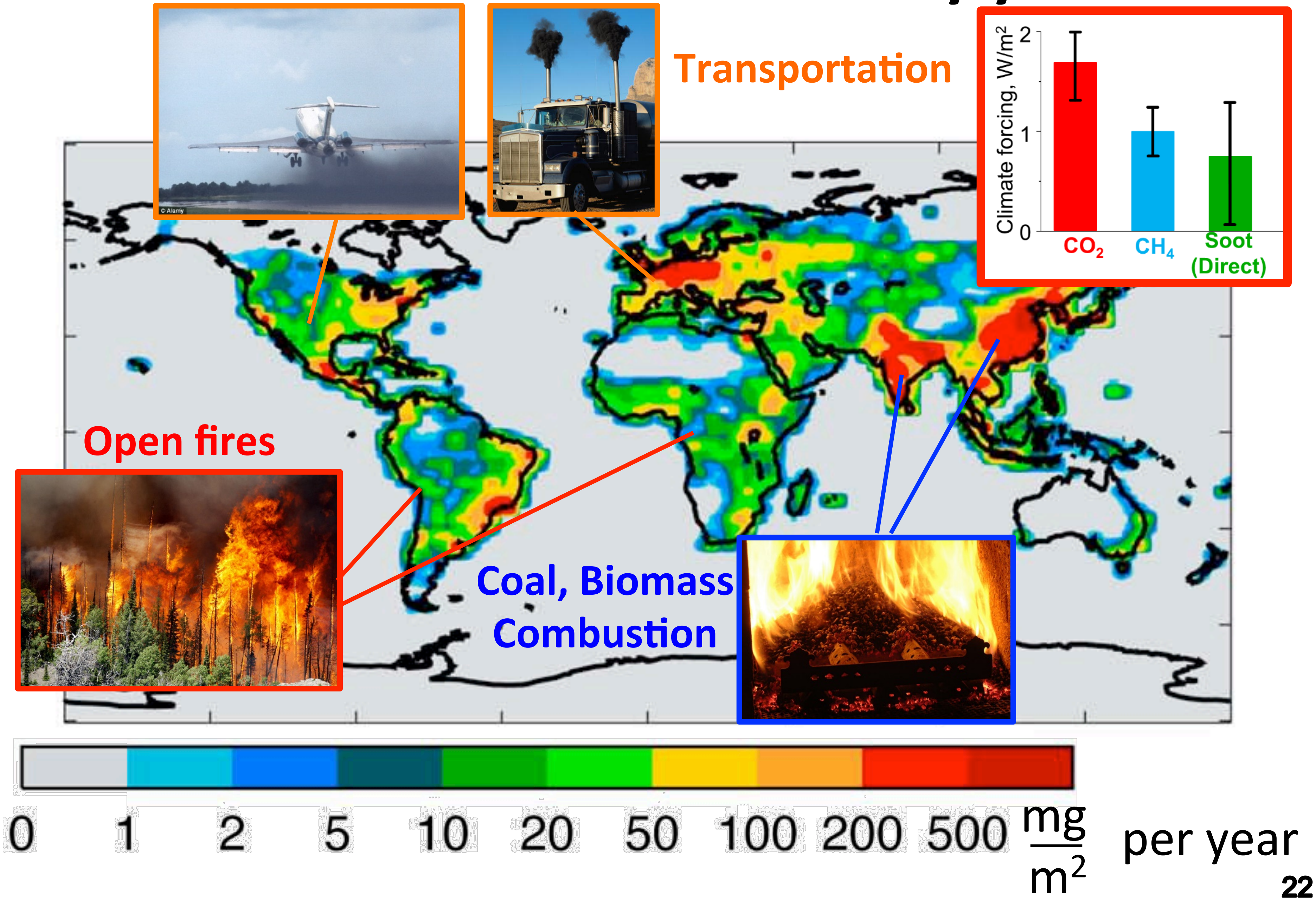
Hydrophilic silica



Extend DEM-DDA for atmospheric aging

Kelesidis, G.A.; Furrer, F.M.; Wegner, K.; Pratsinis, S.E. Langmuir 2018, 34, 8532.

8 Mt of soot emissions every year!



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

Ackowledgements

- Prof. Dr. Sotiris E. Pratsinis

ETH Zurich

- Prof. Dr. Eirini Goudeli
  (University of Melbourne, Australia)
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- Dr. Karsten Wegner

Siemens AG, Zug

- Dr. Aleksandar Duric
- Martin Allemann
- Julian Robertz

BSc and MSc students:

- Florian M. Furrer
- Joel Zurcher
- Natalia Smatsi
- Daniel Gao

ETH Foundation Zürich

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FNSNF
FONDS NATIONAL SUISSE
SCHWEIZERISCHER NATIONALFONDS
FONDO NAZIONALE SVIZZERO
SWISS NATIONAL SCIENCE FOUNDATION

Thank you for your attention!

ETH zürich

Impact of humidity on silica nanoparticle agglomerate morphology and size distribution

Georgios A. Kelesidis, Florian M. Furrer, Karsten Wegner, Sotiris E. Pratsinis

Particle Technology Laboratory, ETH Zürich, Switzerland

PTL Particle Technology Laboratory

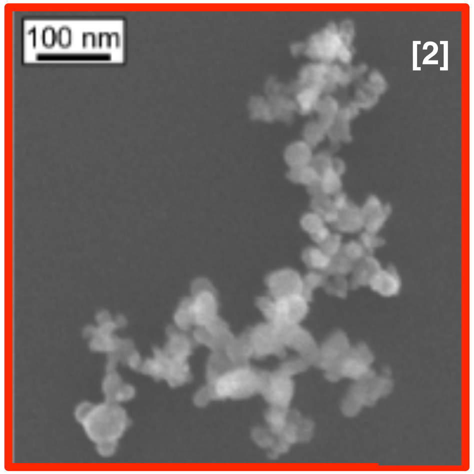
Silica: A flame-made nano-commodity

A 3 billion industry $ including:

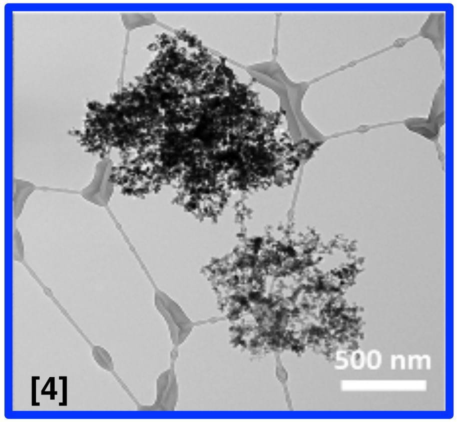
Pharmaceutics

Cosmetics

Dry conditions during flame synthesis



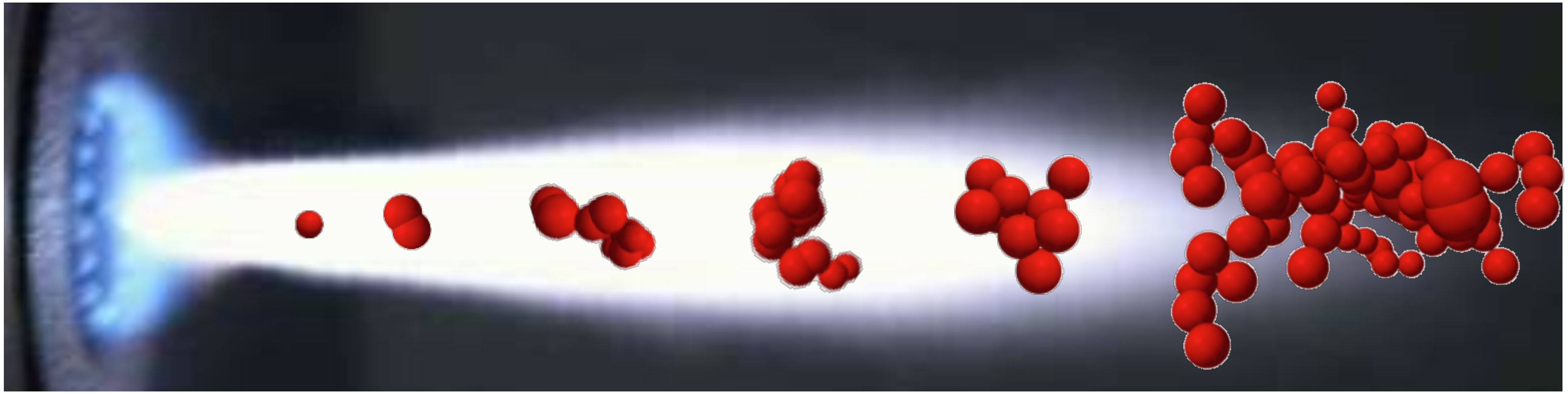
Storage & Processing with humidity!

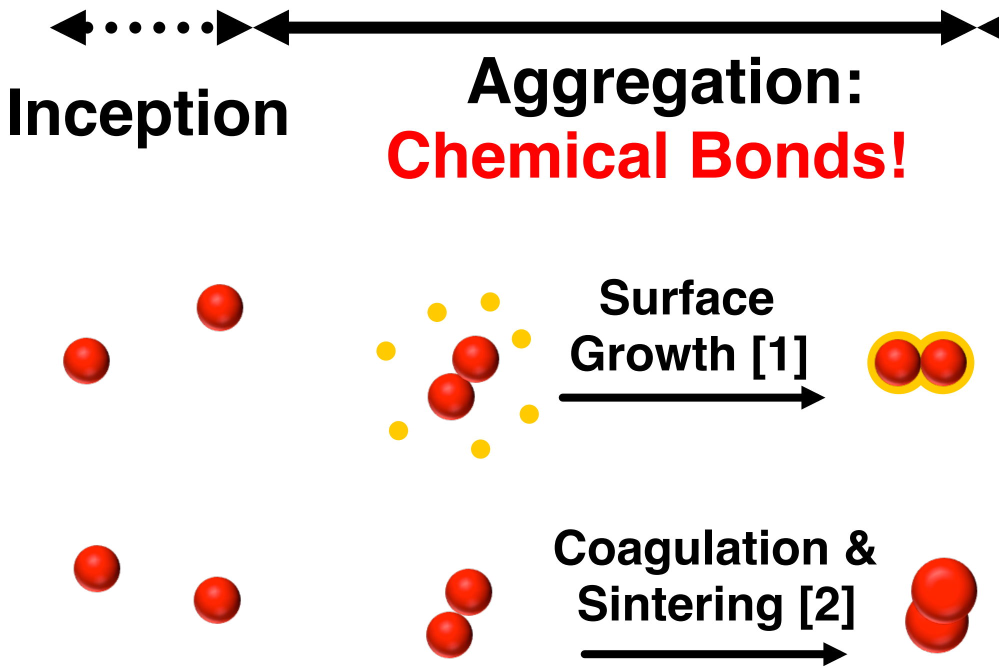


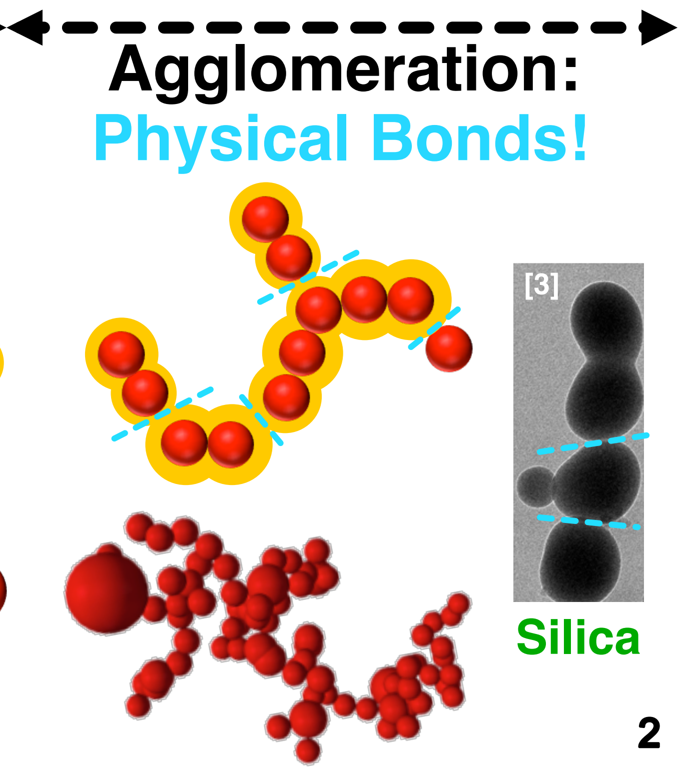
Fluidized agglomerates

[1] Courtesy of Cabot.
[2] J.H. Scheckman, P.H. McMurry, S.E. Pratsinis (2009) *Langmuir* **25**, 8248.
[3] Courtesy of Prof. Lin, Iowa State University.
[4] A. Fabre, T. Steur, W.G. Bouwman, M.T. Kreutzer, J.R. van Ommen (2016) *J. Phys. Chem. C* **120**, 20446.

