From agglomerates to aggregates by sintering – coalescence

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Swiss Commission for Technology and Innovation

Aerosol-made nanostructured materials

Tires (~30 wt%)

Carbon Black

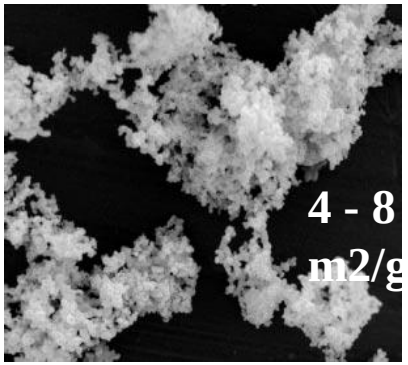
Paints

Courtesy of Dupont

TiO_2

Optical fibers

Inks



Courtesy of Inco

Ni for batteries

ZnO as vulcanizing agent

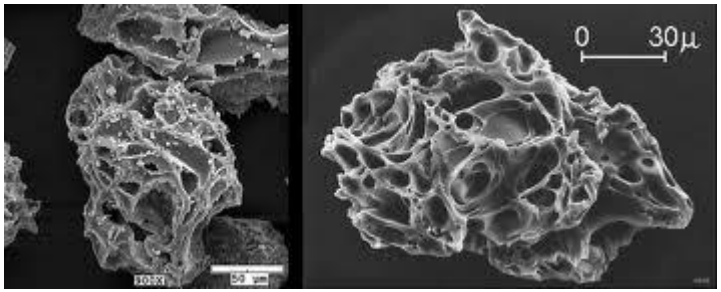
Courtesy of Umicore

Courtesy of Cabot

SiO_2

Flowing aid

Volcanic Aerosols

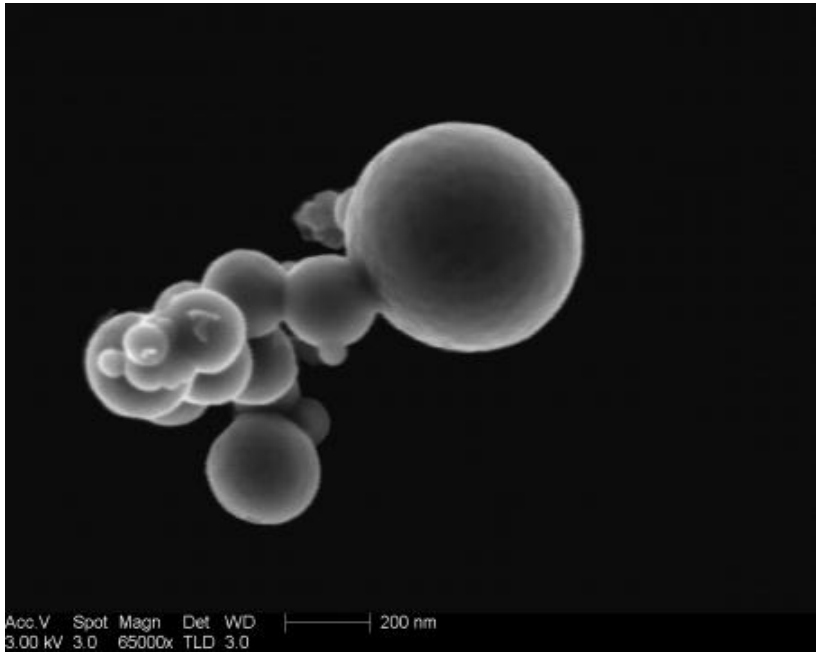


images by Pavel Izbekov and Jill Shipman, Alaska Volcano Observatory / University of Alaska Fairbanks, Geophysical Institute. U.S. Geological Survey.

Exhaust aerosols

Iceland, April, 2010

Power Plant Ply ash

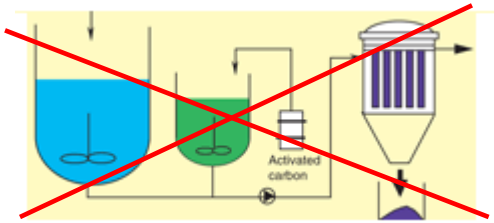


AluminoSilicate, by Esther Coz of CIEMAT/IDAEA-CSIC at RJ Lee Group, Inc.

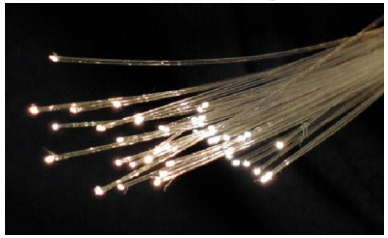
Advantages of aerosol synthesis of materials

Aerosol-based Technologies in Nanoscale Manufacturing: from Functional Materials to Devices through Core Chemical Engineering, *AIChE J.* 56, 3028-3035 (2010)

1. No liquid by-products

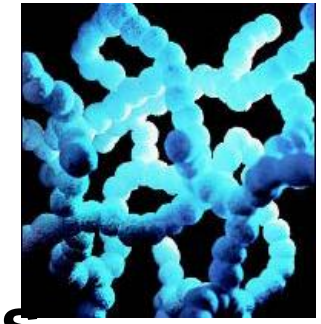


2. Easier particle collection from gases than liquids



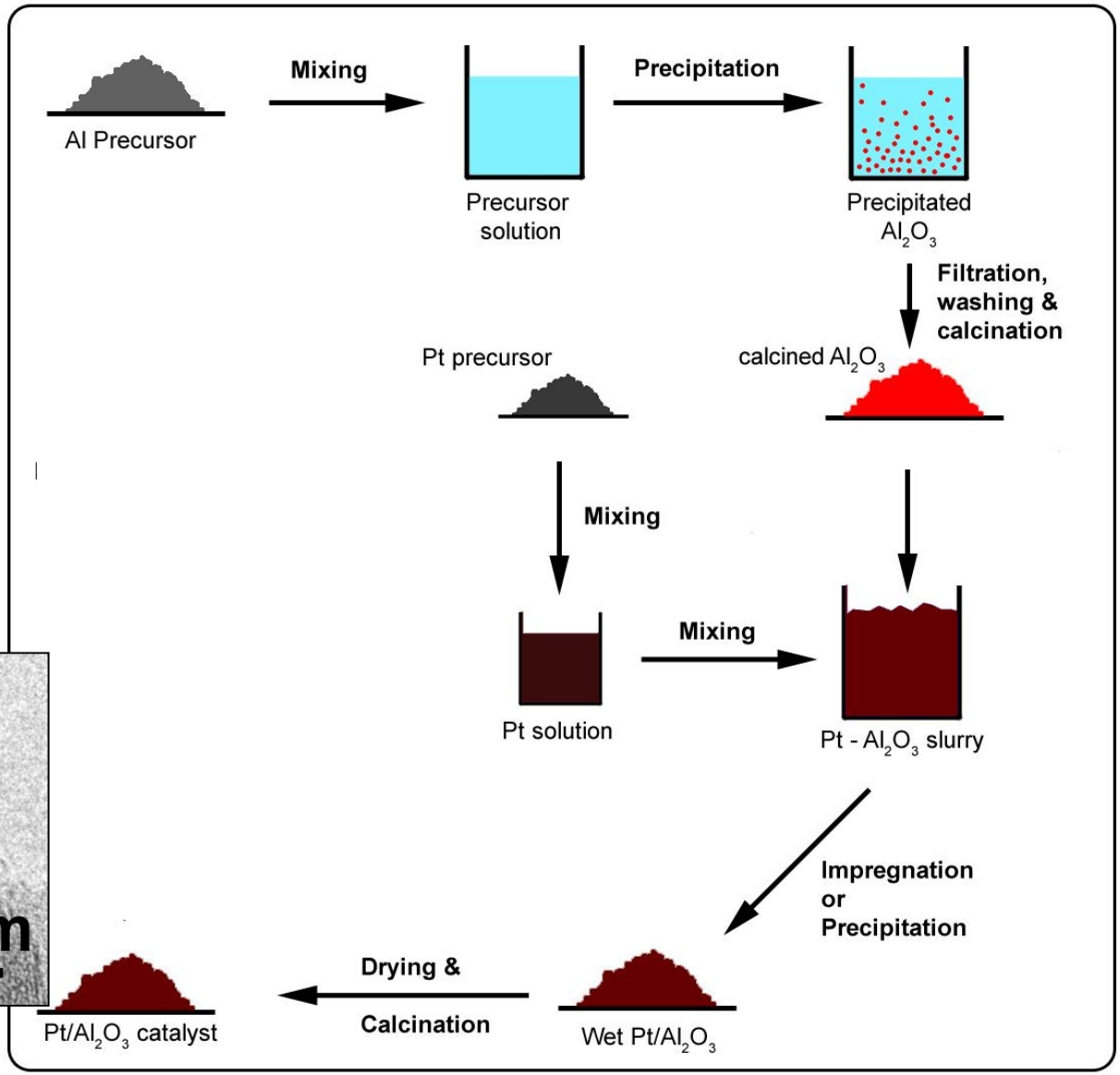
3. High purity products

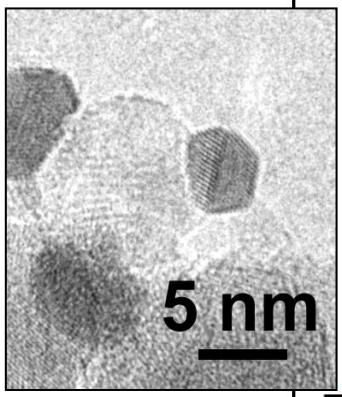
4. Special morphology facilitating reactant & product transport to & from the catalyst **surface**



5. Efficiency: Few and fast unit operations

Synthesis of heterogeneous catalysts





1. Process Efficiency

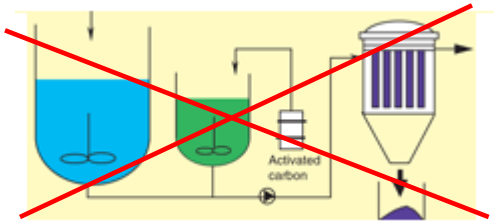
2. Novel (e.g. metastable) materials

Aerosol flame synthesis of catalysts: a Review, *Adv. Powder Technol.*, 17, 457-80 (2006).

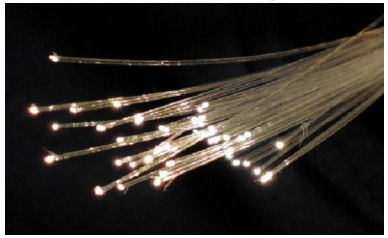
Advantages of aerosols in materials synthesis

Aerosol-based Technologies in Nanoscale Manufacturing: from Functional Materials to Devices through Core Chemical Engineering, *AIChE J.* 56, 3028-3035 (2010)

1. No liquid by-products



2. Easier particle collection from gases than liquids



3. High purity products

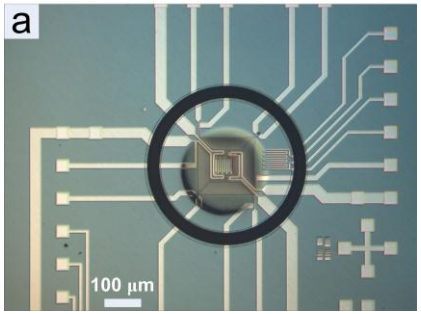
4. Special morphology (fillers in composites)

5. Efficiency: Few and fast unit operations

6. Unique metastable phases by rapid heating-cooling

7. Transport (e.g. diffusion) in gases is better understood facilitating process design from **first principles**.

Sensors

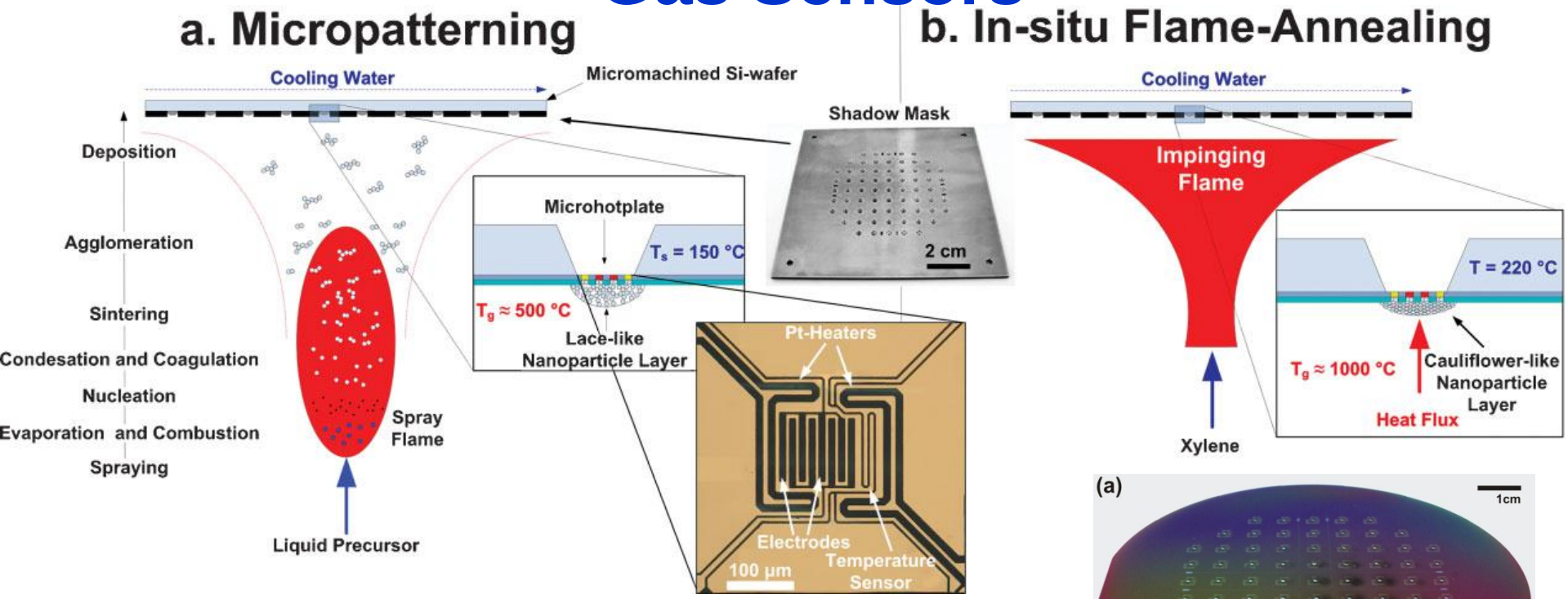


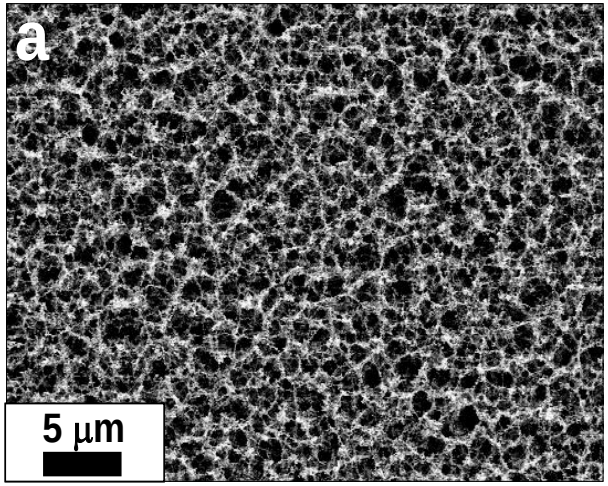
Catalysts

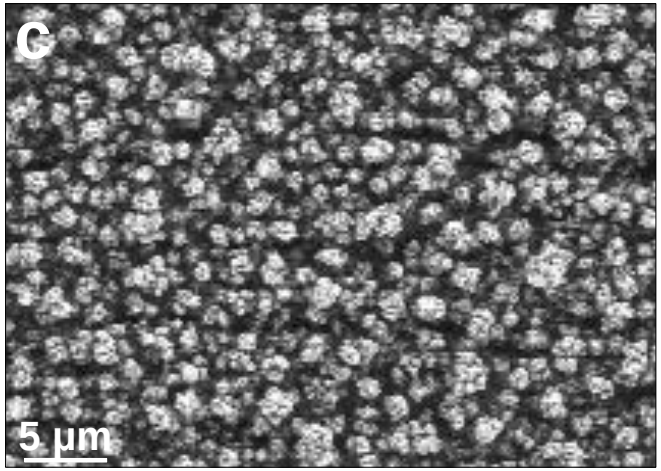
some future aerosol - made materials

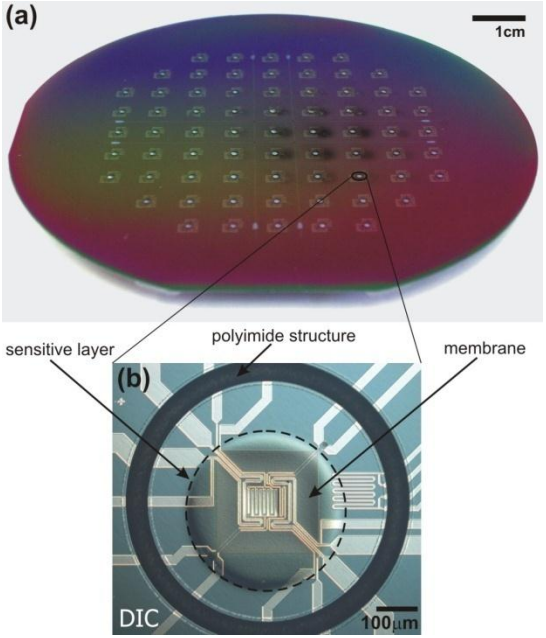
Flame aerosol synthesis of smart nanostructured materials *J. Mater. Chem.* **17,** 4743 - 56 (2007)