Nanoparticle Agglomerate Morphology

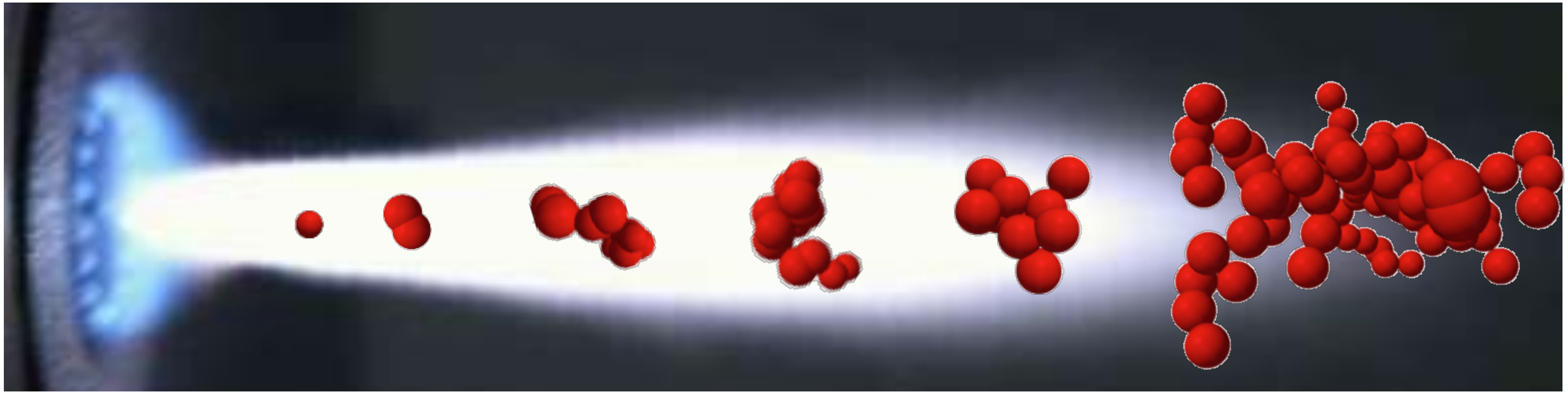


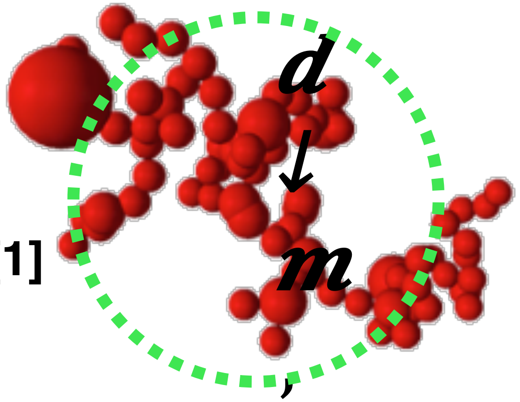




[1] G.A. Kelesidis, E. Goudeli, S.E. Pratsinis (2017) *Proc. Combust. Inst.* **36**, 29.
[2] S. Tsantilis, S.E. Pratsinis (2000) *AIChE J.* **46**, 407.
[3] S. Tsantilis, S.E. Pratsinis, S. E. (2004) *Langmuir* **20**, 5933.

Nanoparticle Agglomerate Morphology



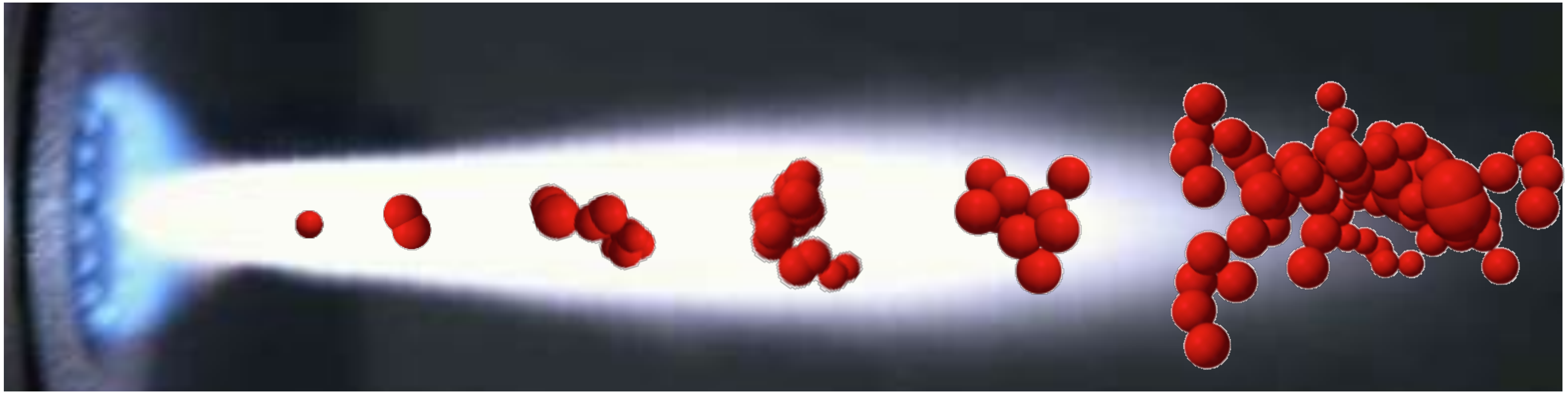


[1]

$$\rho_{eff}/\rho = (d_m/d_p)^{-0.78}$$

[1] G.A. Kelesidis, E. Goudeli, S.E. Pratsinis (2017) *Carbon* **121**, 527.

Nanoparticle Agglomerate Morphology



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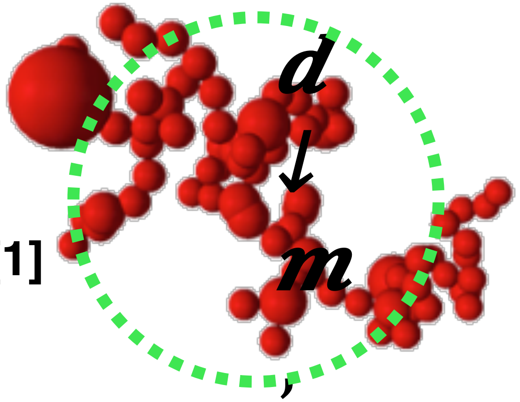
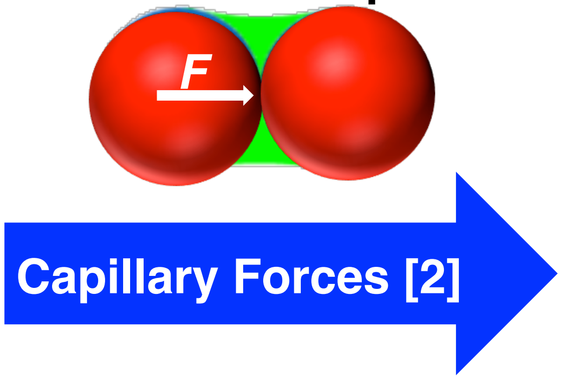
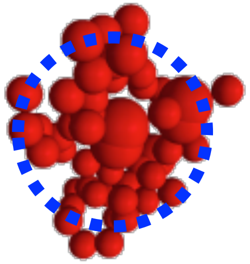


$d_{m,o}$

$$\rho_{eff}/\rho = (d_m/d_p)^{-0.78}$$

Water Condensation/Evaporation



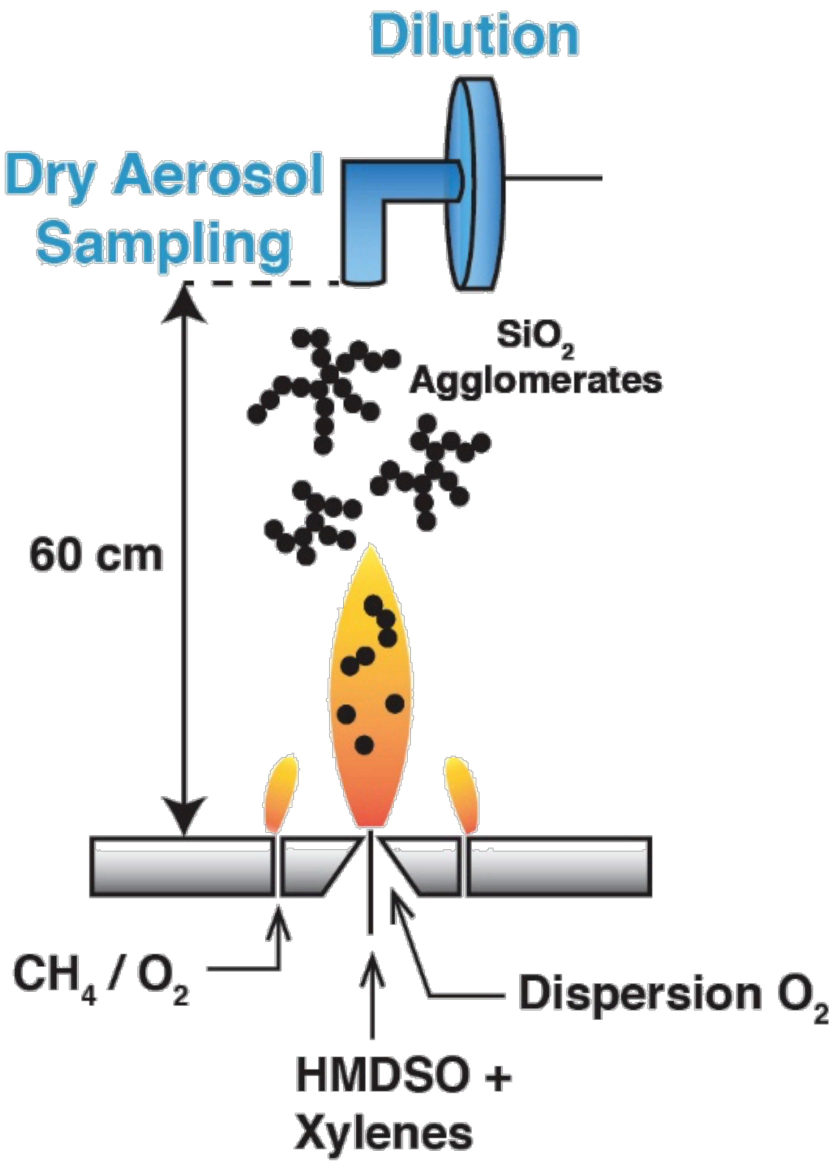


$d_m < d_{m,o}$

$$\rho_{eff}/\rho = ?$$

[1] G.A. Kelesidis, E. Goudeli, S.E. Pratsinis (2017) *Carbon* **121**, 527.
[2] S. Kütz S, A. Schmidt-Ott (1992) *J. Aerosol Sci.* **23**, S357.

Experimental Set Up



Flame Spray Pyrolysis

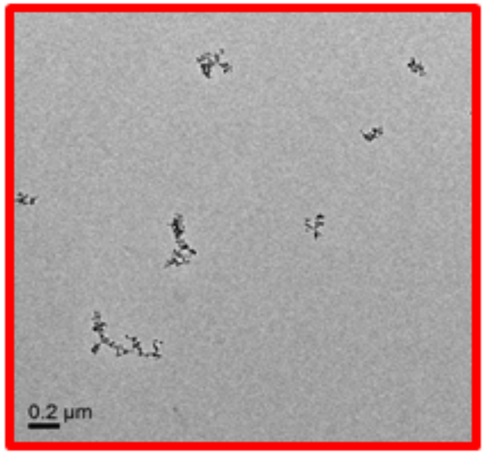
d_m, d_p, ρ_{ef}

[1] G. A. Kelesidis, F.M. Furrer, K. Wegner, S.E. Pratsinis (2018) *Langmuir* **34**, 8532.

Morphology dynamics by Humidity

Water condensation & evaporation with:

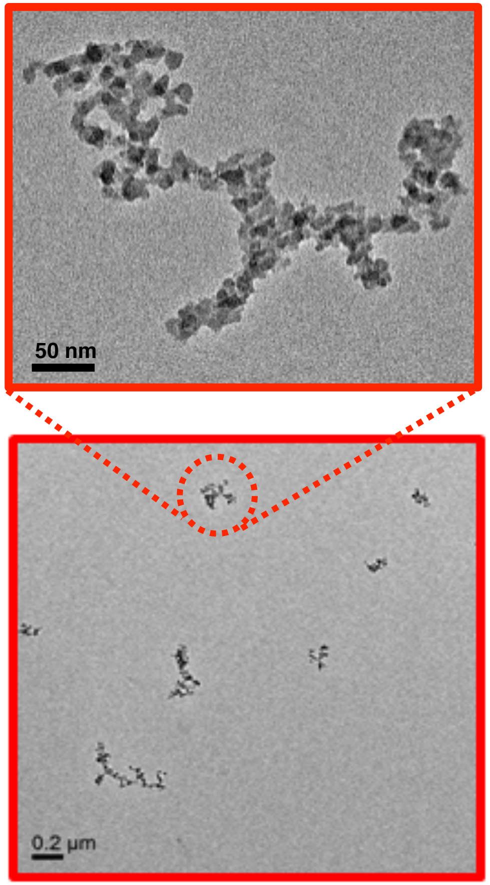
S = 0.2 (dry)



Morphology dynamics by Humidity

Water condensation & evaporation with:

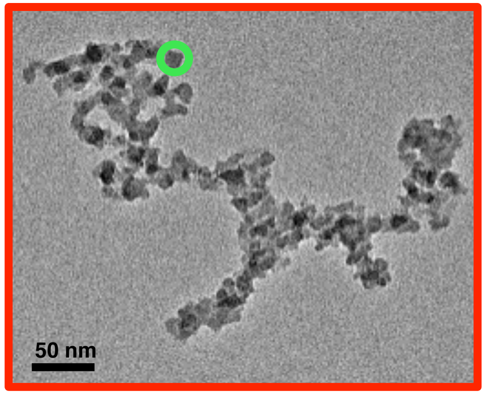
S = 0.2 (dry)

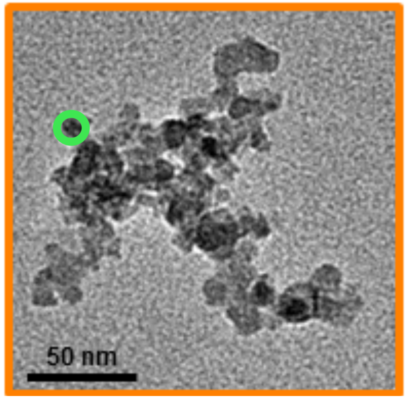


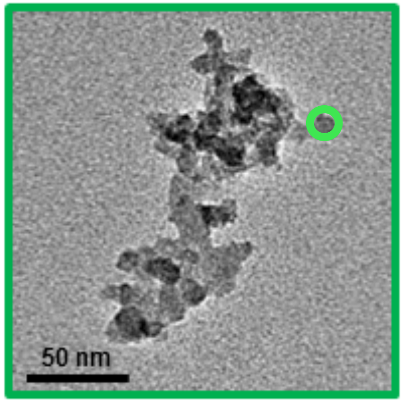
Morphology dynamics by Humidity

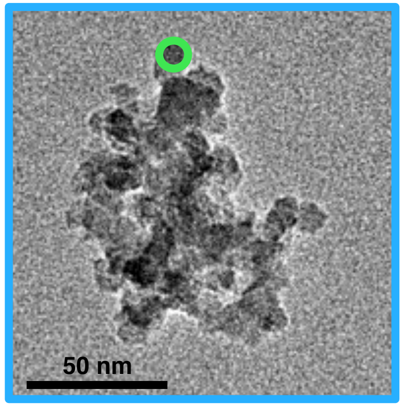
Water condensation & evaporation with:

S = 0.2 (dry) | 1.1 | 1.3 | 1.5









ρ_{eff} = 427 kg/m^3 | 445 kg/m^3 | 491 kg/m^3 | 640 kg/m^3

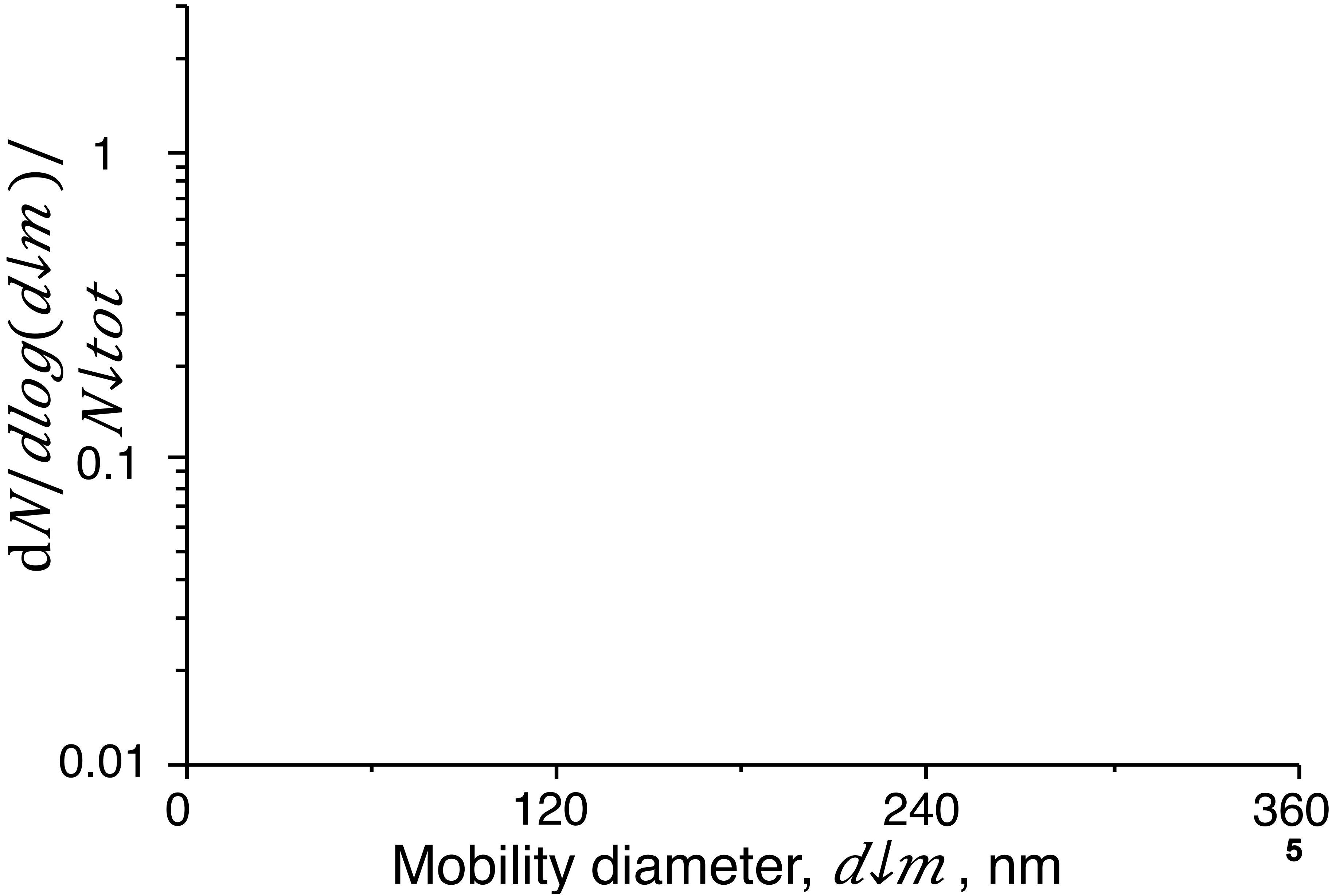
Bulk silica density,
ρ = 2200 kg/m^3

50 % ρ_{eff} increase!

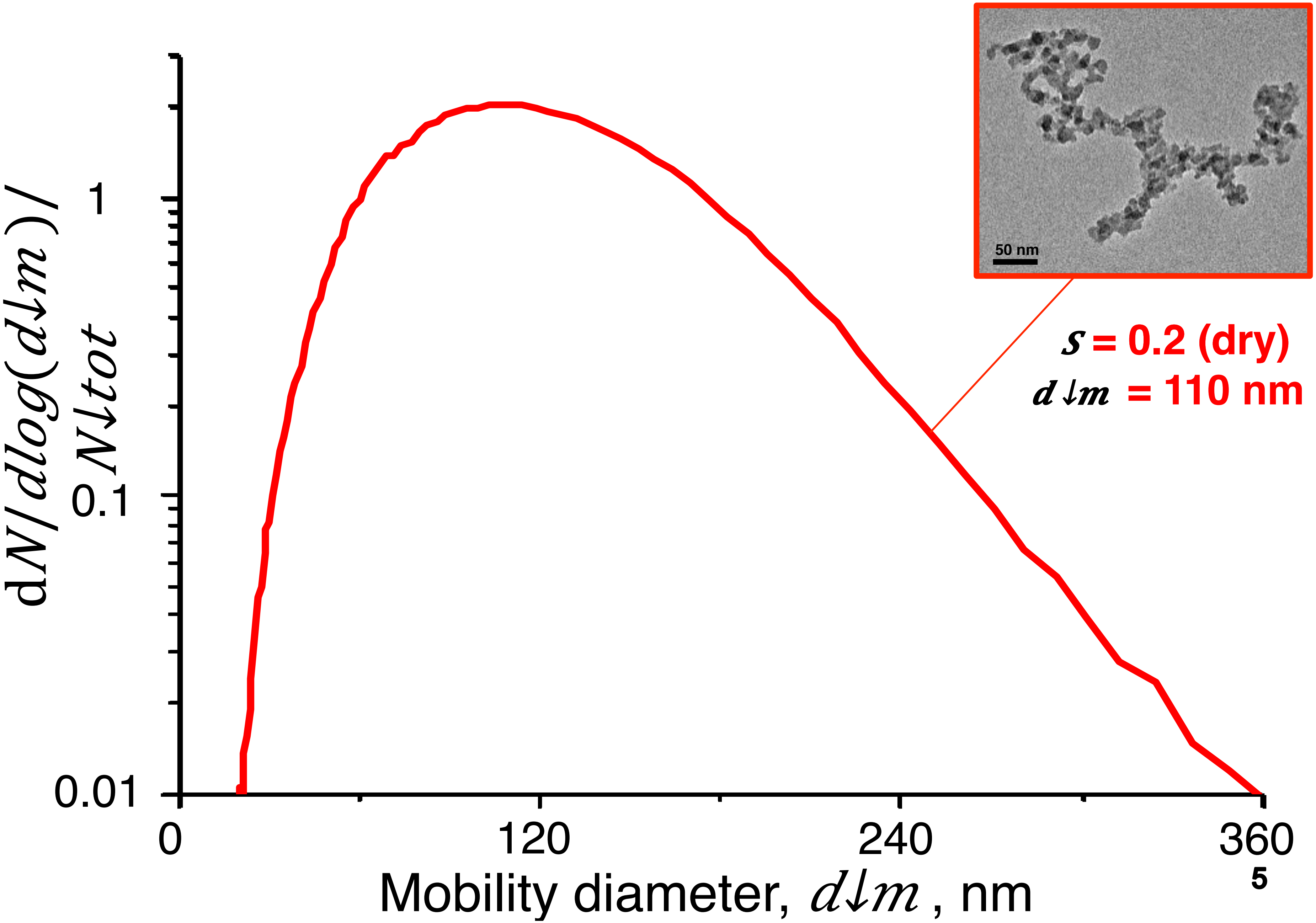
Primary particle diameter, d_p = 12 nm

Not affected by humidity!

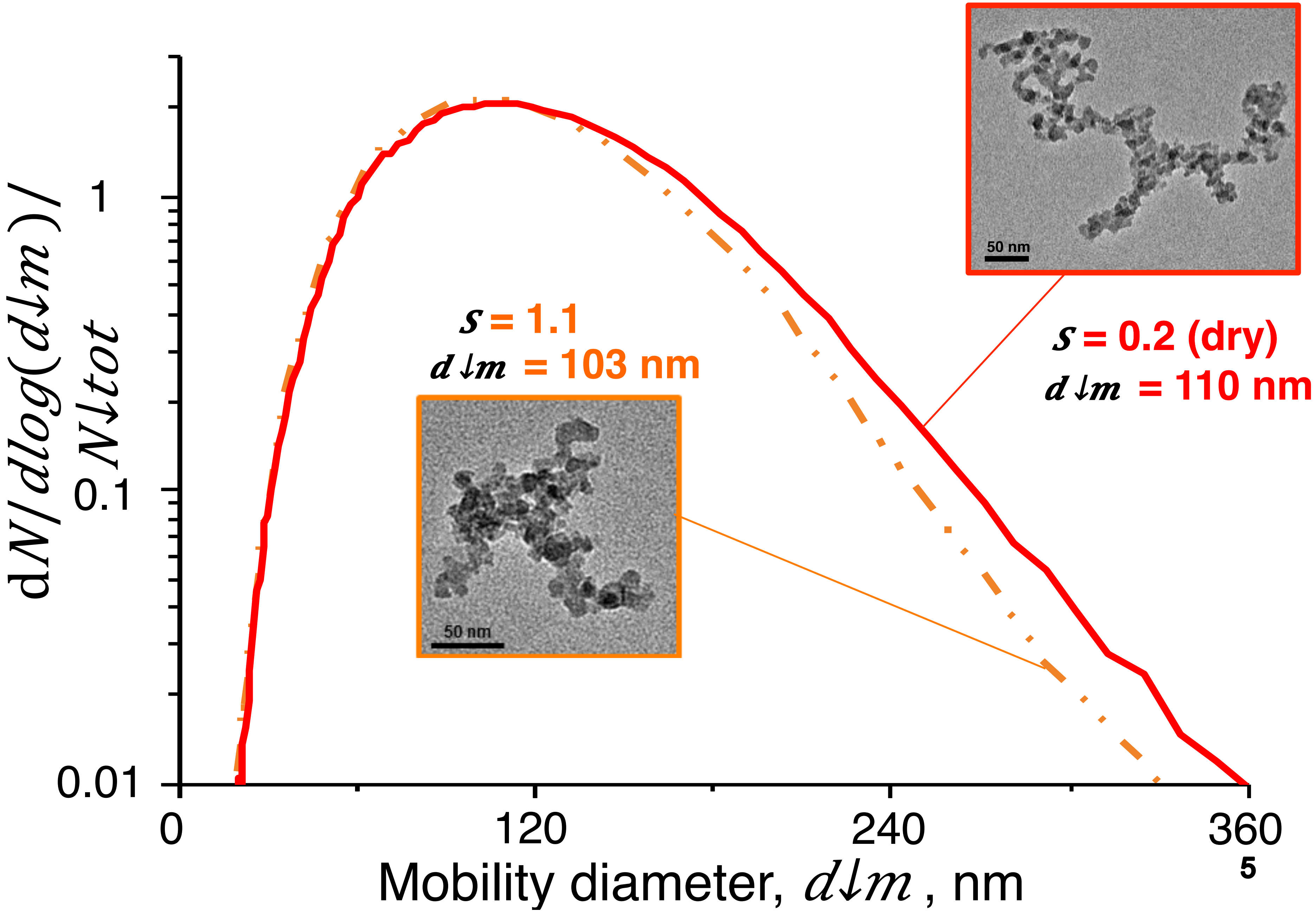
Restructuring dynamics of silica agglomerates



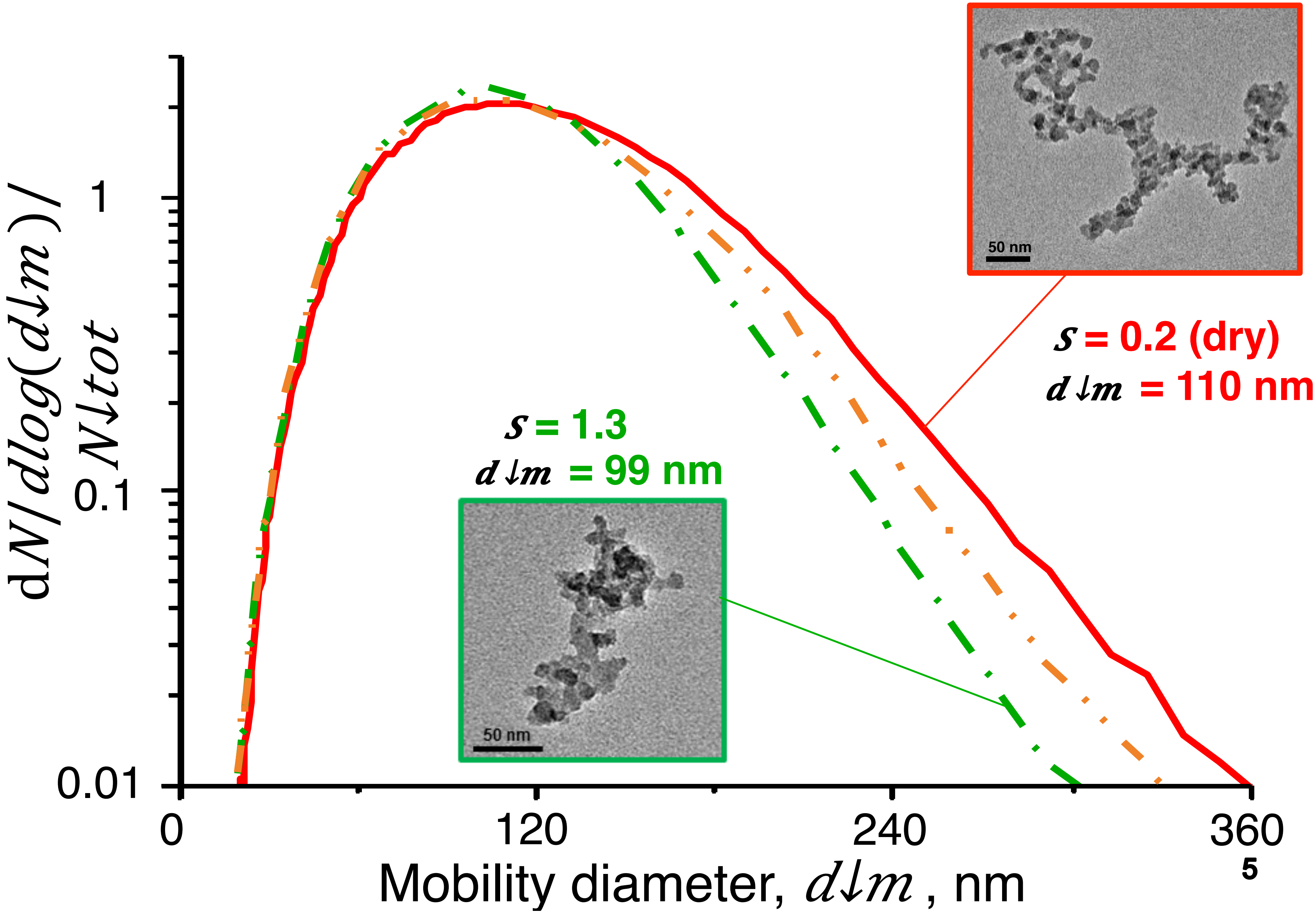
Restructuring dynamics of silica agglomerates