Gas Sensors





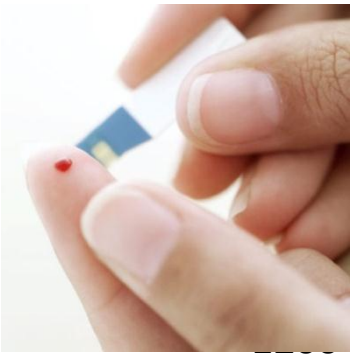


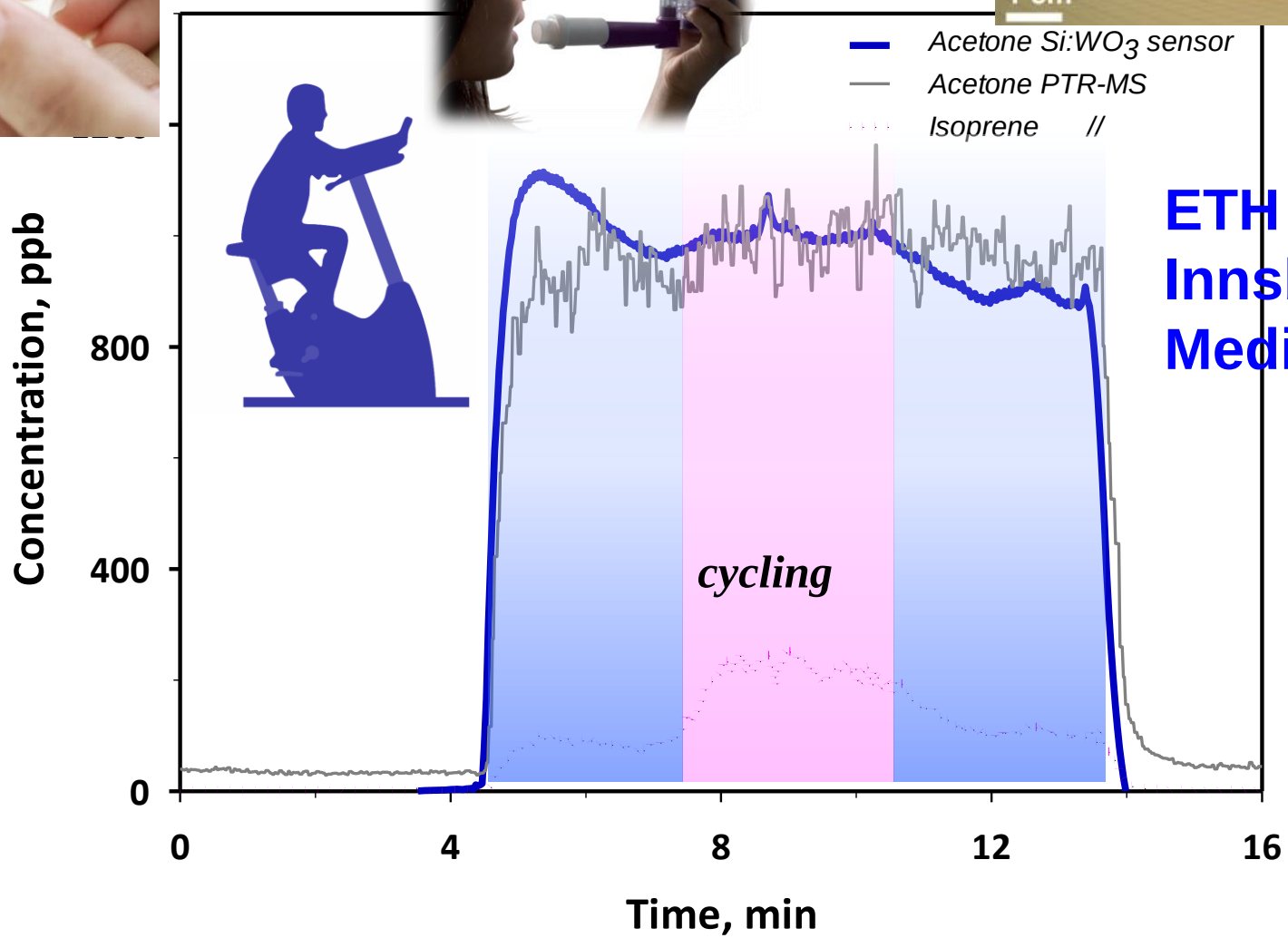


Micropatterning Layers by Flame Aerosol Deposition - Annealing *Adv. Mater.*, **20**, 3005-10 (2008).

Wafer-level flame-spray-pyrolysis deposition of gas-sensitive layers on microsensors *J. Micromech. Microeng.* 18, 035040 (2008).

Diabetes monitoring by acetone breath analysis





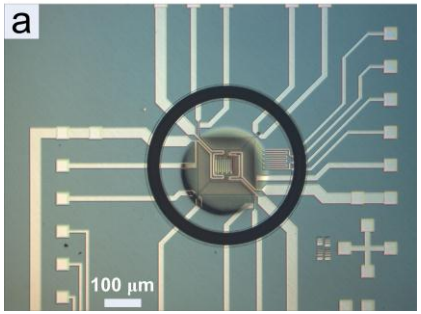
ETH Zurich & Innsbruck Medical Univ.

Acetone in the human breath by portable Si:WO_3 gas sensors, *Anal. Chem. Acta*, in review (2012)

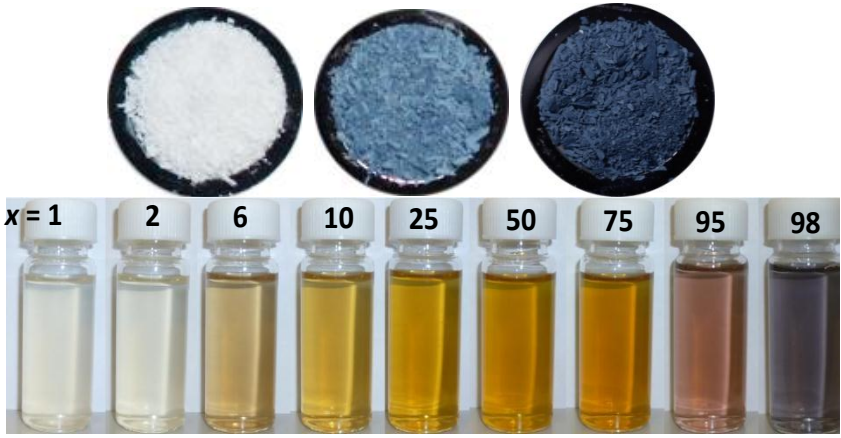
some future aerosol - made materials

Dental fillers & bone replacement

Sensors



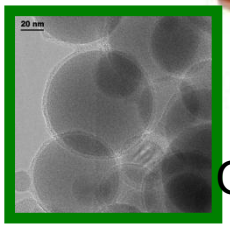
Advanced Pigments



Catalysts

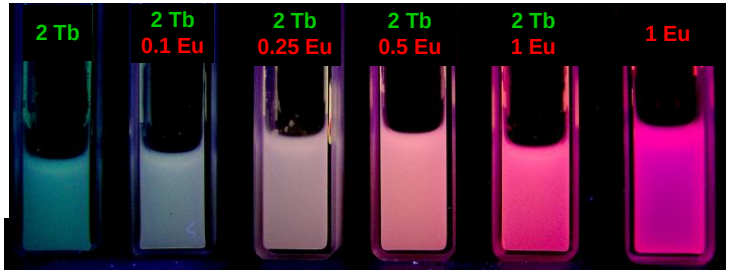
Nutrition

Batteries

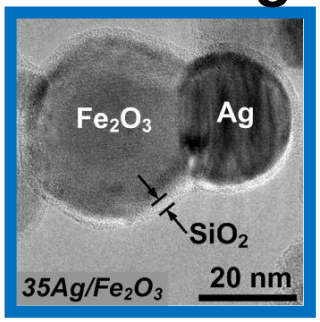


C-$LiFePO_4$

Phosphors

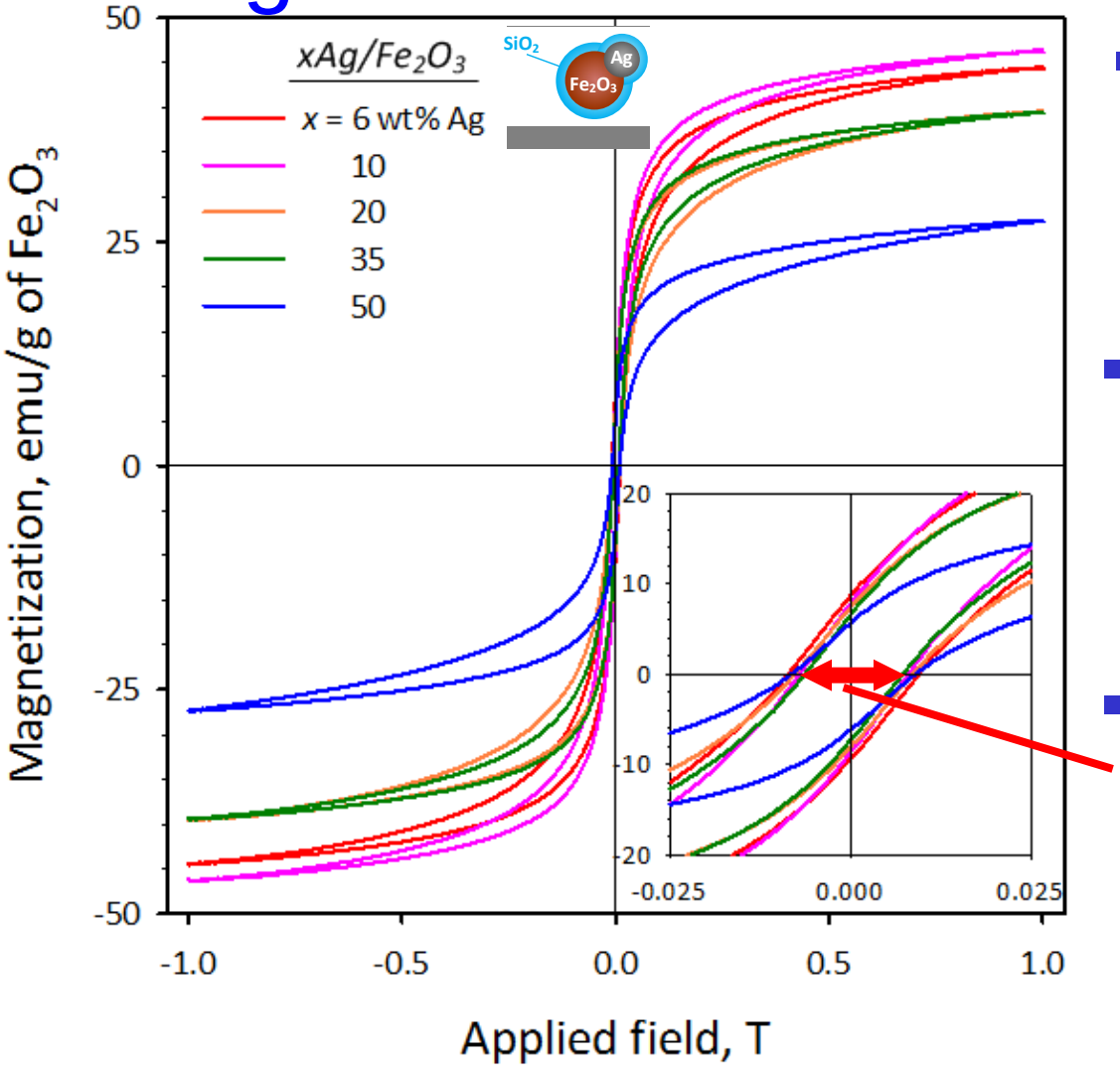


SPION/Ag



Flame aerosol synthesis of smart nanostructured materials *J. Mater. Chem.* **17,** 4743 - 56 (2007)

Magnetization of silica-coated Ag/Fe_2O_3



- **Comparable magnetization for pure flame-made Fe_2O_3[1]**
- **Lower magnetization for *x* = 50 wt% Ag**
  - **Higher α-Fe_2O_3 content**
- **Near superparamagnetic behavior**

[1] Teleki, Suter, Kidambi, Ergeneman, Krumeich, Nelson, Pratsinis, *Chem. Mater.* 21, 2094 (2009).