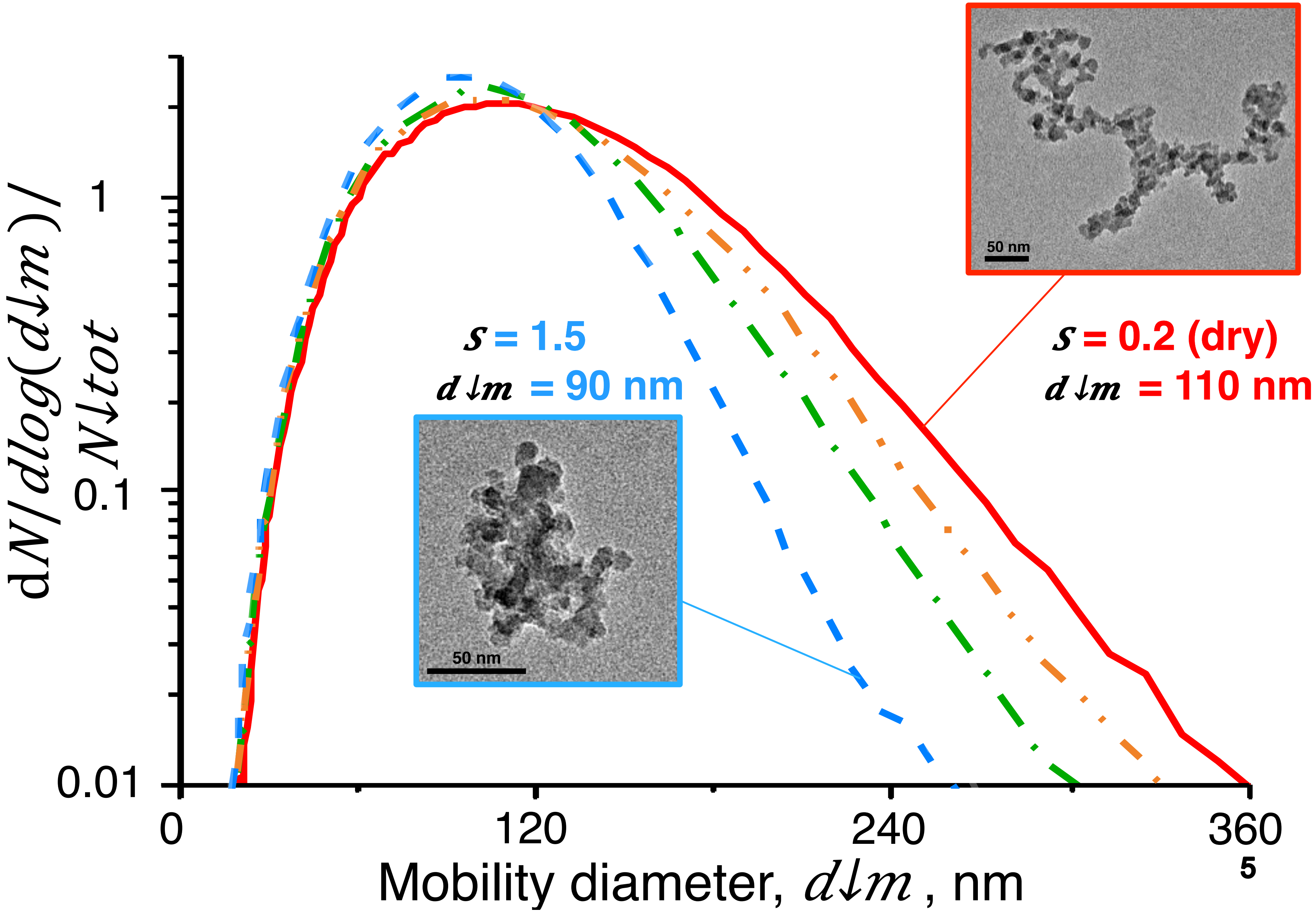
Restructuring dynamics of silica agglomerates



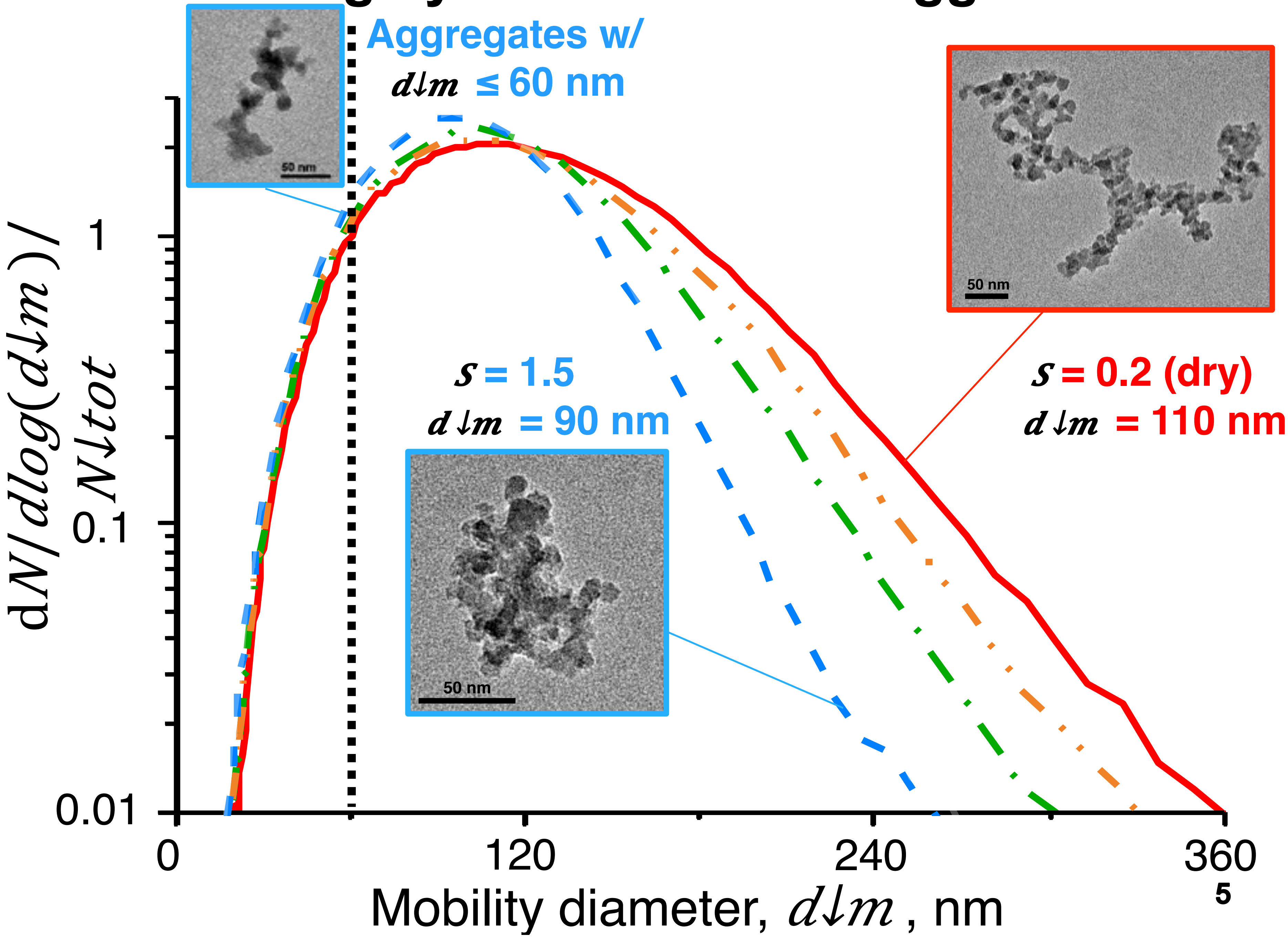
Restructuring dynamics of silica agglomerates



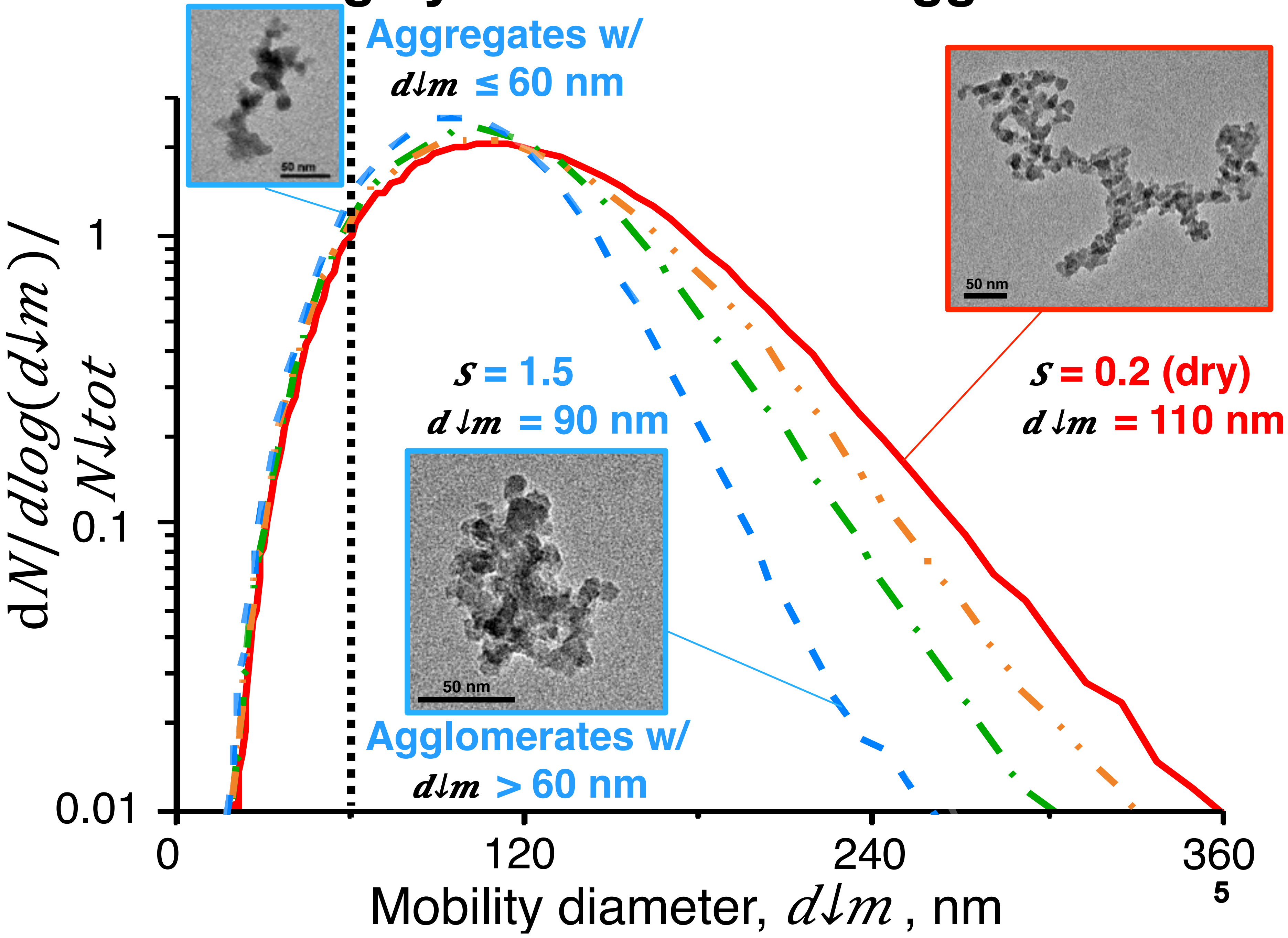
Restructuring dynamics of silica agglomerates



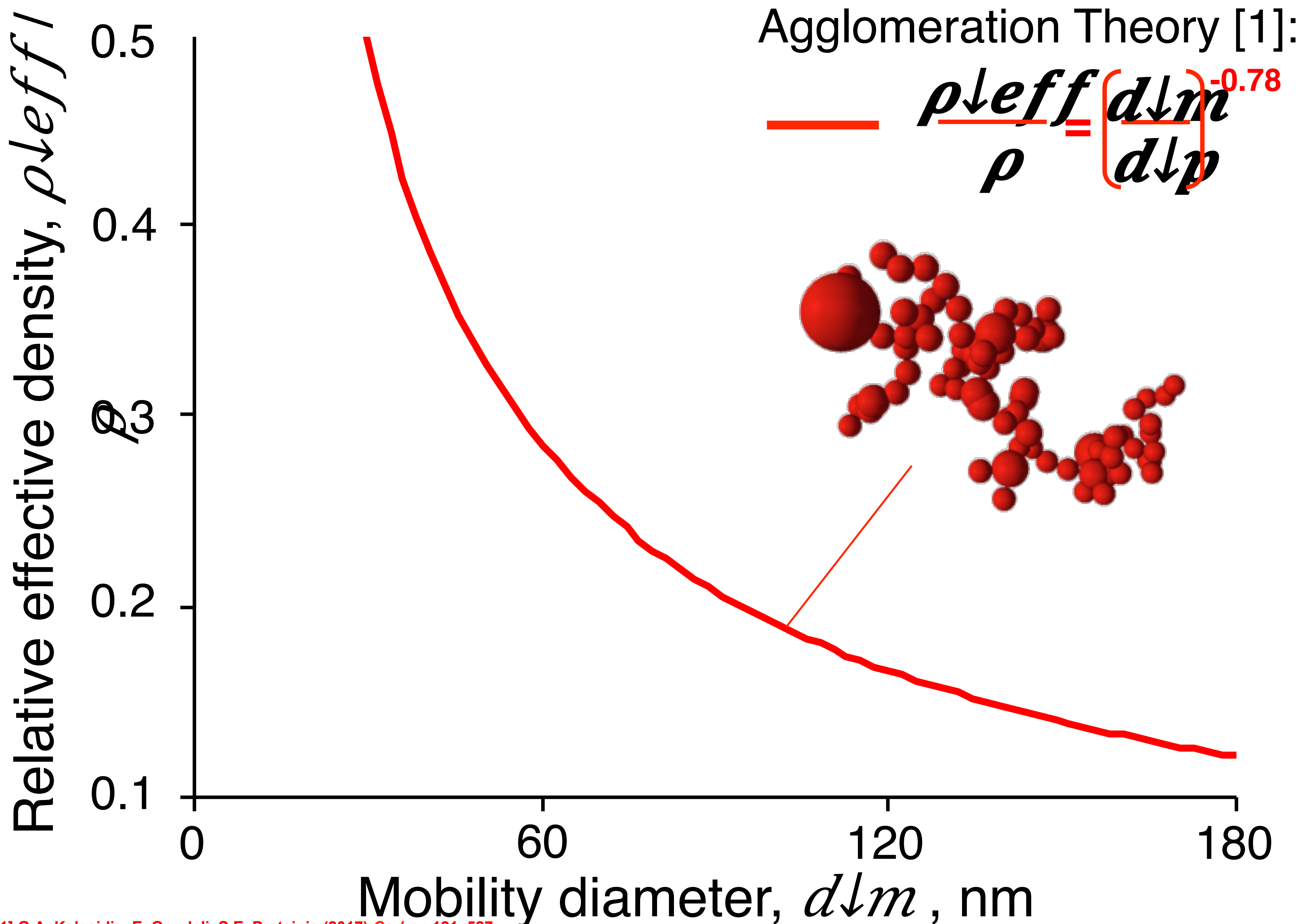
Restructuring dynamics of silica agglomerates