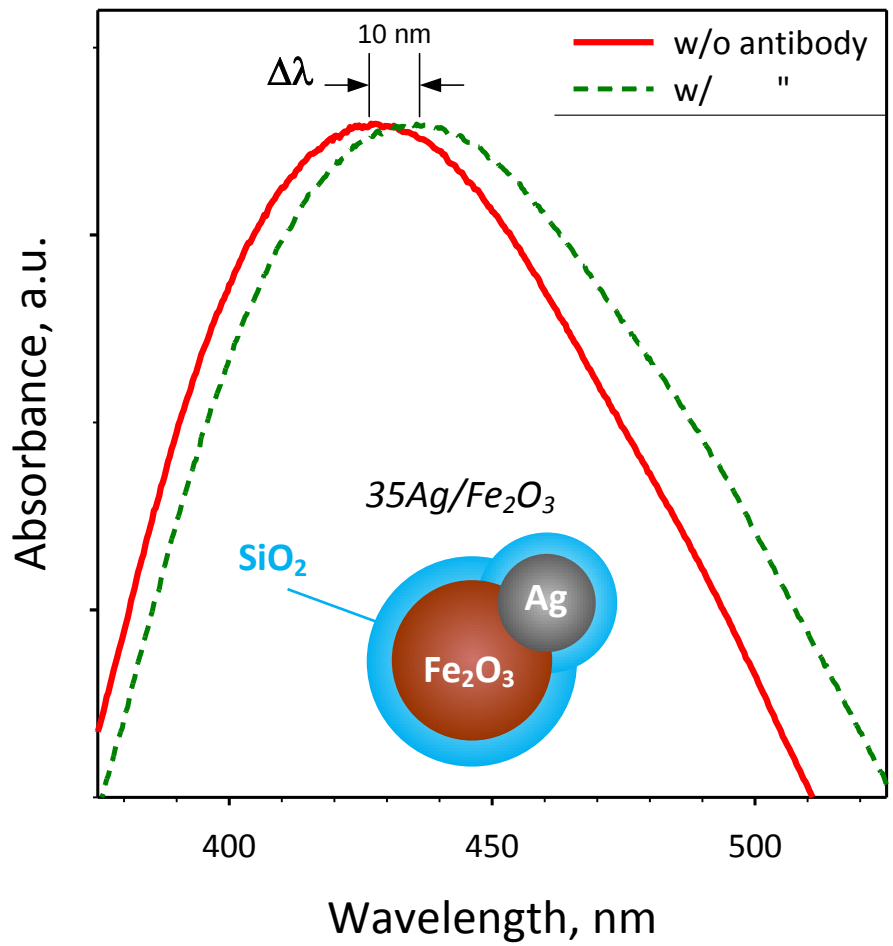
Flame aerosol reactors for synthesis up to 1 kg/h of Nanocomposite particles

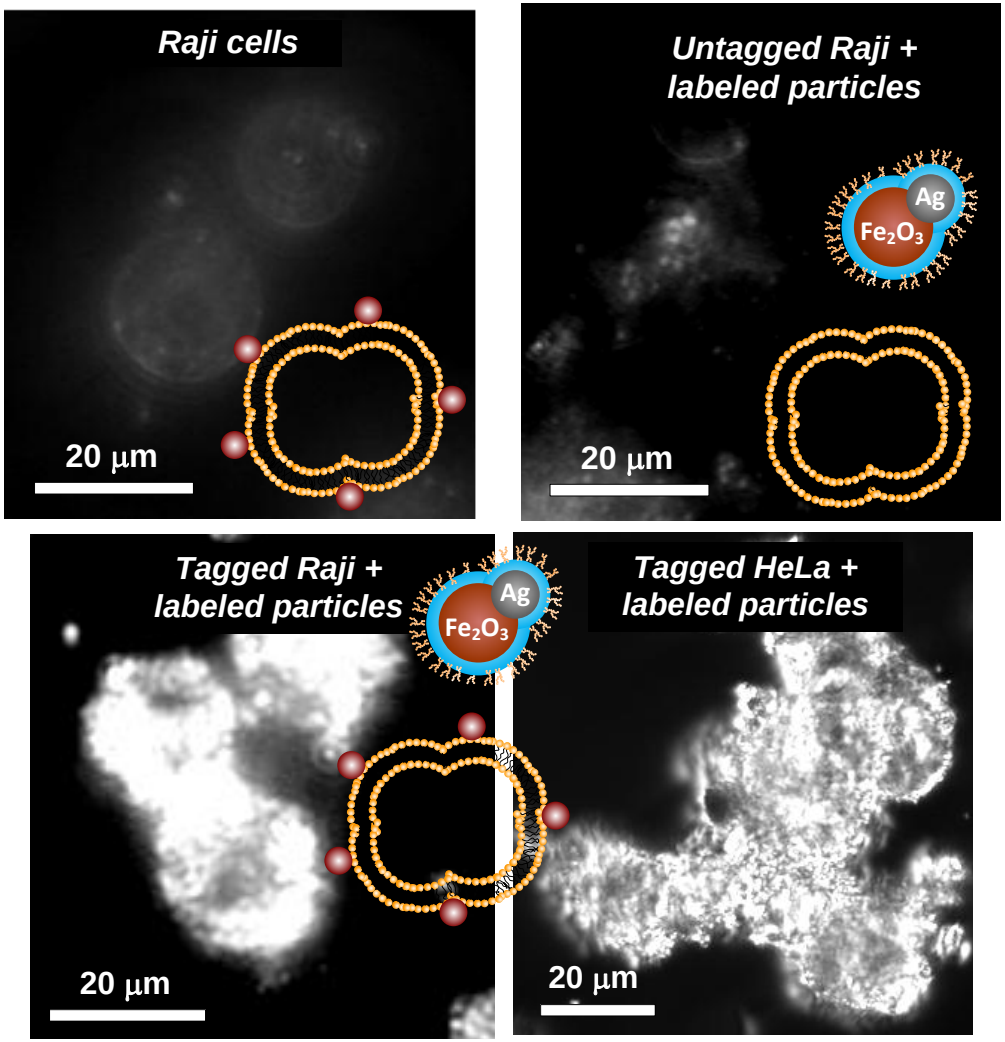
Flame Spray Pyrolysis Reactor & Control Unit

Baghouse filter

Flame aerosol synthesis of smart nanostructured materials *J. Mater. Chem.*, **17**, 4743 (2007).

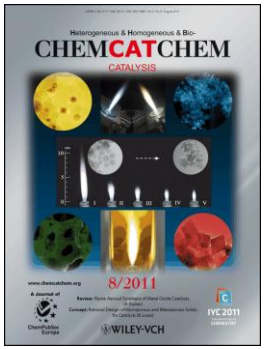
Biofunctionalization – Cell detection





Sotiriou, Sannomiya, Teleki, Krumeich, Vörös, Pratsinis, *Adv. Funct. Mater.* 20, 4250 (2010).
Sotiriou, Hirt, Lozach, Teleki, Krumeich, Pratsinis, *Chem. Mater.* 23, 1985 (2011).

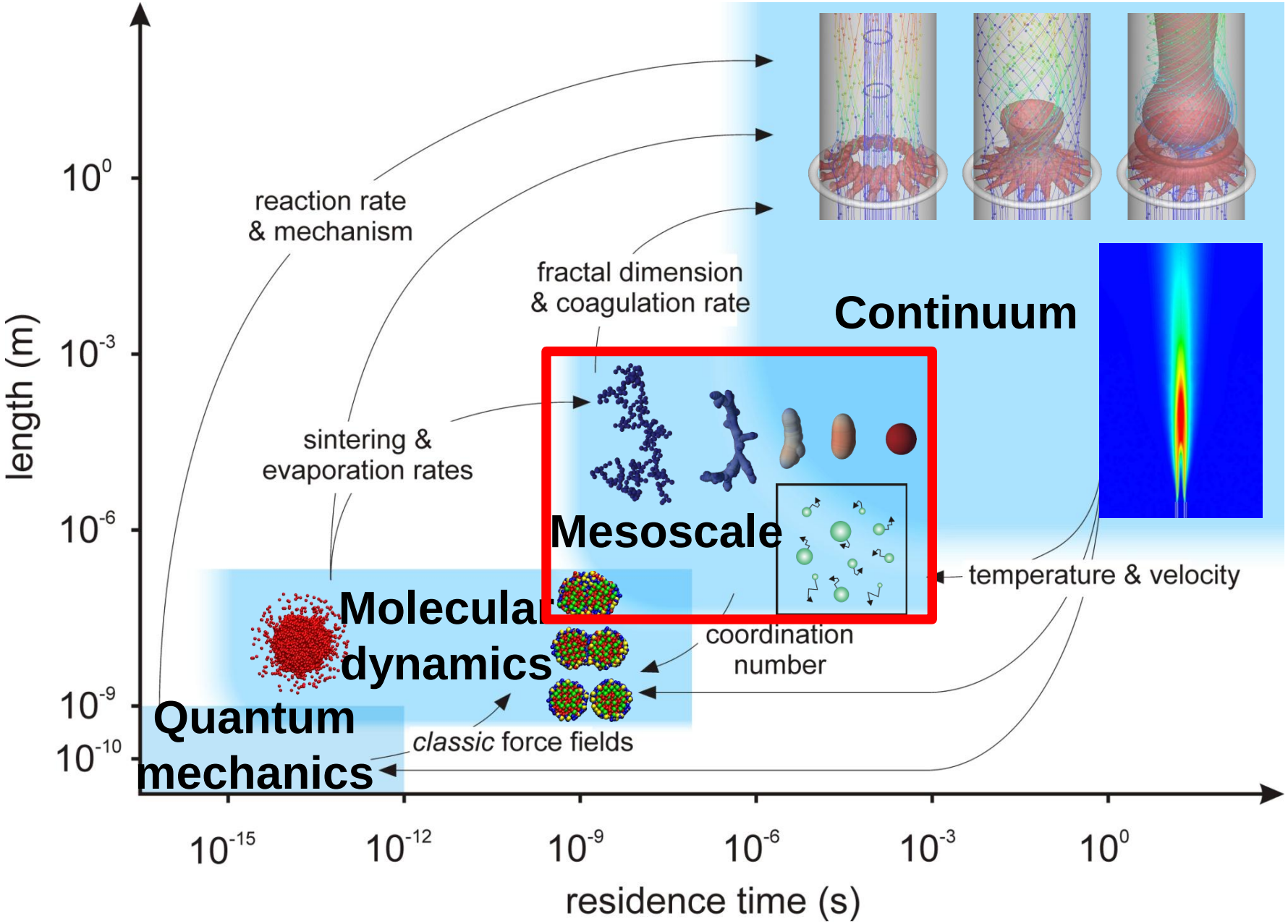
Flame reactor pilot plant, Johnson Matthey Research Center, Reading, UK



History of the Manufacture of Fine Particles in High-Temperature Aerosol Reactors" in *"Aerosol Science and Technology: History and Reviews"*, ed. D.S. Ensor & K.N. Lohr, RTI Press, Ch. 18, pp.475-507, 2011.

Flame Spray Pyrolysis pilot plant at ARCI in Hyderabad, India

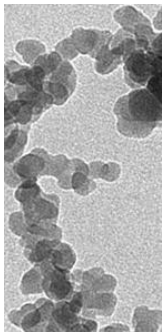
K. Wegner, B. Schimmöller, B. Thiebaut, C. Fernandez, T.N. Rao, "Pilot Plants for Industrial Nanoparticle Production by Flame Spray Pyrolysis", *KONA Powder and Particle*, 29, 251-265 (2011)

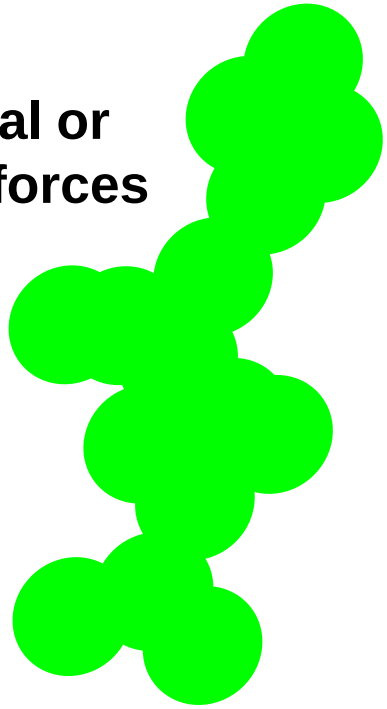


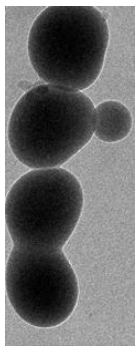
Design of Nanomaterial Synthesis by Aerosol Processes *Annual Rev. Chem. Biomol. Eng.*, 3, 103–127 (2012).

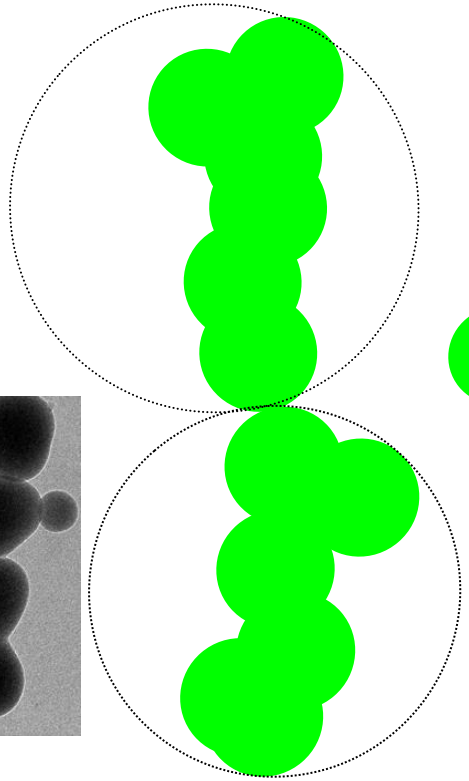
Aggregates and Agglomerates

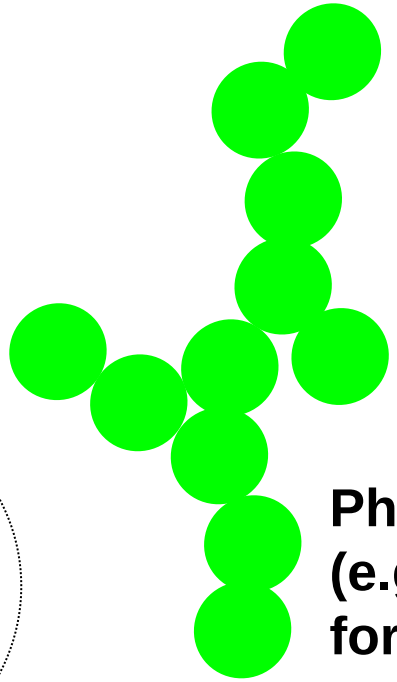
Chemical or Sinter-forces

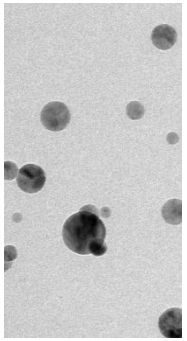












Physical (e.g.vdW) forces

Catalysts, lightguides, devices

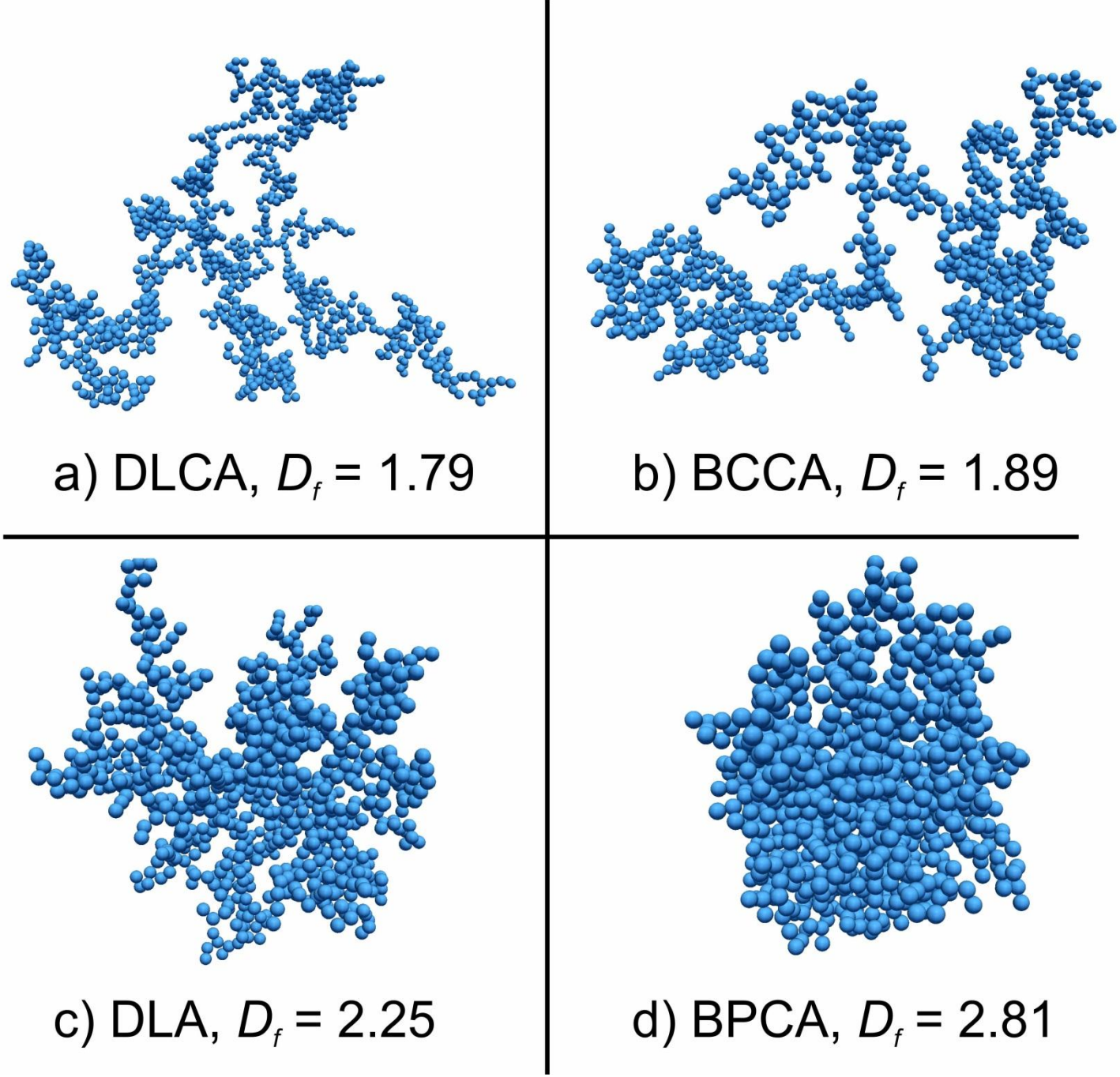
Nanocomposites, paints

Less toxic?

Potentially toxic?

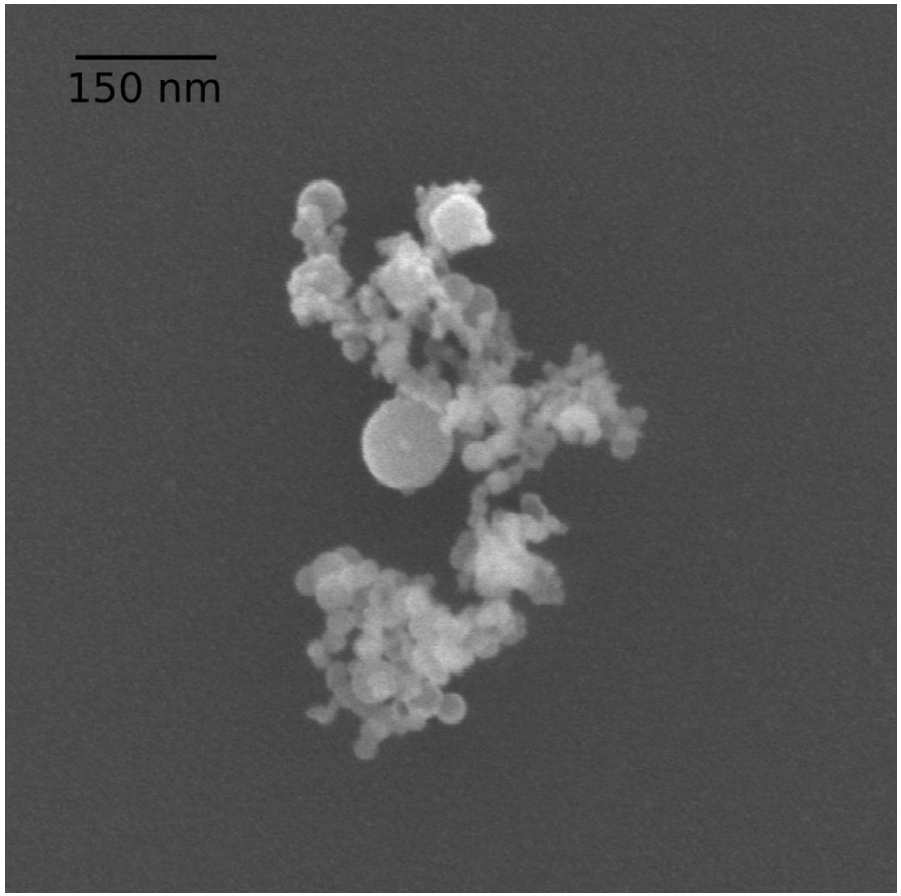
Current instruments cannot distinguish them

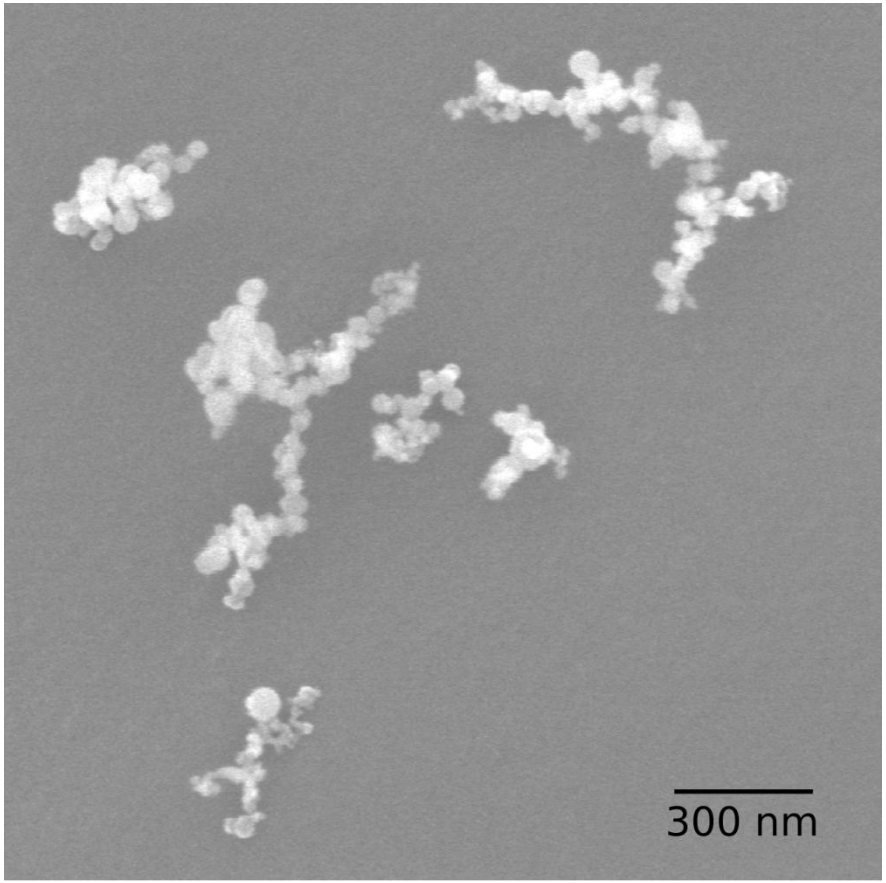
History of the Manufacture of Fine Particles in High-Temperature Aerosol Reactors in *"Aerosol Science and Technology: History and Reviews"*, ed. D.S. Ensor & K.N. Lohr, RTI Press, Ch. 18, pp.475-507, 2011.



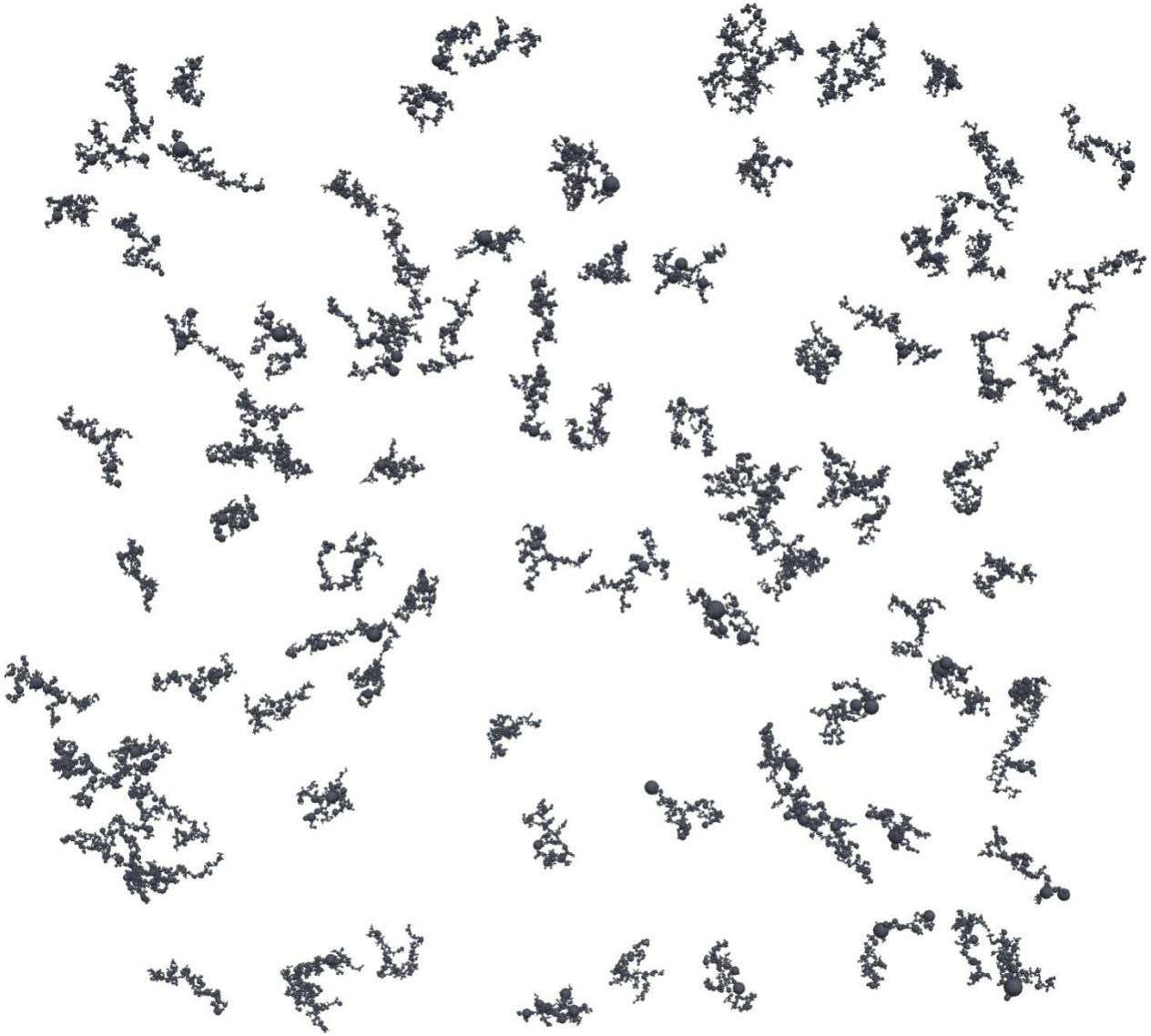
Mandelbrot, B.B. (1982). The Fractal Geometry of Nature. Freeman. SF.

Flame-made SiO_2 agglomerates and aggregates

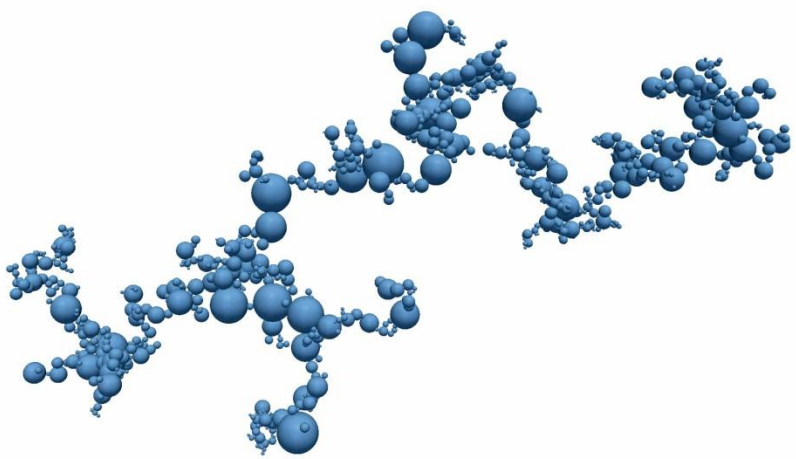




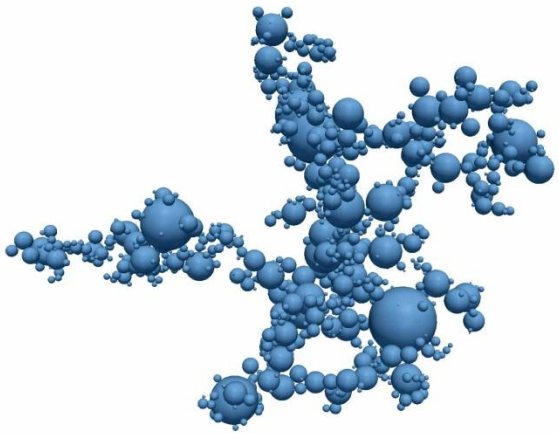
J. Scheckman, P.H. McMurry, S.E. Pratsinis, Rapid Characterization of Agglomerate Aerosols by in situ Mass-Mobility Measurements, *Langmuir*, 25, 8248–8254 (2009).