Restructuring dynamics of silica agglomerates

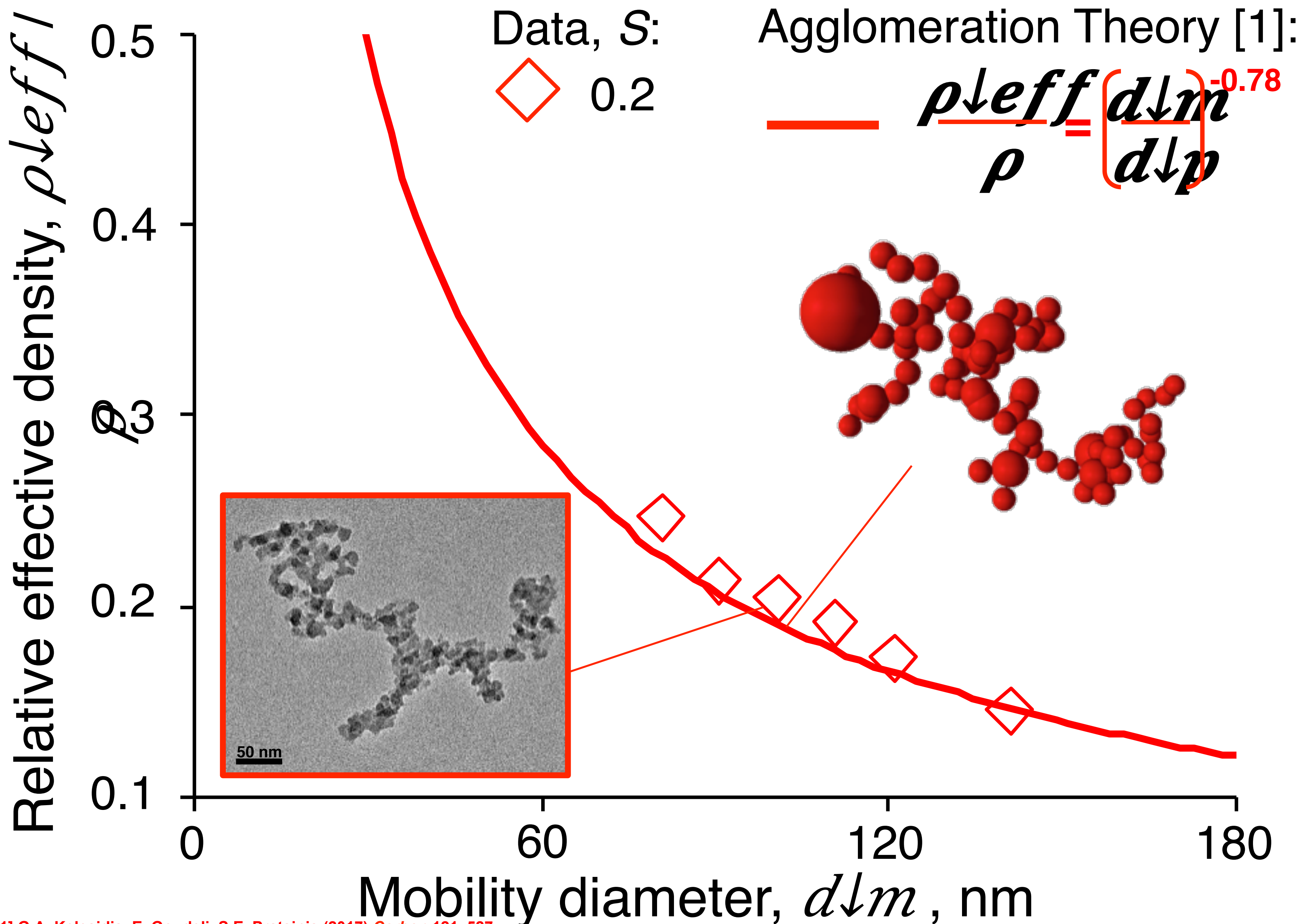


Impact of humidity on agglomerate morphology



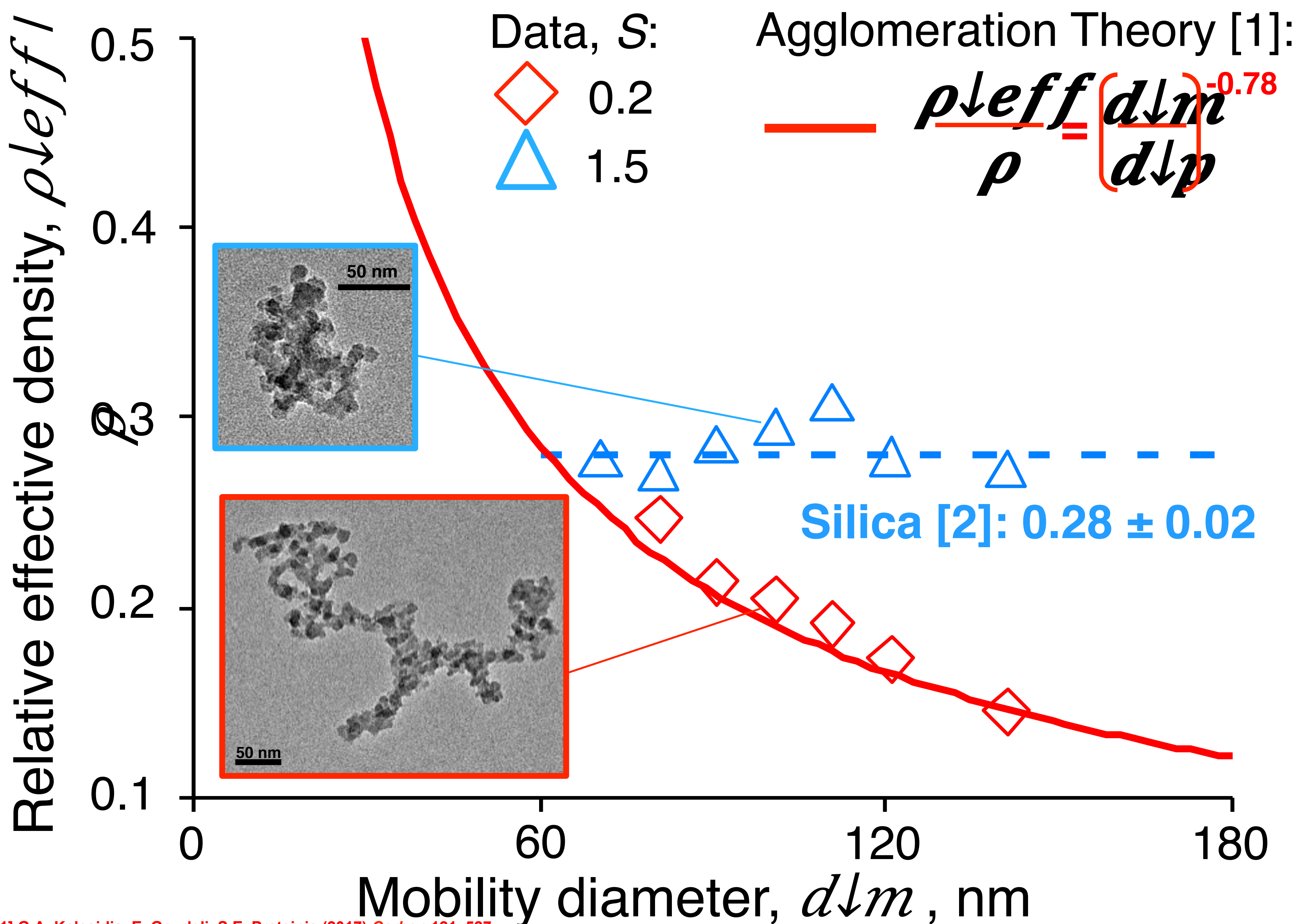
[1] G.A. Kelesidis, E. Goudeli, S.E. Pratsinis (2017) *Carbon* 121, 527.

Impact of humidity on agglomerate morphology



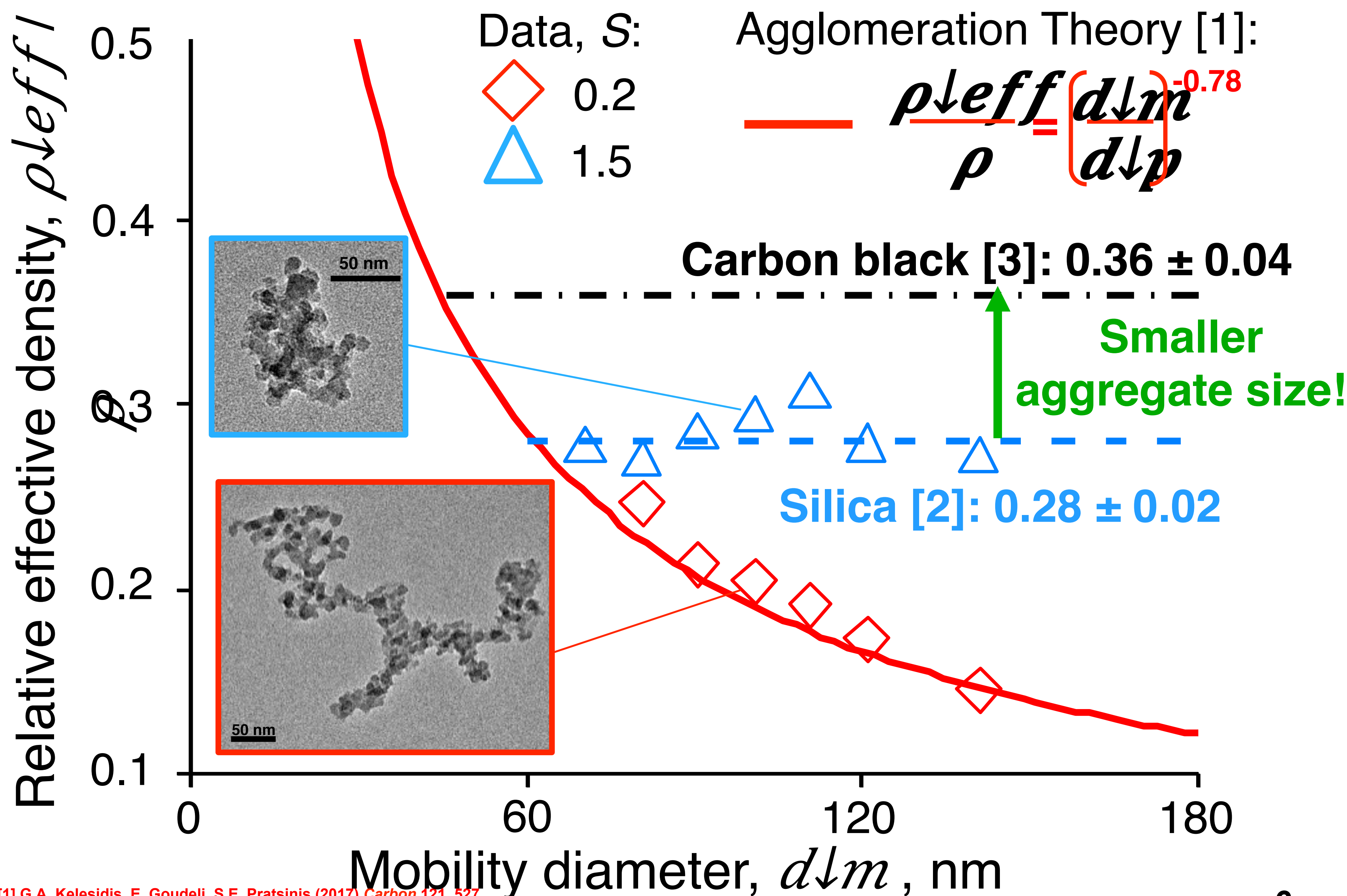
[1] G.A. Kelesidis, E. Goudeli, S.E. Pratsinis (2017) *Carbon* 121, 527.

Impact of humidity on agglomerate morphology



[1] G.A. Kelesidis, E. Goudeli, S.E. Pratsinis (2017) *Carbon* 121, 527.
[2] G.A. Kelesidis, F.M. Furrer, K. Wegner, S.E. Pratsinis (2018) *Langmuir* 34, 8532.