The Structure of Agglomerates consisting of Polydisperse Particles, *Aerosol Sci. Technol.*, **46**, 347–353 (2012)

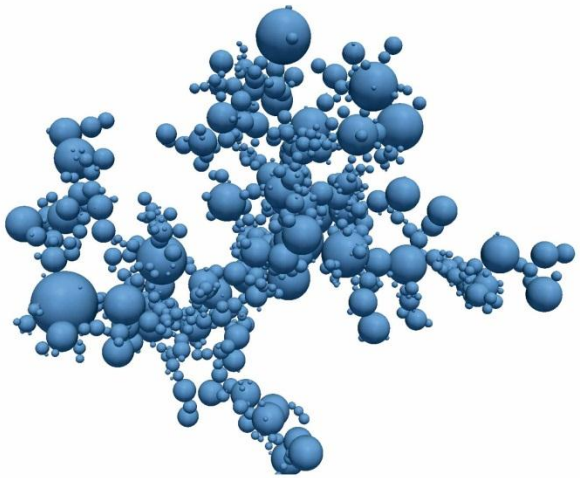


a) DLCA, D_f = 1.68

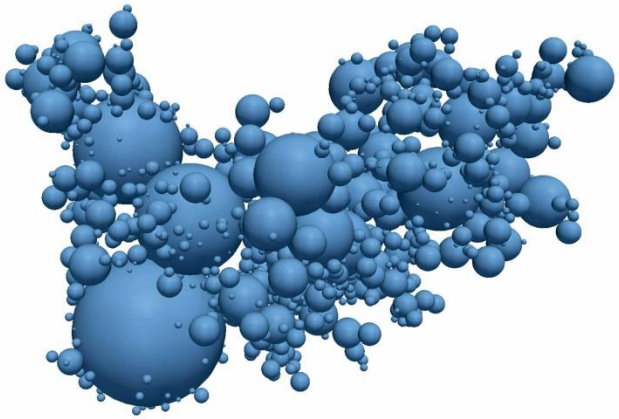


b) BCCA, D_f = 1.74

$\sigma_g = 2$

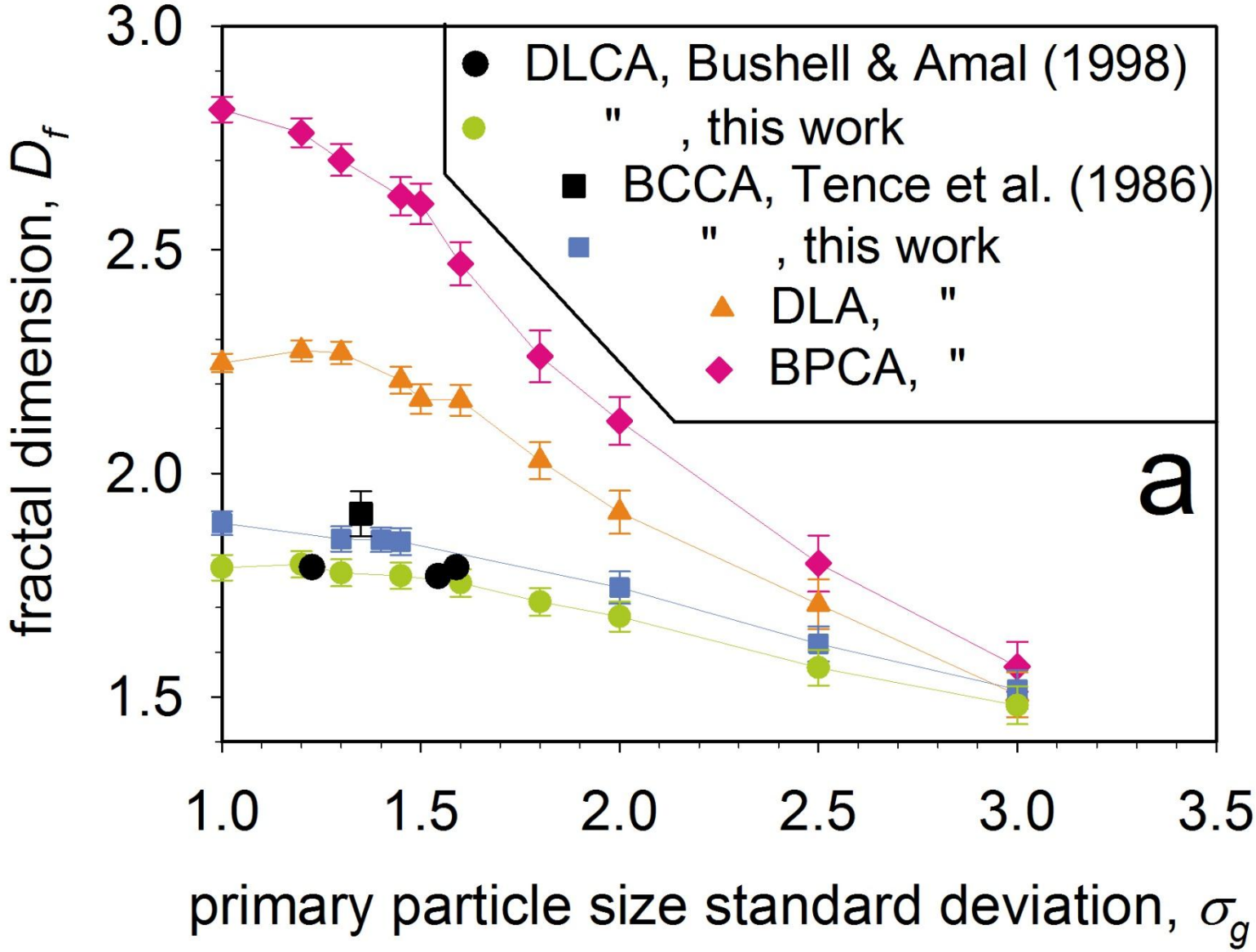


c) DLA, D_f = 1.91



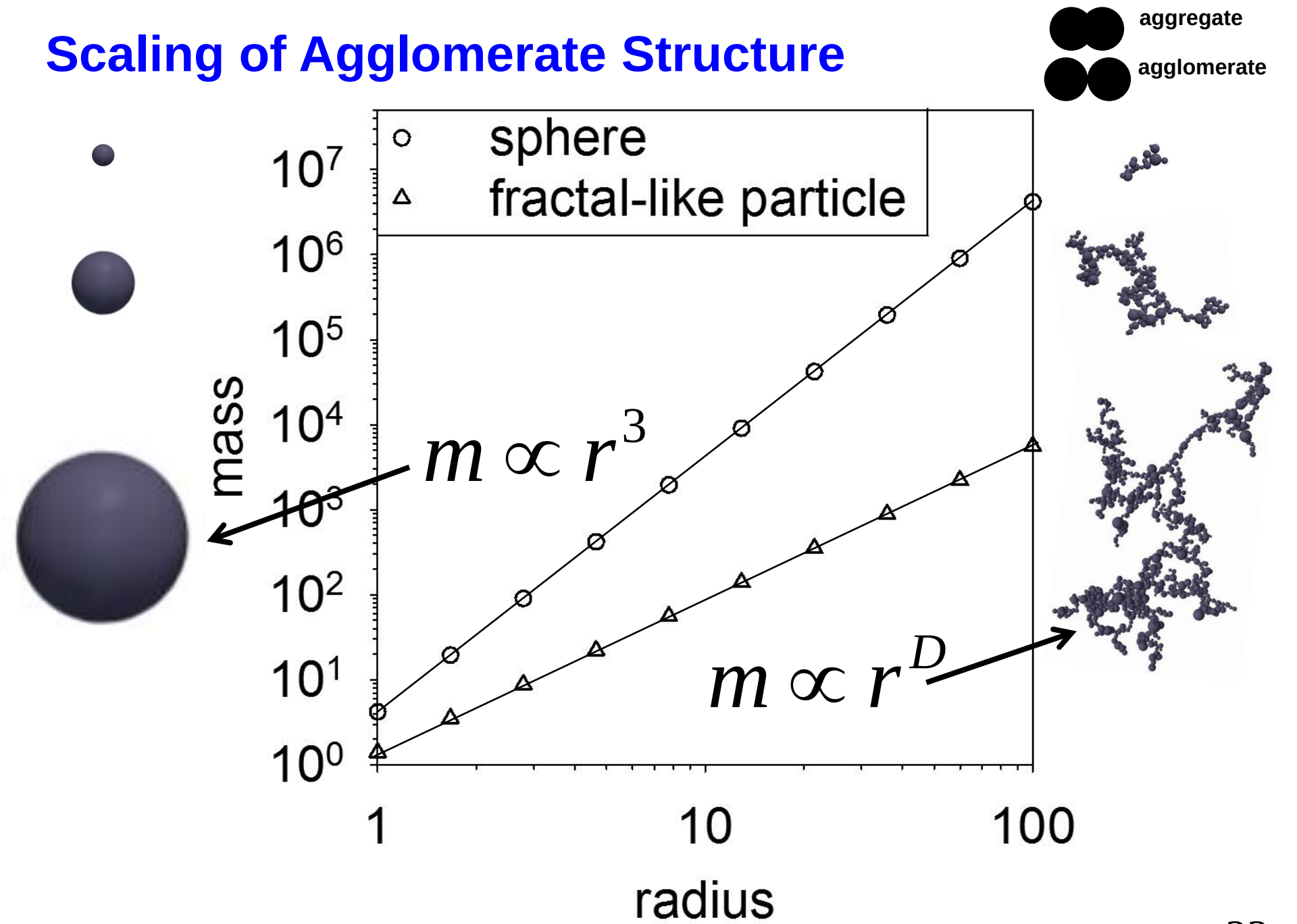
d) BPCA, D_f = 2.12

The Structure of Agglomerates consisting of Polydisperse Particles
Aerosol Sci. Technol., **46,** 347–353 (2012)



The Structure of Agglomerates consisting of Polydisperse Particles, *Aerosol Sci. Technol.*, **46**, 347–353 (2012)

Scaling of Agglomerate Structure



Characteristic Agglomerate Radius

aggregate

agglomerate

Mass fractal dimension[1],

D_f

$$\frac{m}{m_p} = k_n \left(\frac{r_g}{r_p} \right)^{D_f}$$

Mass-mobility exponent[3],

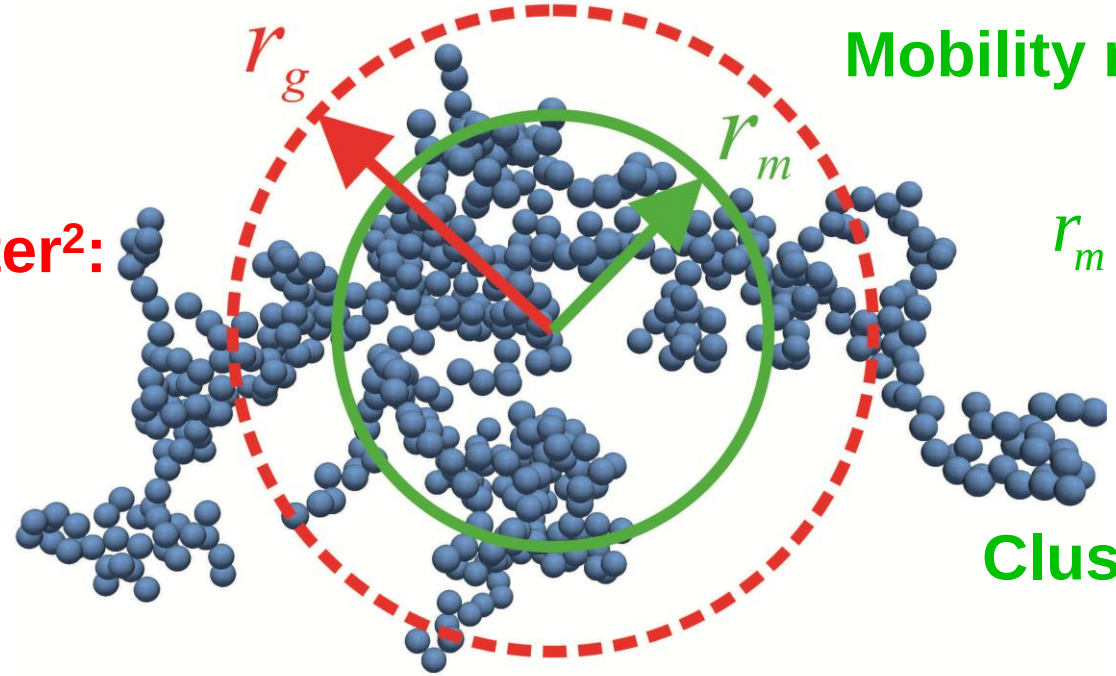
D_{fm}

$$\frac{m}{m_p} = k_m \left(\frac{r_m}{r_p} \right)^{D_{fm}}$$

Radius of gyration

Cluster-cluster[2]:

$D_f \approx 1.8$



Mobility radius

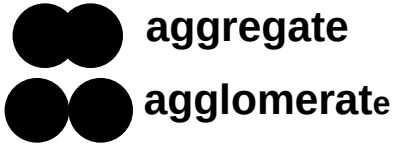
$$r_m = \sqrt{\frac{a_a}{\pi}}$$

Cluster-cluster[2]:

$D_{fm} \approx 2.15$

1. S.R. Forrest & T. A. Witten, *J. Phys. A: Math. Gen.* 12 (1979) L109-L117.
2. C.M. Sorensen, *Aerosol Sci. Technol.* 45 (2011) 755-769.
3. K. Park, F. Cao, D.B. Kittelson & P.H. McMurry, *Environ. Sci. Technol.* 37 (2003), 577-583.

Sintering by Viscous Flow

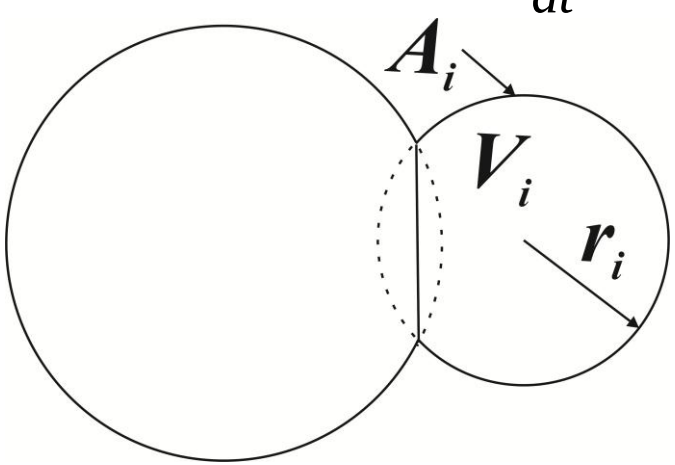


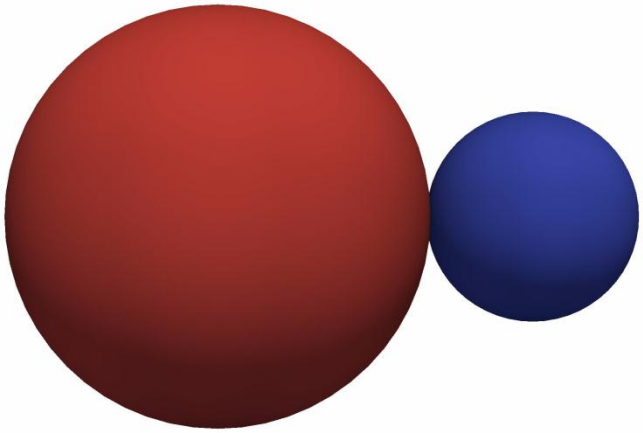
Constant strain rate ε in particle

1. Energy balance[1] $\gamma \dfrac{dA_i}{dt} = \iiint 3\eta\dot{\varepsilon}^2 dV_i = 3\eta\dot{\varepsilon}^2 V_i$

Change in surface energy = viscous dissipation

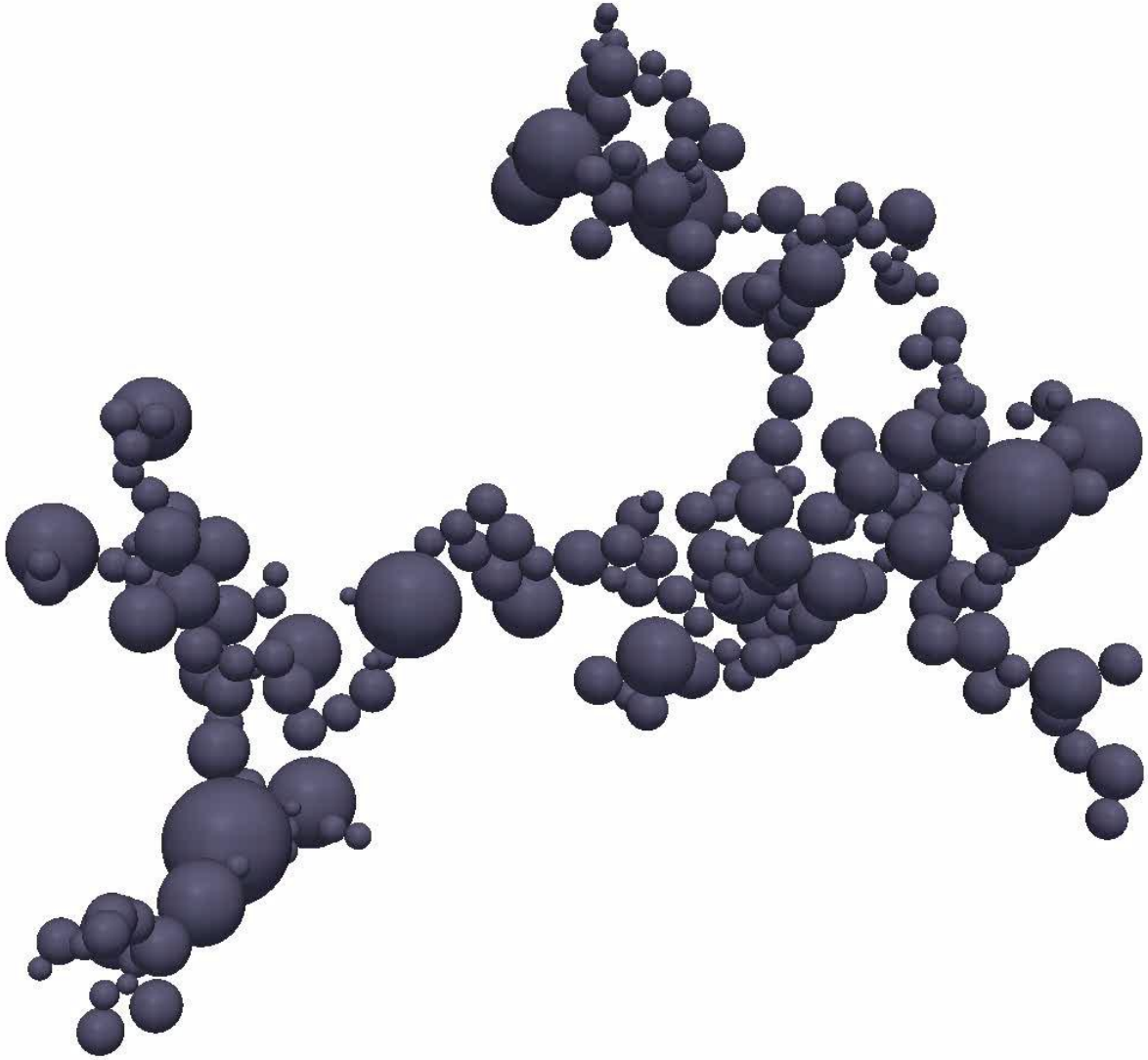
2. Mass balance[2] $\dfrac{dV_i}{dt} = 0$





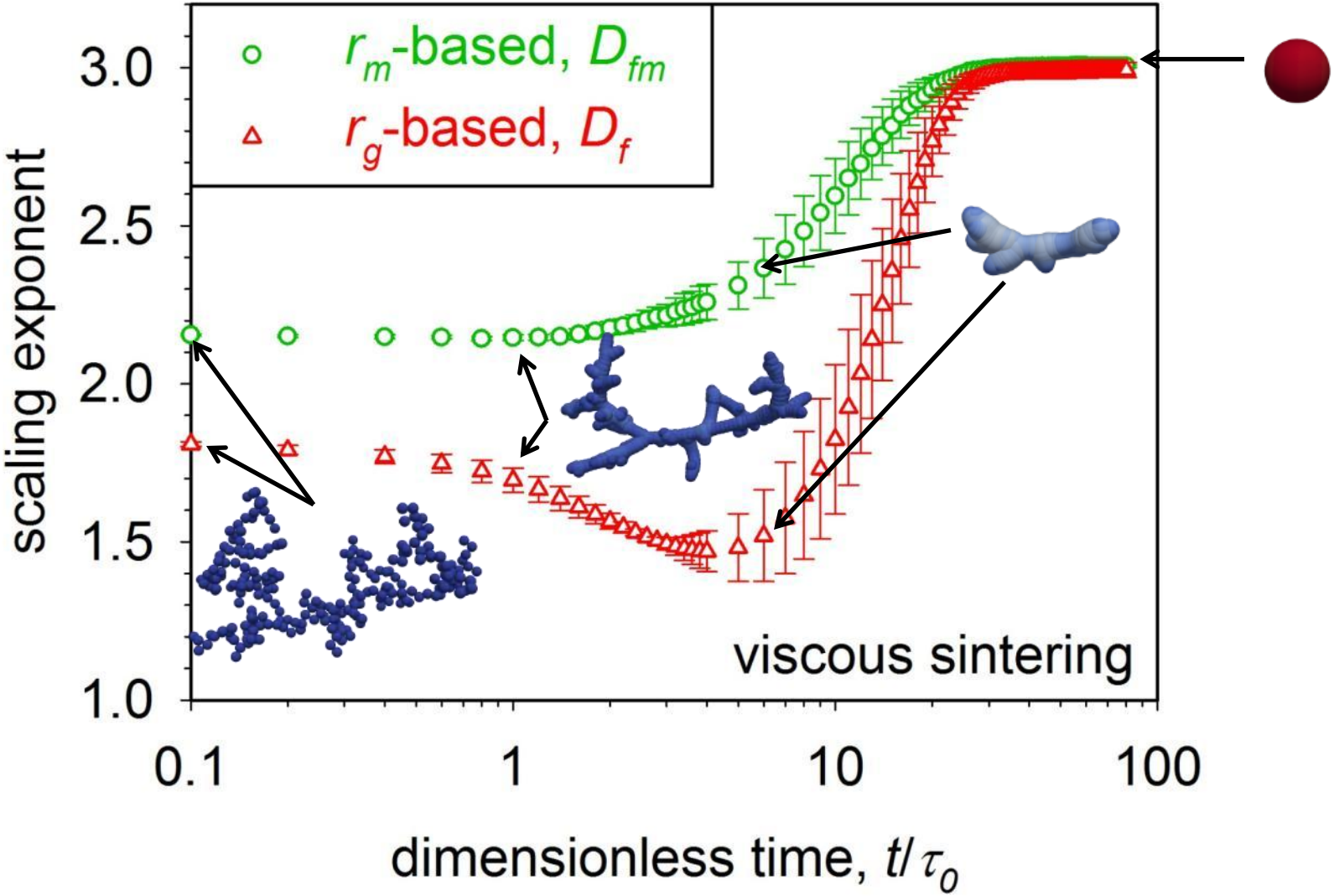
1. J. Frenkel, *J. Phys.* 9 (1945) 385-391.
2. R.M. Kadushnikov, V.V. Skorokhod, I.G. Kamenin, V.M. Alievskii, E.Y. Nurkanov, D.M. Alievskii, *Powder Metall. Met. C+ 40* (2001) 154-163.

Sintering - Coaleascence



Evolution of D_f & D_{fm}

Ensemble average over 200 clusters with 16-512 PPs

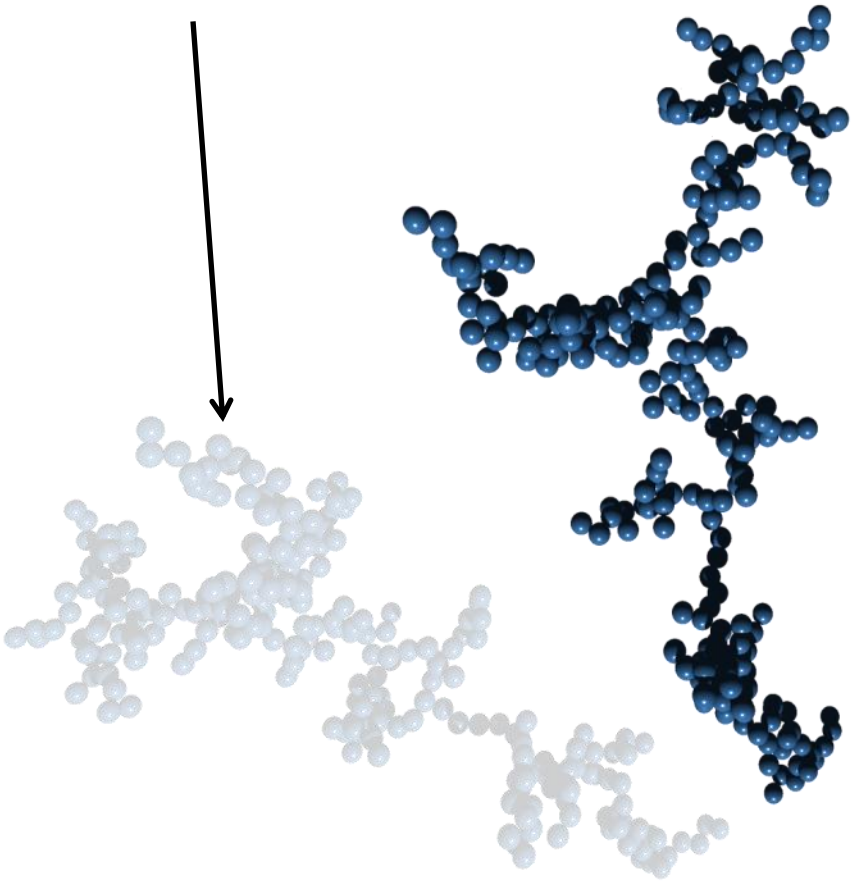


Aggregate morphology evolution by sintering: Number and diameter of primary particles, *J. Aerosol Sci*. **46,** 7-19 (2012) **.**

Projected Area of Aggregate[1] during Sintering

$$n_{va} = k_a \left(\frac{a_a}{a_{va}} \right)^{D_\alpha}$$

a_a: projected area



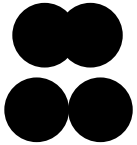
d_{va}: average PP diameter

$$d_{va} = d_{BET} = \frac{6v}{a}$$

n_{va}: average number of PPs

$$n_{va} = \frac{v}{\pi d_{va}^3 / 6}$$

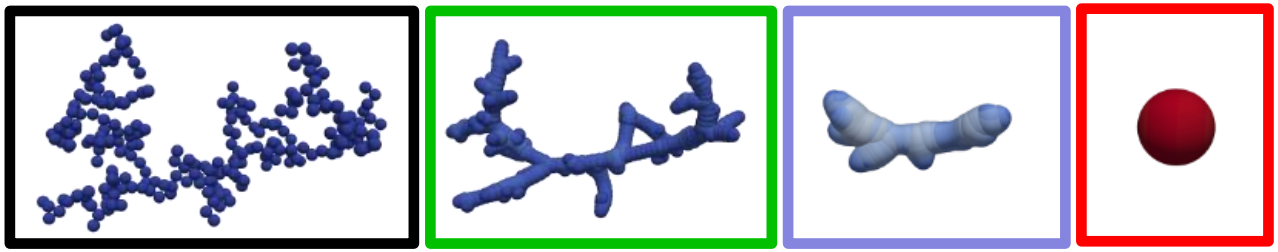
1. A.I. Medalia, *J. Colloid Interface Sci*. 24 (1967) 393-404.



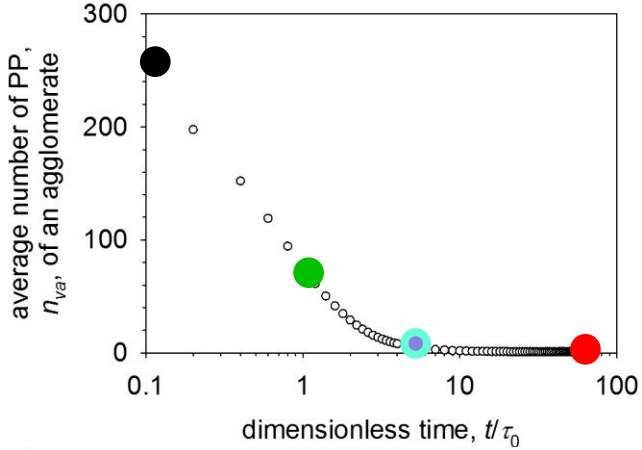
aggregate

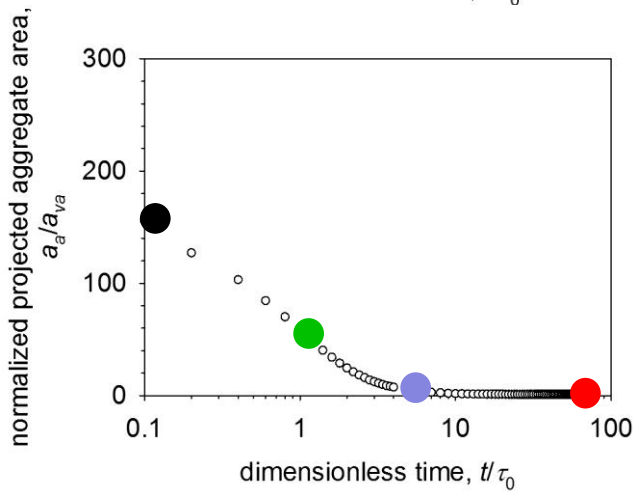
agglomerate

Projected Aggregate[1] Area during Sintering

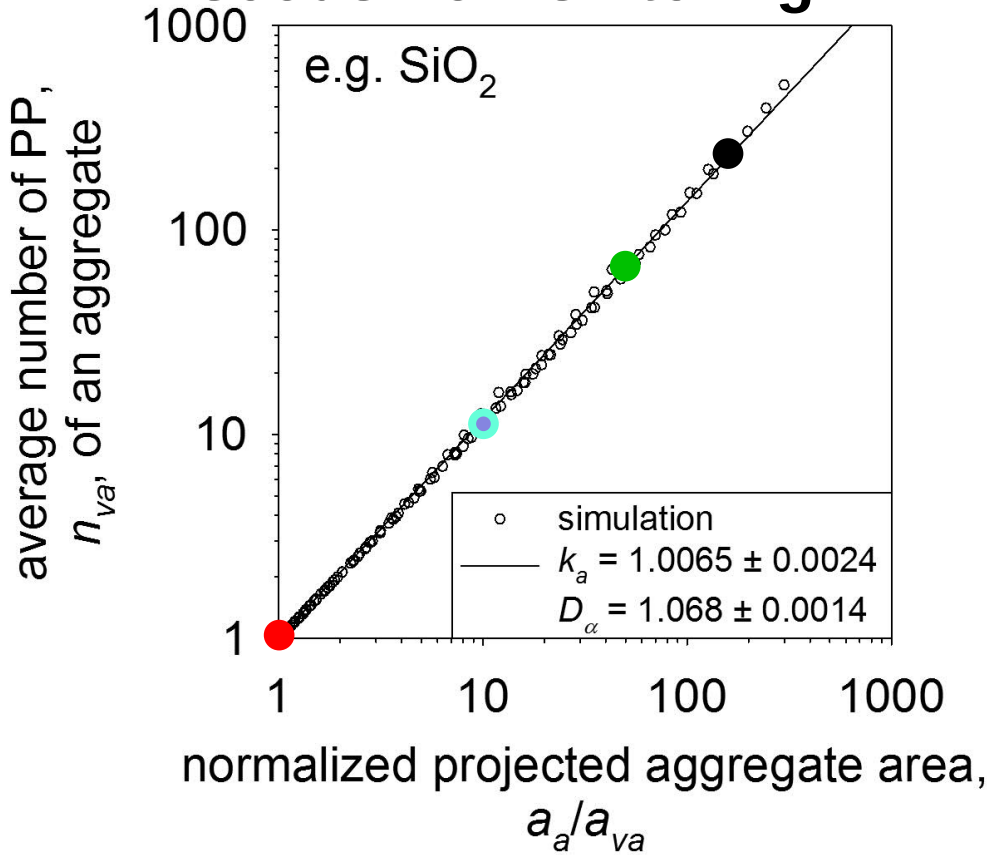


$$n_{va} = k_a \left(\frac{a_a}{a_{va}} \right)^{D_\alpha}$$





viscous flow sintering[2]