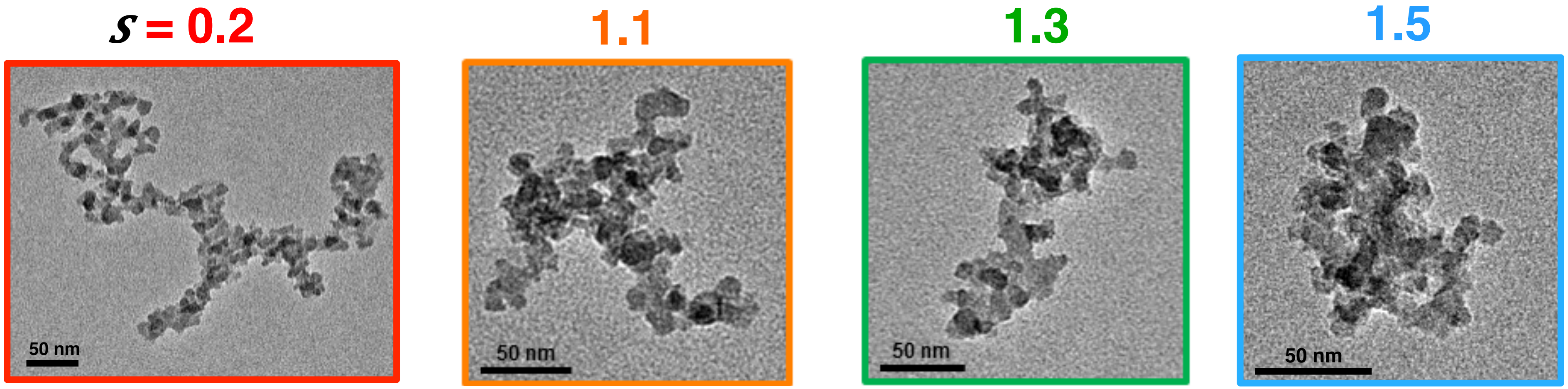
Impact of humidity on agglomerate morphology



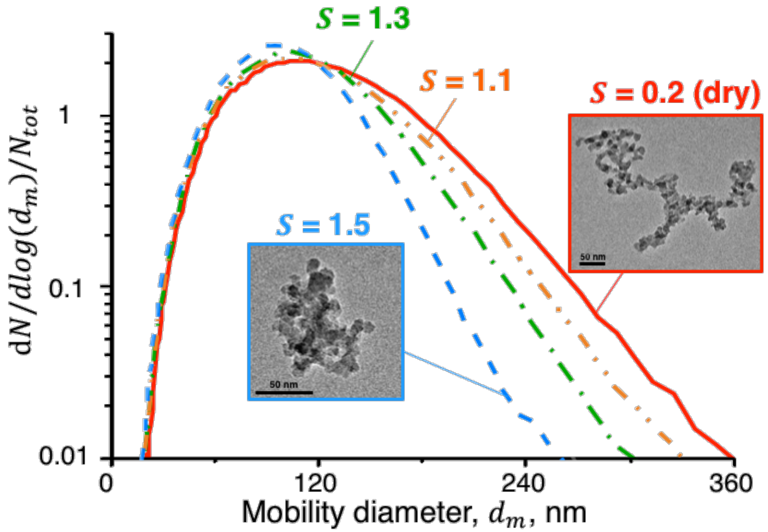
[1] G.A. Kelesidis, E. Goudeli, S.E. Pratsinis (2017) *Carbon* 121, 527.
[2] G.A. Kelesidis, F.M. Furrer, K. Wegner, S.E. Pratsinis (2018) *Langmuir* 34, 8532.
[3] C.D. Zangmeister, J.G. Radney, L.T. Dockery, J.T. Young, X.F. Ma, R.A. You, M.R. Zachariah (2014) *PNAS* 111, 9037.

Conclusions

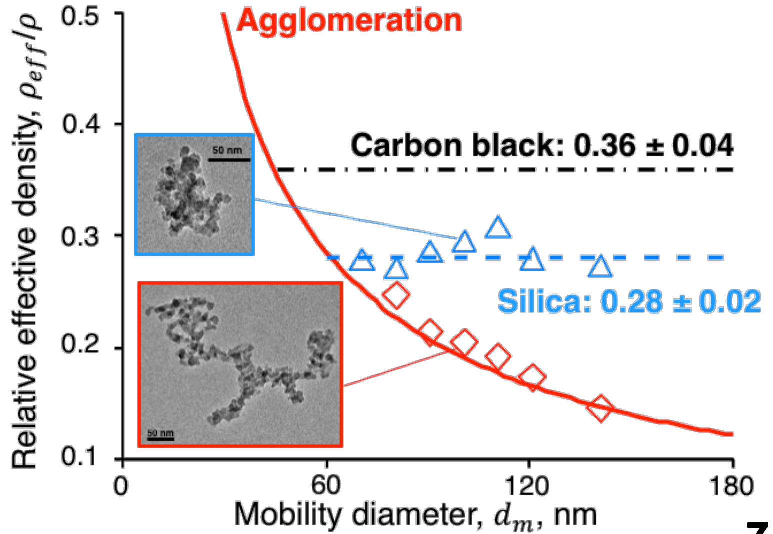
- Nanoparticle Processing & Storage w/ $S > 1.3$ changes drastically their agglomerate morphology!



- Up to 20 % d_m reduction.



- Unique ρ_{eff} distribution!

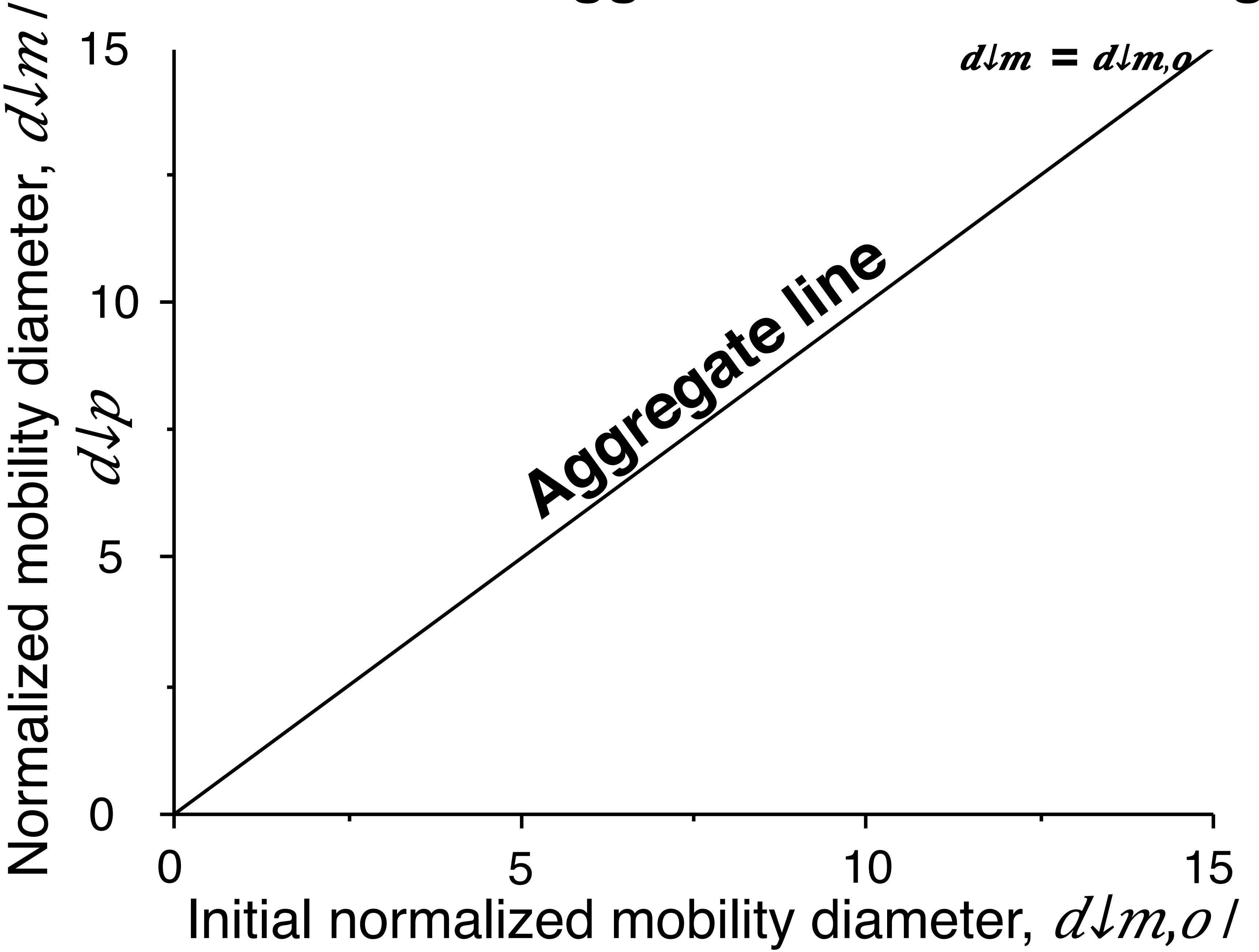


[1] G. A. Kelesidis, F.M. Furrer, K. Wegner, S.E. Pratsinis (2018) *Langmuir* **34**, 8532.

Thank you for your attention!

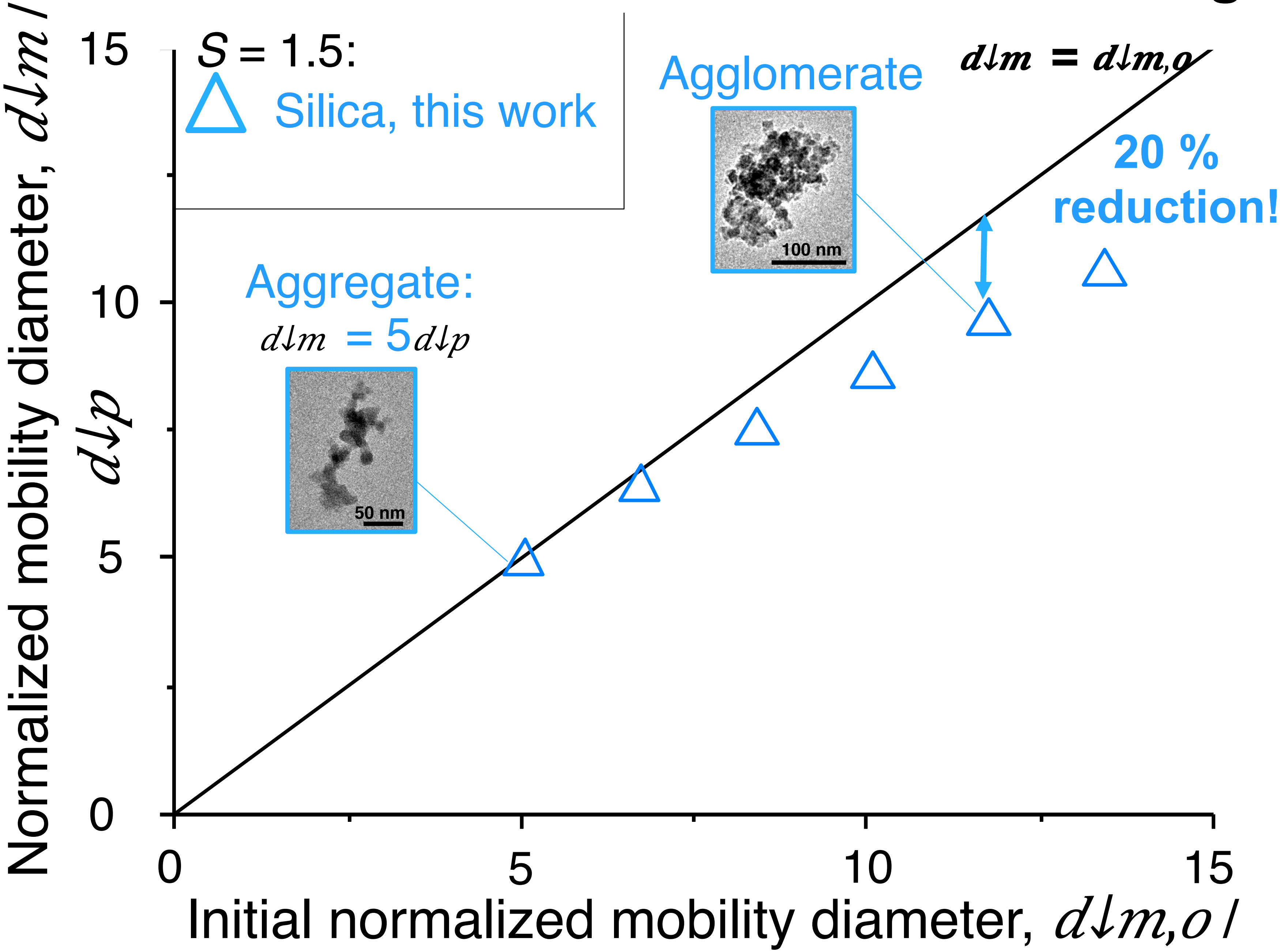
Back-up Slides

Silica vs Soot agglomerate restructuring



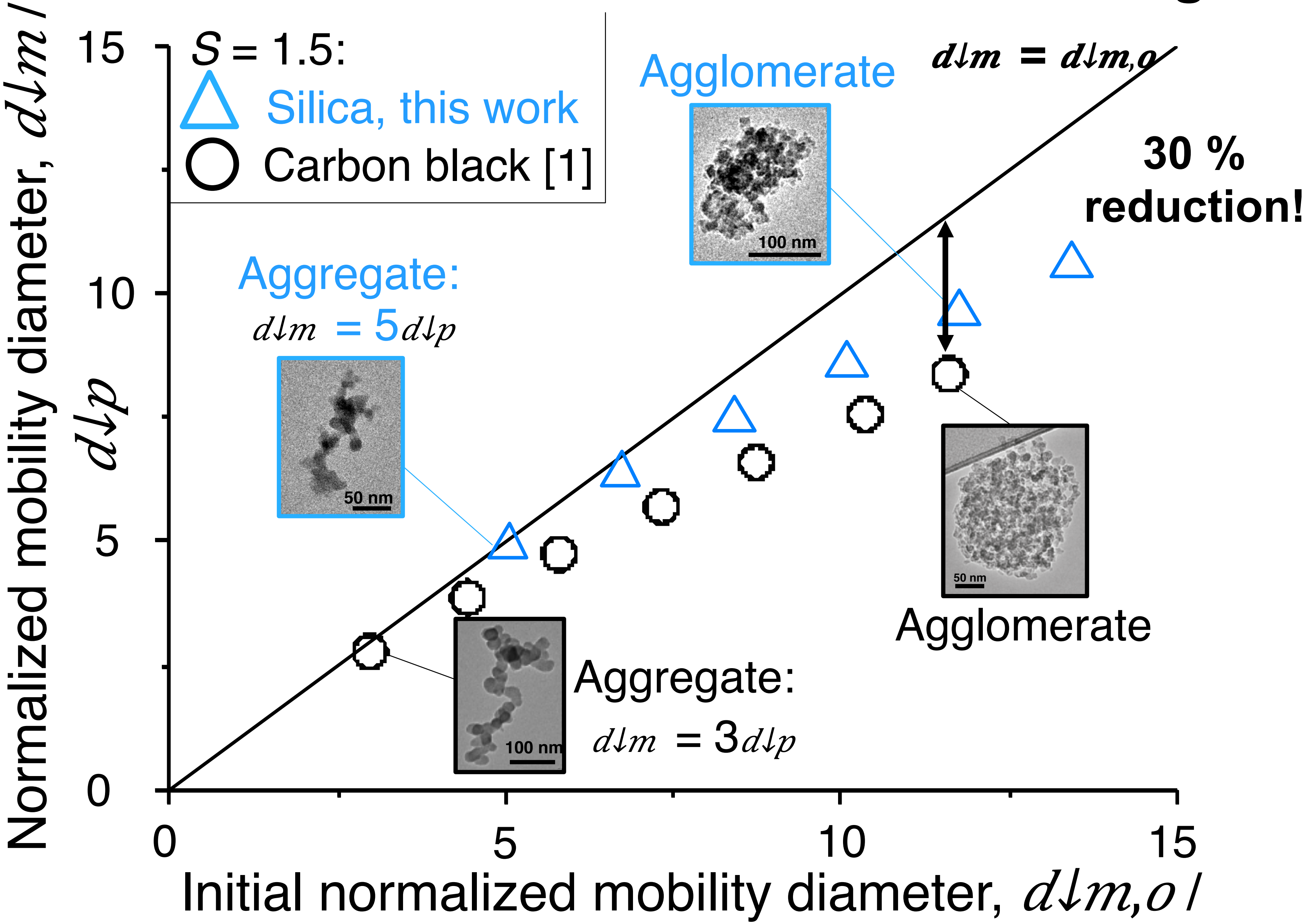
[1] X.F. Ma, C.D. Zangmeister, J. Gigault, G.W. Mulholland, .R. Zachariah (2013), *J. Aerosol Sci.* 66 209-219.

Silica Vs Carbon black Restructuring



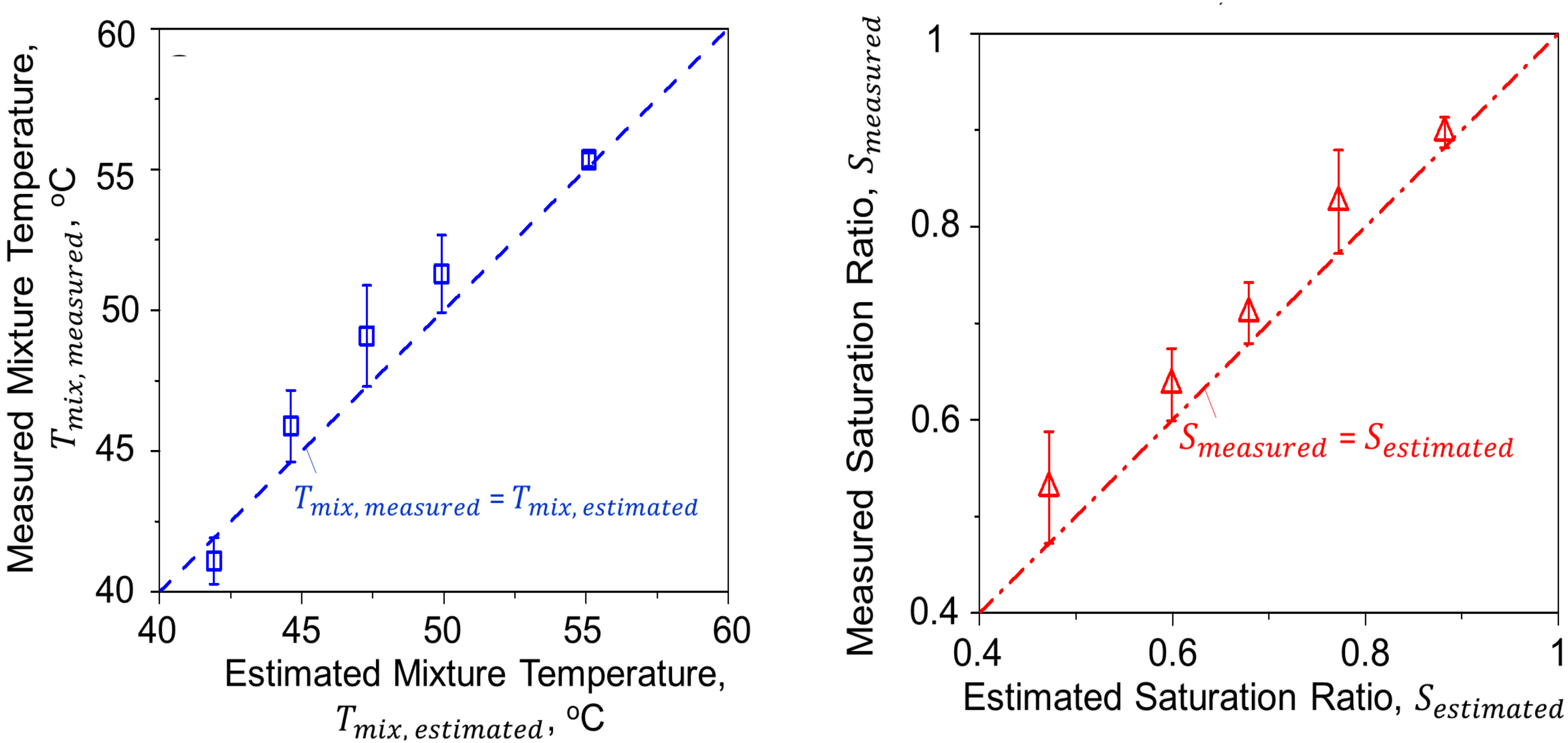
[1] X.F. Ma, C.D. Zangmeister, J. Gigault, G.W. Mulholland, M.R. Zachariah (2013) *J. Aerosol Sci.* 66 209-219.

Silica Vs Carbon black Restructuring

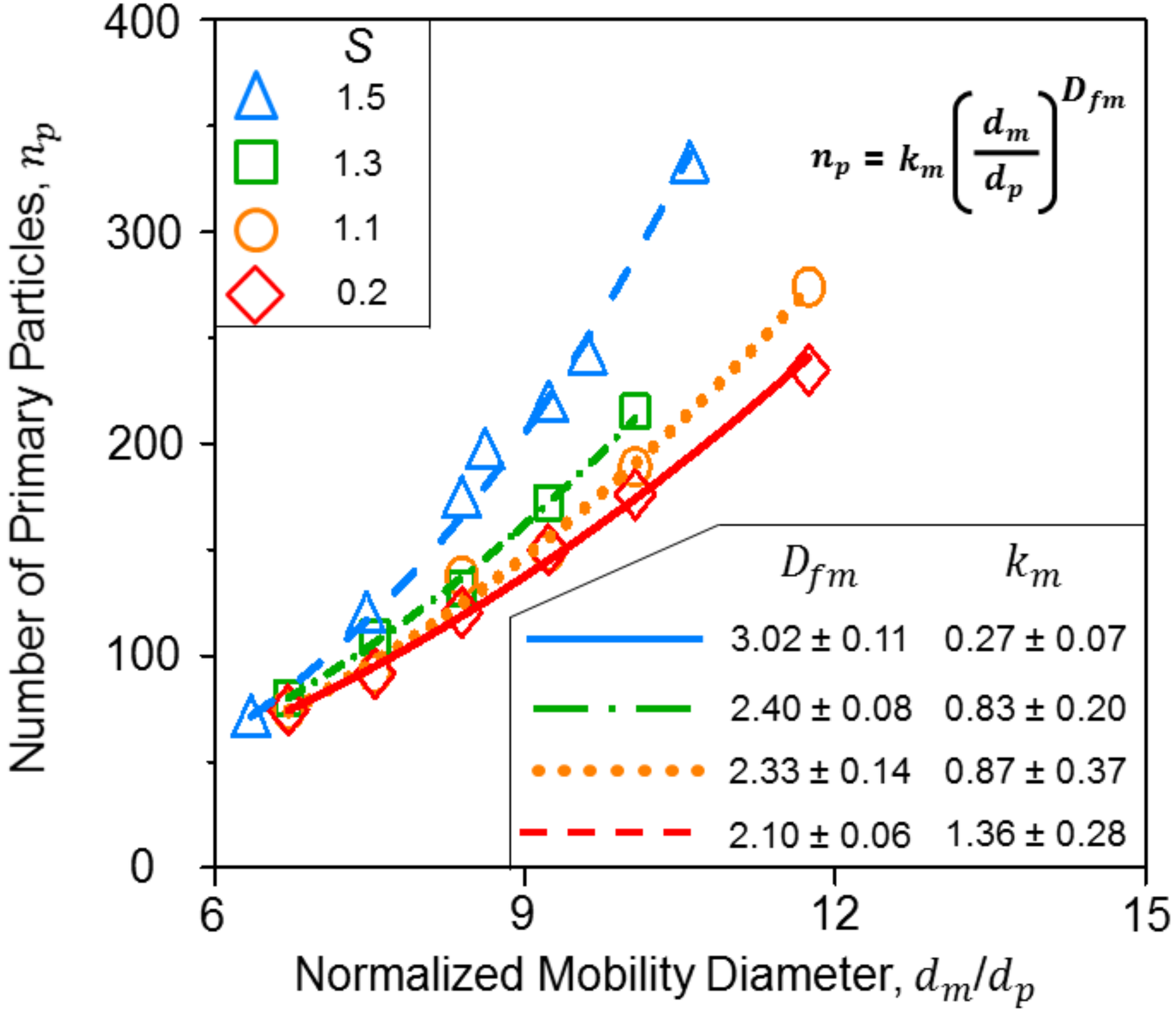


[1] X.F. Ma, C.D. Zangmeister, J. Gigault, G.W. Mulholland, M.R. Zachariah (2013) J. Aerosol Sci. 66 209-219.