1. A.I. Medalia, *J. Colloid Interface Sci*. **24** 393-404 (1967) .

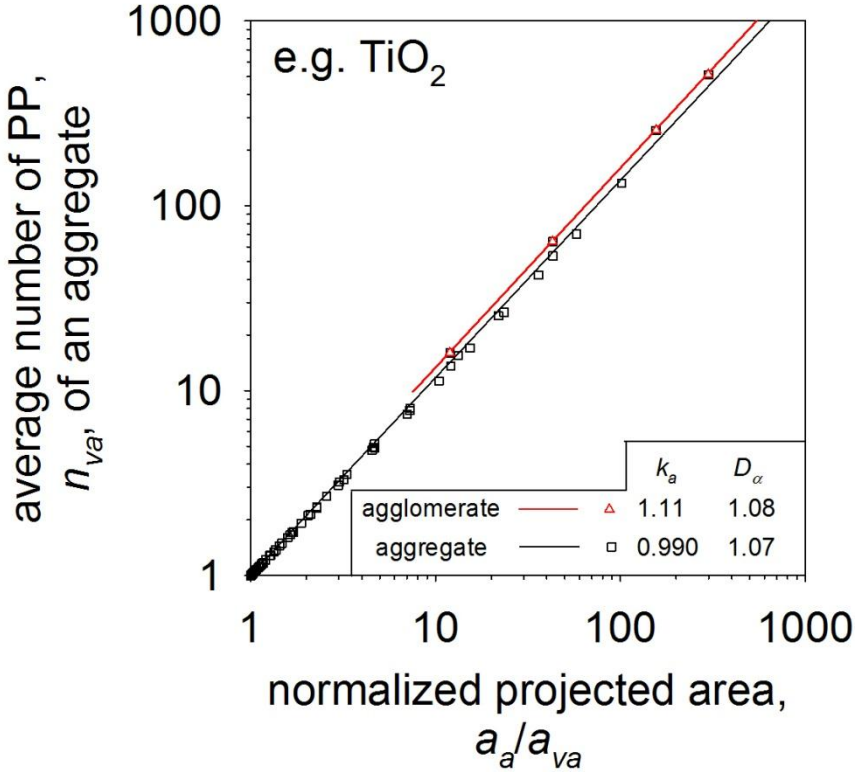
2. Multiparticle Sintering Dynamics: From Fractal-like Aggregates to Compact Structures, *Langmuir,* **27,** 6358-6367 (2011) .

Projected Aggregate[1] Area during Sintering

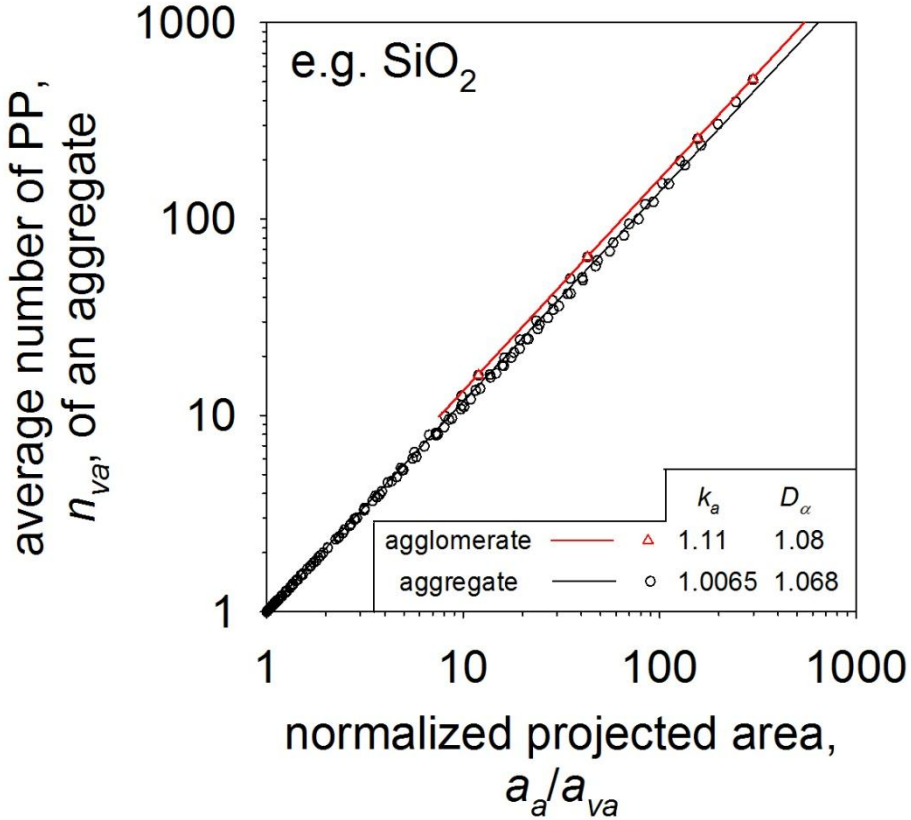
k_a = 1 & D_α = 1.07 are practically independent of sintering mechanism

$$n_{va} = k_a \left(\frac{a_a}{a_{va}} \right)^{D_\alpha}$$

grain boundary diffusion[3]



viscous flow sintering[2]



1. A.I. Medalia, *J. **Colloid Interface Sci.*** **24,** 393-404 (1967).
2. Multiparticle Sintering Dynamics: From Fractal-like Aggregates to Compact Structures, ***Langmuir,*** **27,** 6358-6367 (2011).
3. Aggregate morphology evolution by sintering: Number and diameter of primary particles, *J. **Aerosol Sci.*** **46,** 7-19 (2012) **.**

Mass - Mobility Relation

Surface area mean diameter:

$$d_{va} = \frac{6v}{a}$$

Average number of primary particles:

$$n_{va} = \frac{v}{v_{va}}$$

Scaling of projected aggregate area:[1]

$$n_{va} = k_a \left(\frac{a_a}{a_p} \right)^{D_\alpha}$$

a_a = projected aggregate area

Mobility in free molecular[2] **and transition regime:**[3]

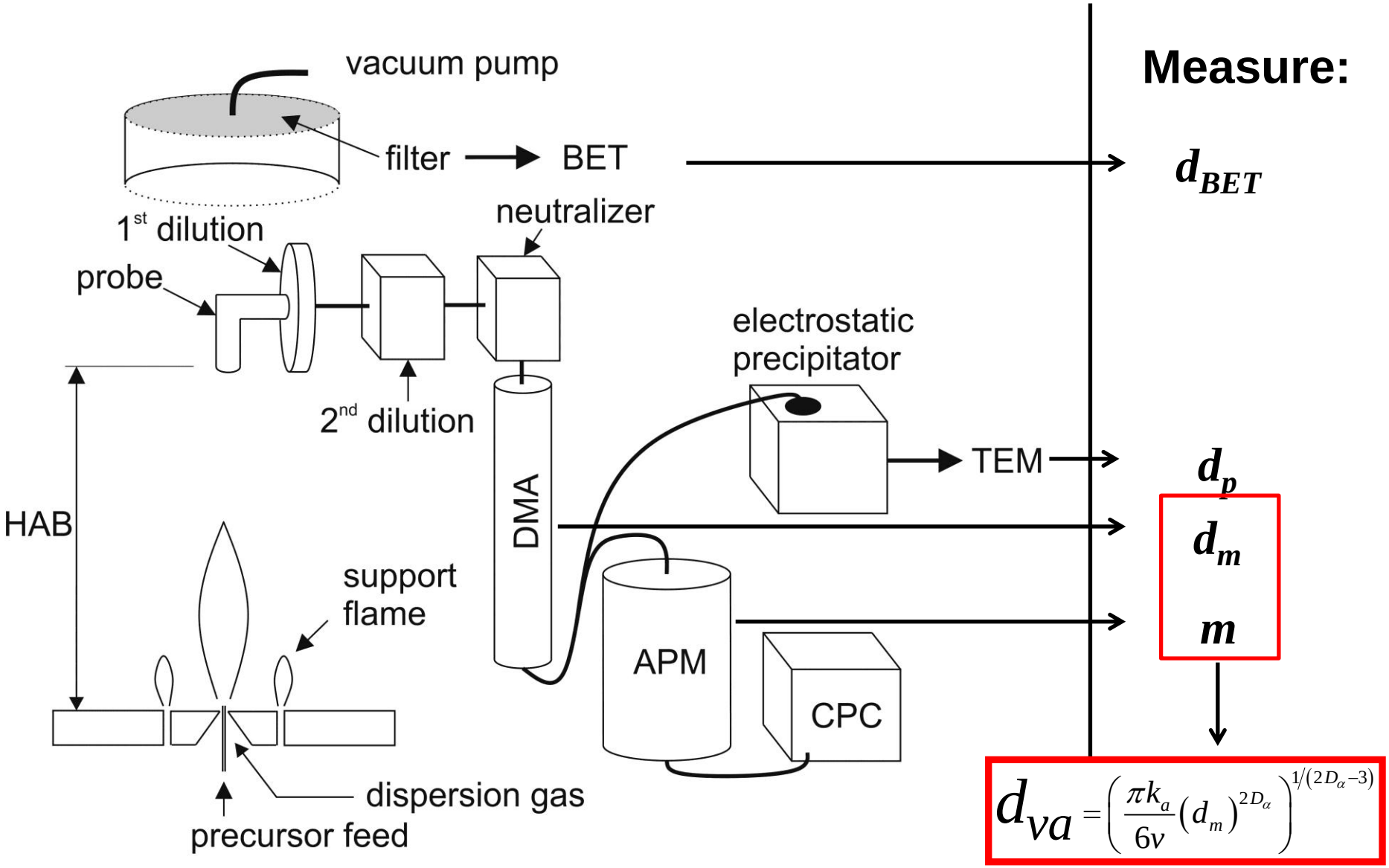
$$d_m = \sqrt{\frac{4a_a}{\pi}}$$

Surface area mean diameter from mobility size and volume

$$d_{va} = \left(\frac{\pi k_a}{6v} \left(d_m \right)^{2D_\alpha} \right)^{1/(2D_\alpha - 3)}$$

1. A.I. Medalia, *J. Colloid Interface Sci*. 24 (1967) 393-404.
2. P. Meakin, *Adv. Colloid Interface Sci.* 28 (1988) 249-331.
3. S.N. Rogak, R.C. Flagan & H.V. Nguyen, *Aerosol Sci. Technol.* 18 (1993) 25-47.

Characterization of ZrO_2 Nanoparticles



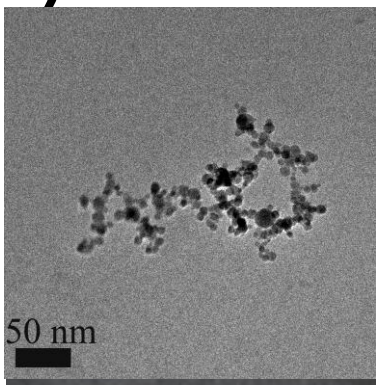
M.L. Eggersdorfer, A.J. Gröhn, C.M. Sorensen, P.H. McMurry & S.E. Pratsinis, Mass-Mobility Characterization of Flame-made ZrO_2 Aerosols: the Primary Particle Diameter & extent of Aggregation, in review. (2012)

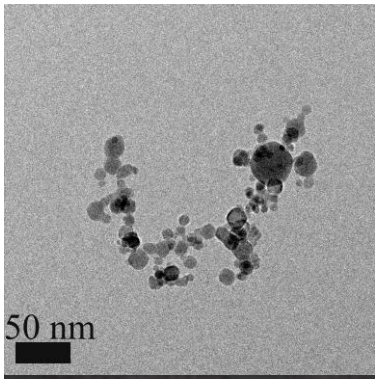
Reality Check: Effect of Liquid Precursor Feed Rate on d_p & D_f

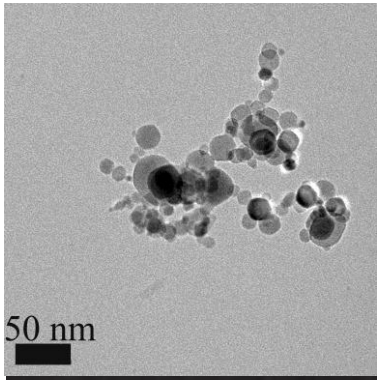
X/Y Flame

X: precursor feed liquid (ml/min)

Y: dispersion gas (l/min)



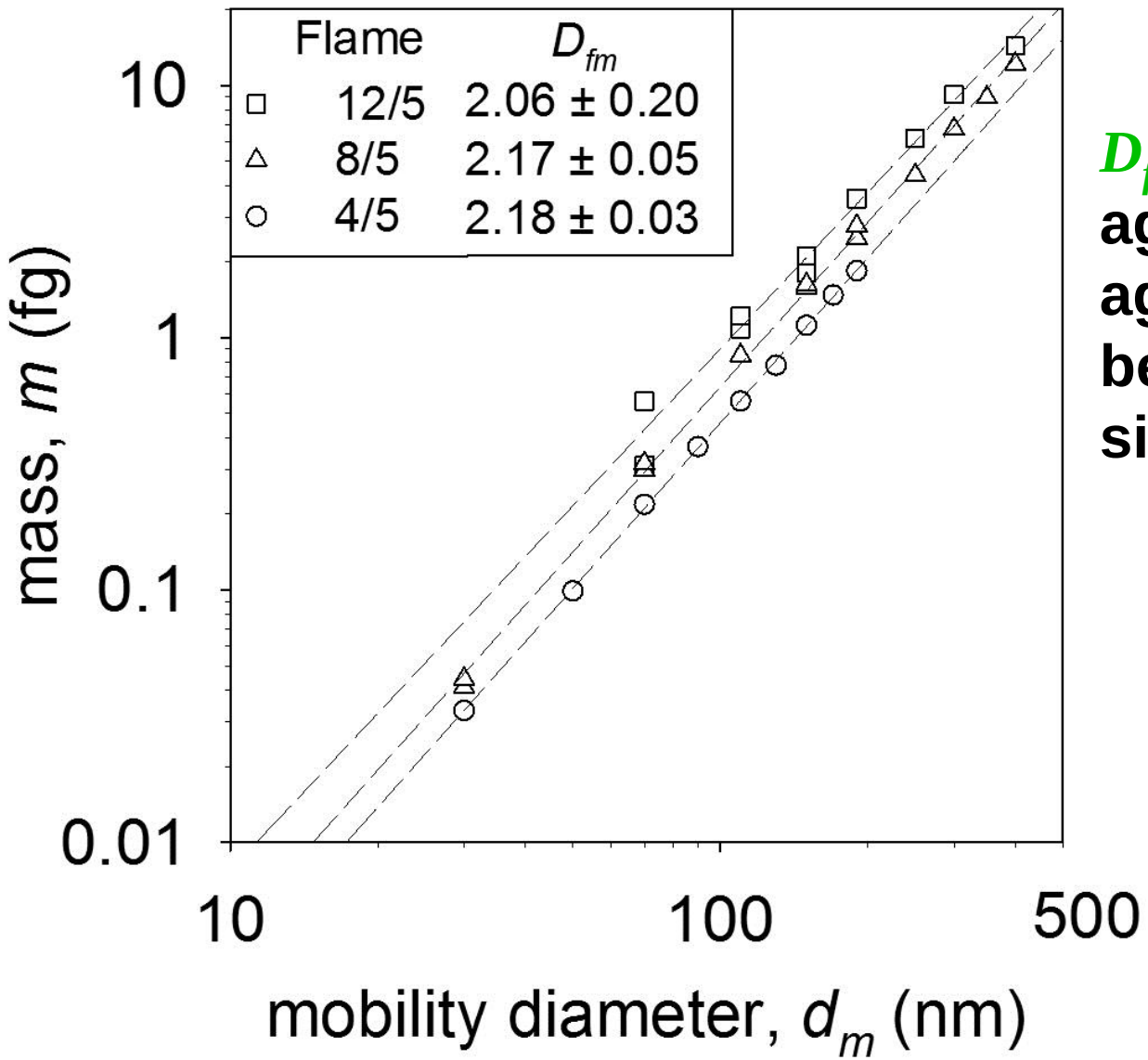




Inreasing liquid precursor feed rate results in faster sintering & coagulation [1]