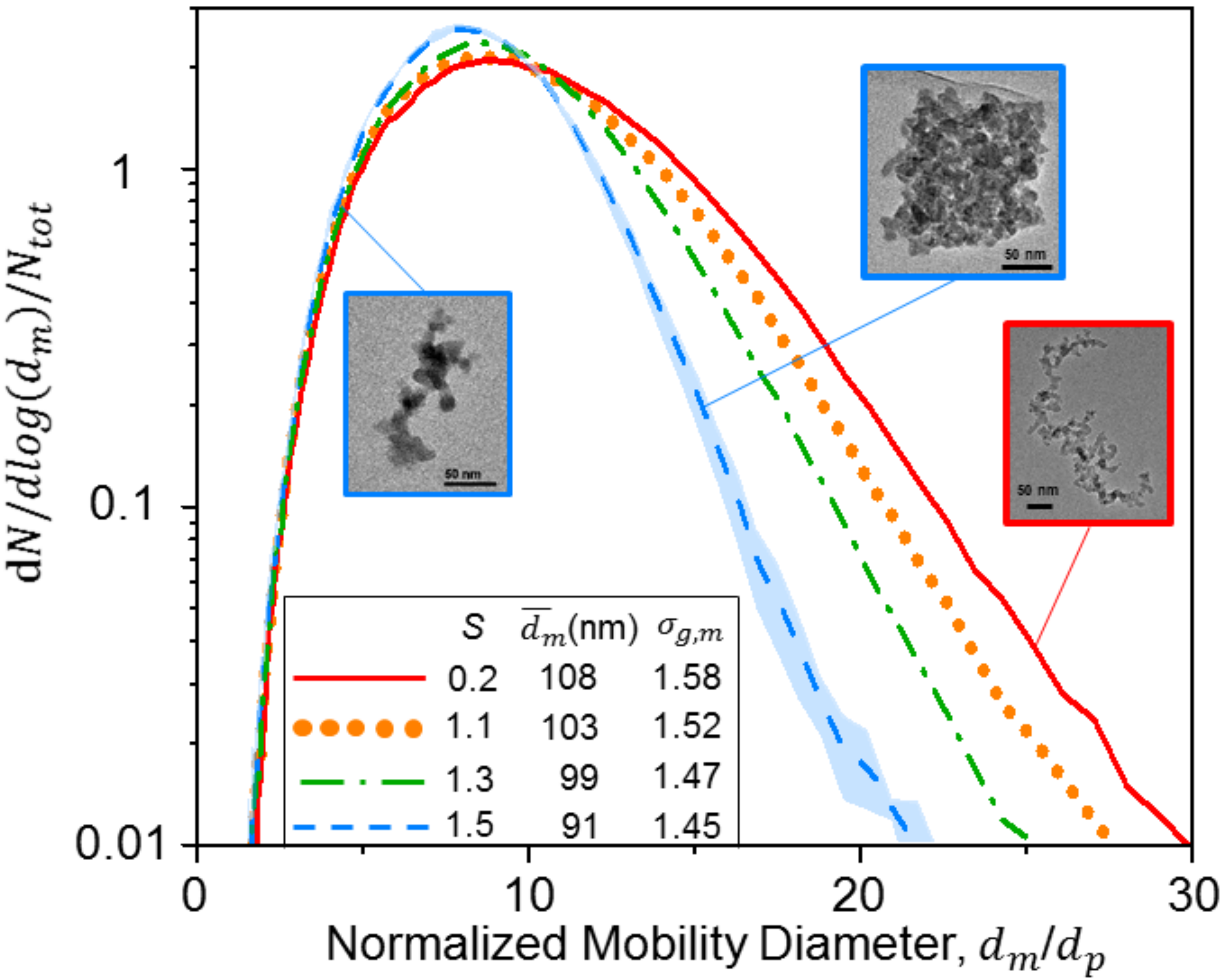
Validation of *S* calculation



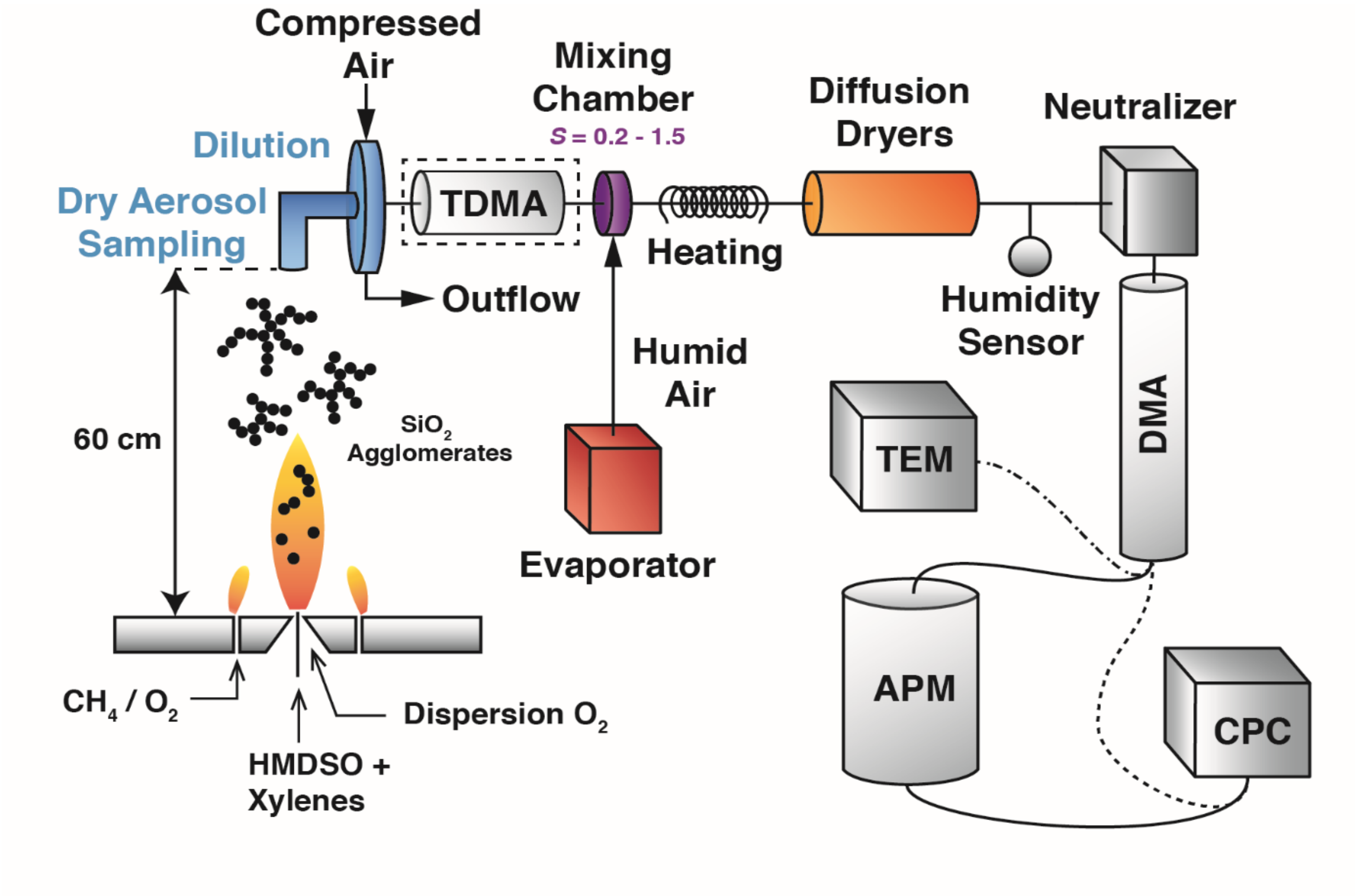
Mass-mobility relationship



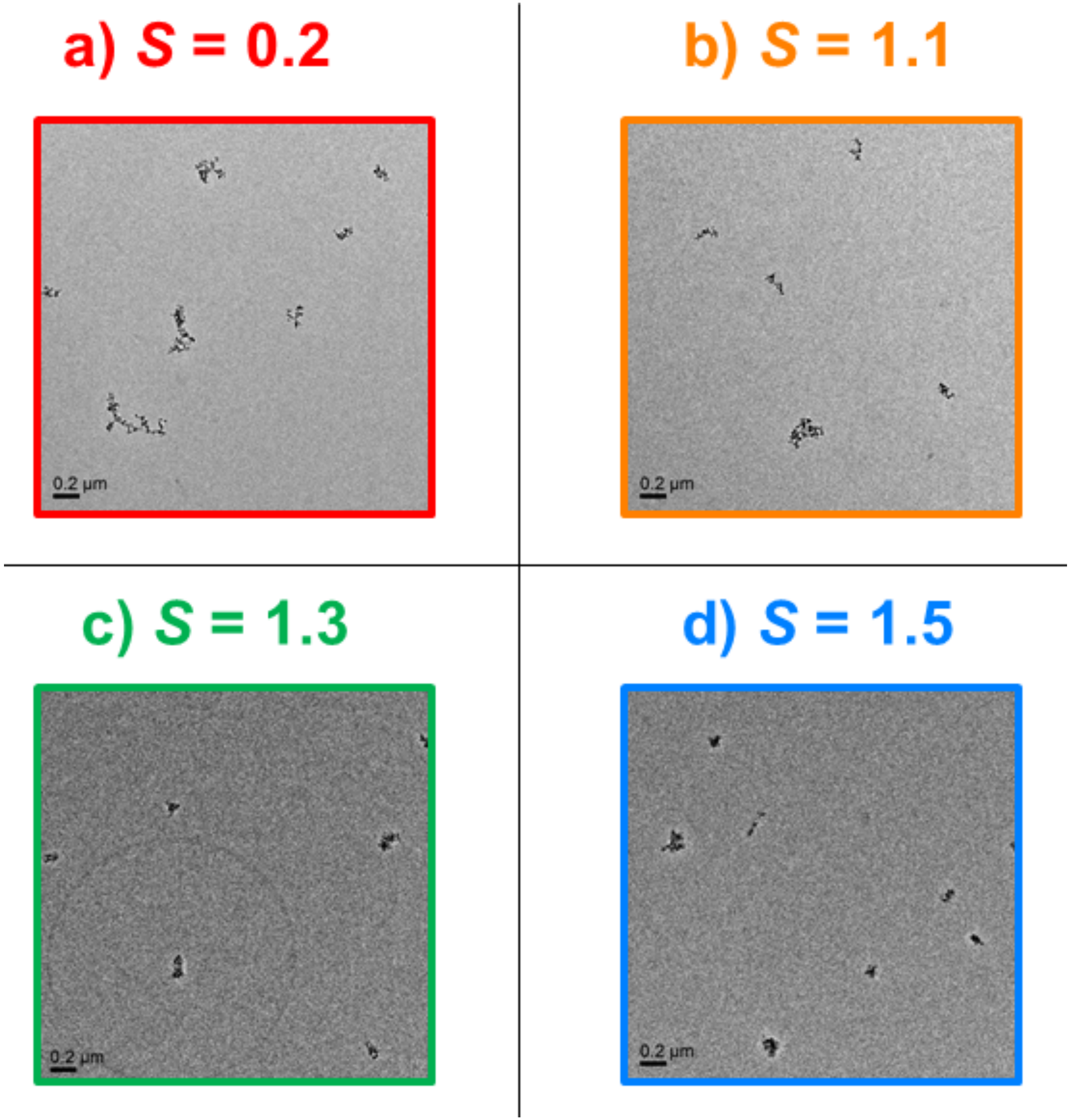
Evolution of mobility size distribution



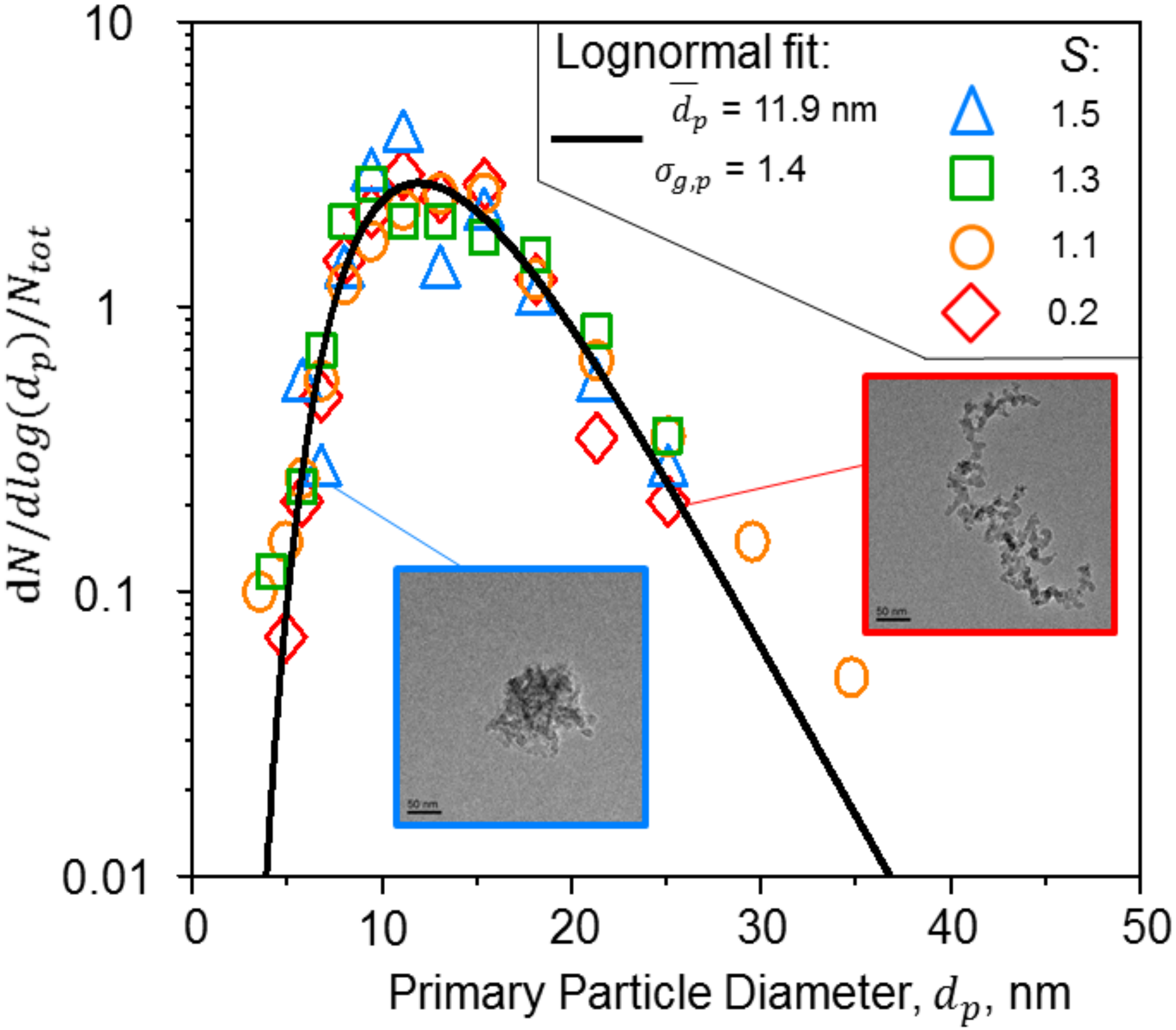
Experimental Set Up

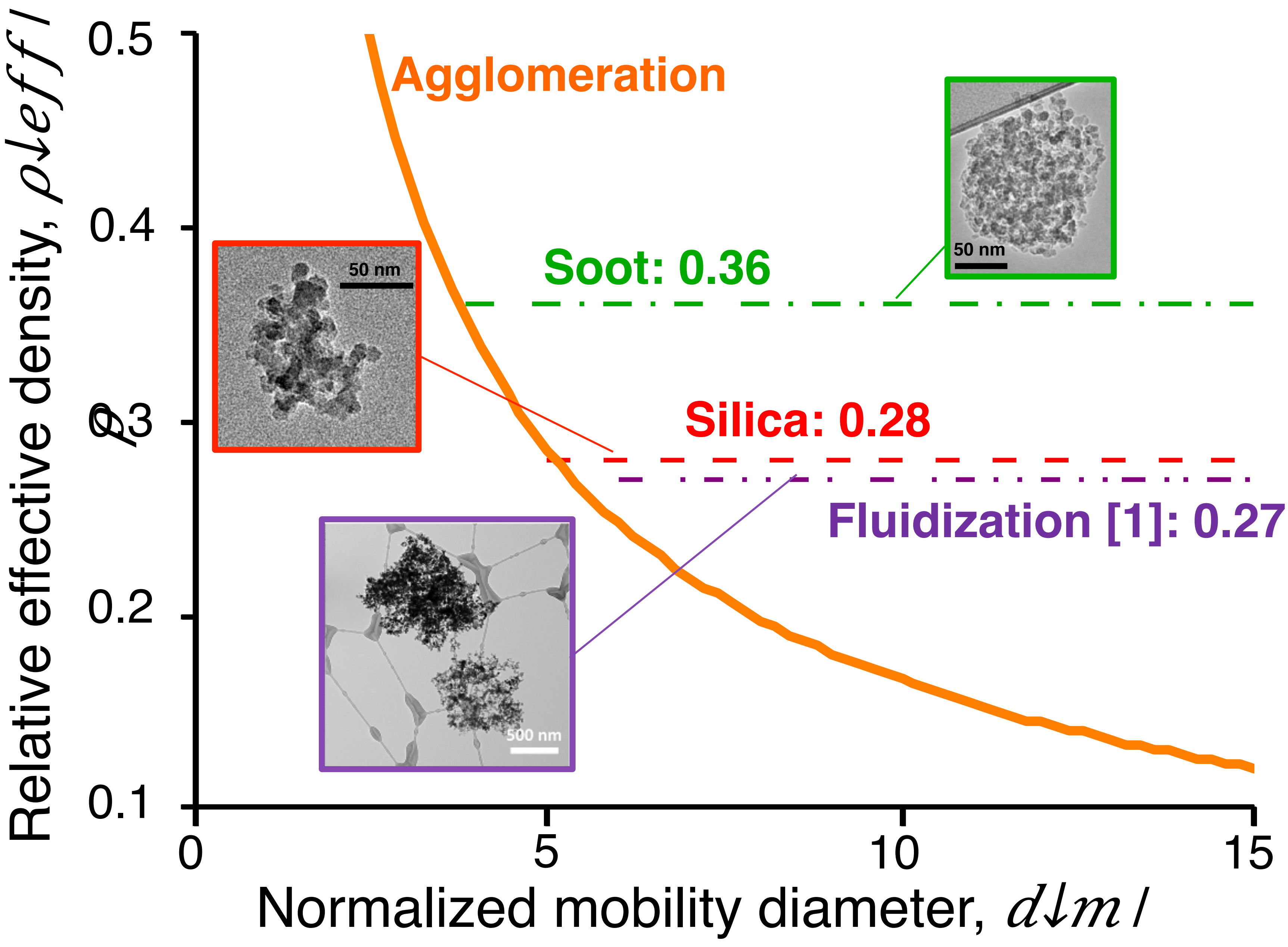


Microscopy images



Primary particle size distribution





[1] A. Fabre, T. Steur, W.G. Bouwman, M.T. Kreutzer, J.R. van Ommen (2016) *J. Phys. Chem. C* **120**, 20446.