1. The Role of Gas Mixing in Flame Synthesis of Titania Powders, *Powder Technol.* **86,** 87-93 (1996).

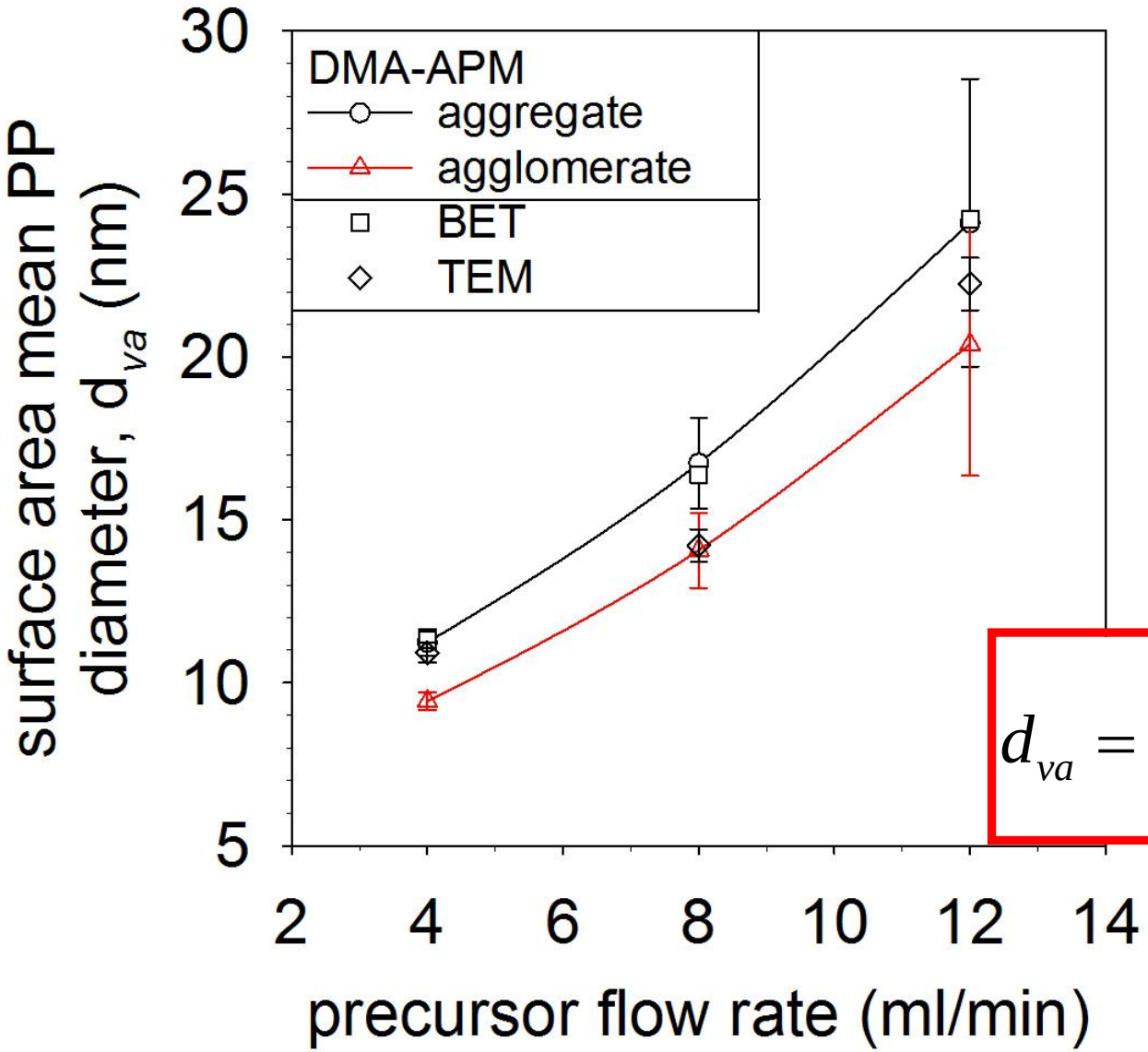
Effect of Precursor Feed Rate: Mass-Mobility



D_{fm} ≈ 2.15: agglomerates or aggregates at beginning of sintering

M.L. Eggersdorfer, A.J. Gröhn, C.M. Sorensen, P.H. McMurry & S.E. Pratsinis, Mass-Mobility Characterization of Flame-made ZrO_2 Aerosols: the Primary Particle Diameter & extent of Aggregation , in review. (2012)

Effect of Liquid Precursor Feed Rate: d_{va}



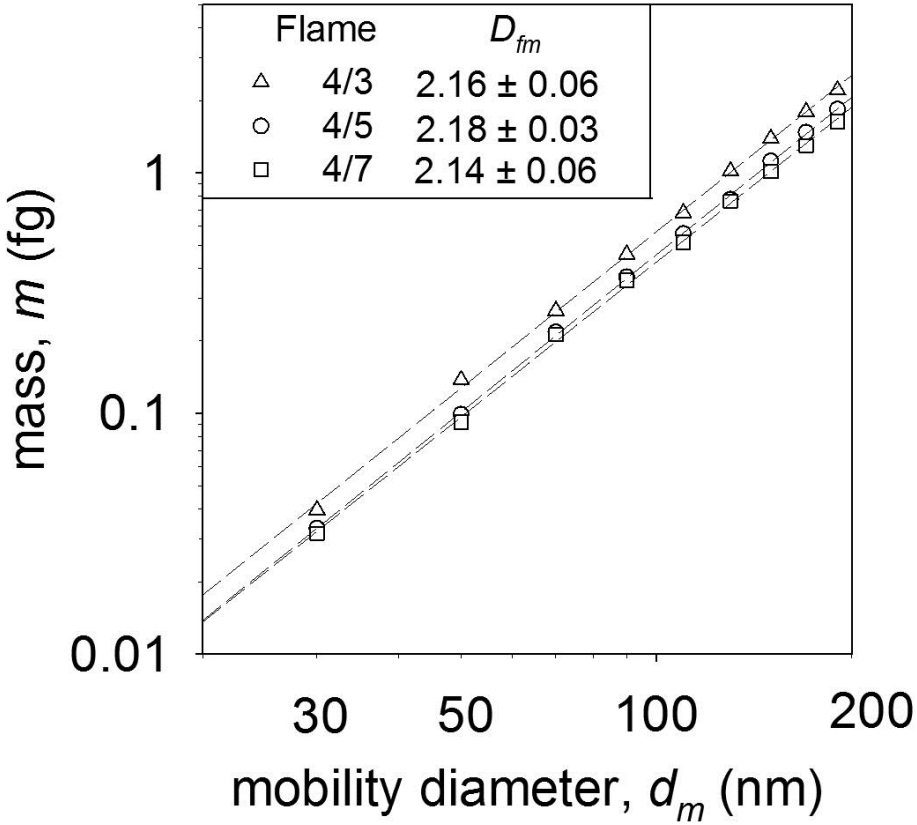
***d_{va}* can be rapidly determined during nanoparticle production by DMA-APM measurements**

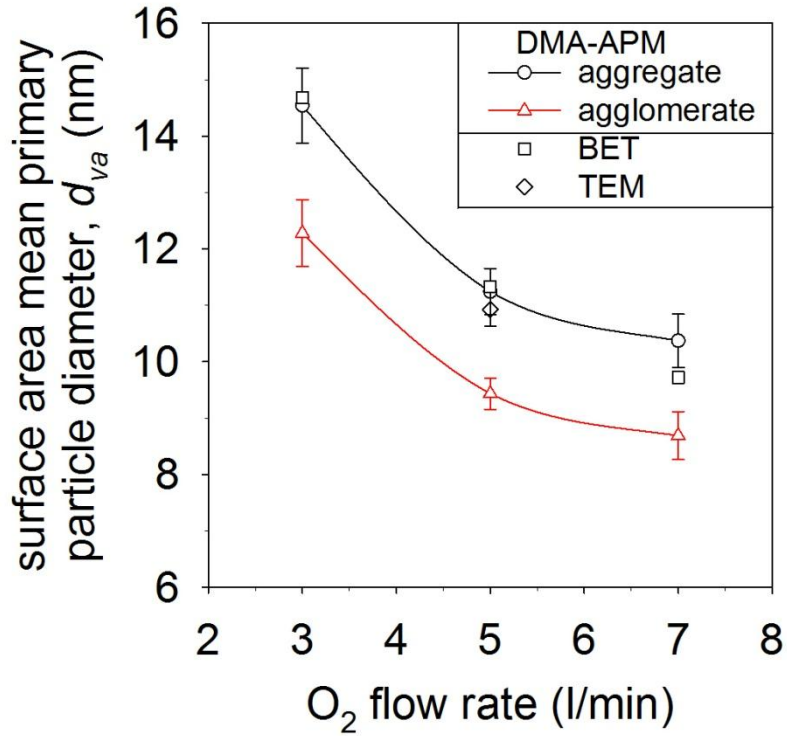
$$d_{va} = \left(\frac{\pi k_a}{6v} \left(d_m \right)^{2D_\alpha} \right)^{1/(2D_\alpha - 3)}$$

M.L. Eggersdorfer, A.J. Gröhn, C.M. Sorensen, P.H. McMurry & S.E. Pratsinis, Mass-Mobility Characterization of Flame-made ZrO_2 Aerosols: the Primary Particle Diameter & extent of Aggregation , in review. (2012)

Effect of Oxygen Dispersion Flow Rate

aggregate
agglomerate





Increasing O_2 flow rate dilutes the aerosol & shortens the high temperature particle residence time resulting in smaller particles[1]

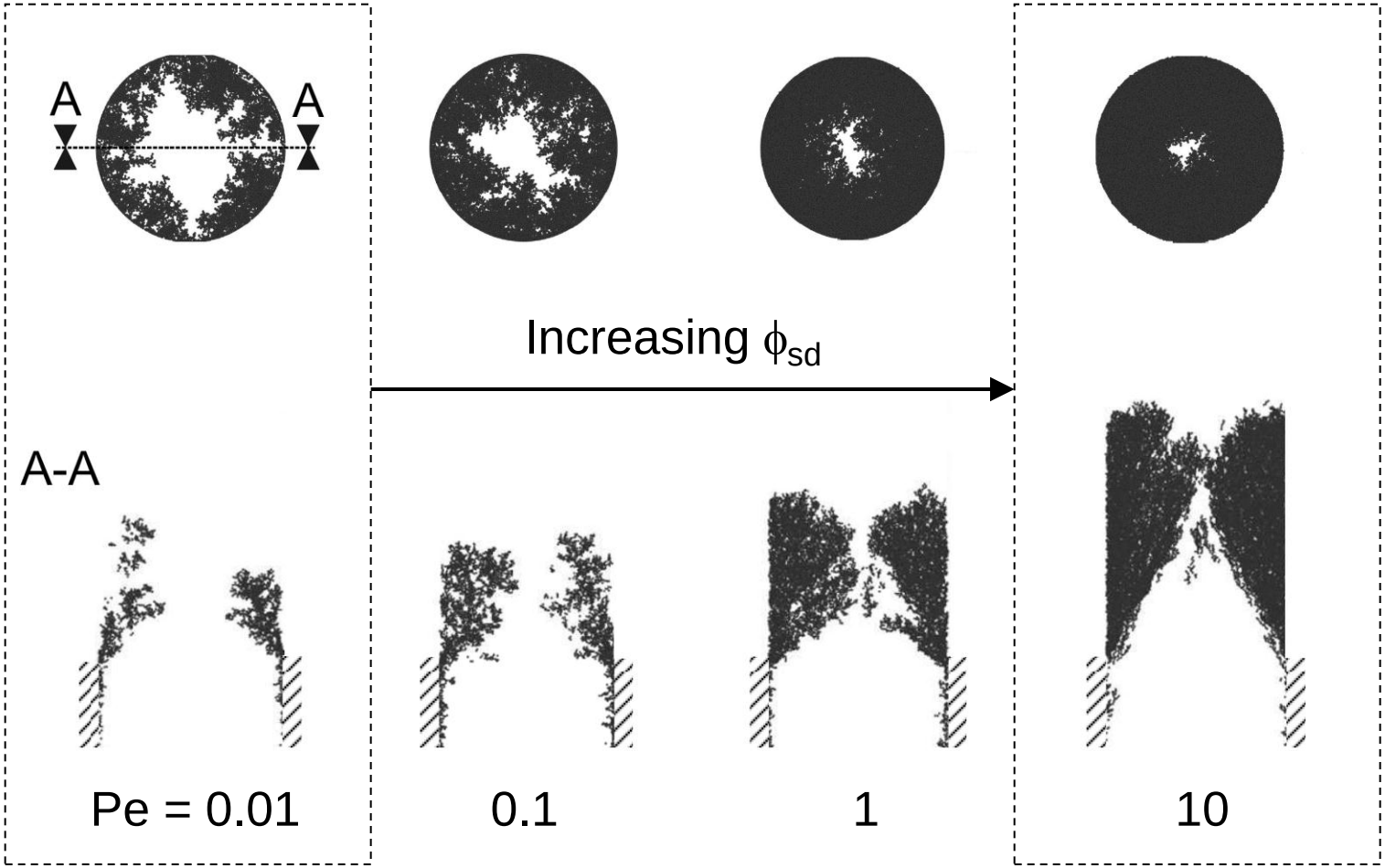
$$d_{va} = \left(\frac{\pi k_a}{6v} \left(d_m \right)^{2D_\alpha} \right)^{1/(2D_\alpha - 3)}$$

1. The Role of Gas Mixing in Flame Synthesis of Titania Powders, *Powder Technol.* **86,** 87-93 (1996).

M.L. Eggersdorfer, A.J. Gröhn, C.M. Sorensen, P.H. McMurry & S.E. Pratsinis, Mass-Mobility Characterization of Flame-made ZrO_2 Aerosols: the Primary Particle Diameter & extent of Aggregation, in review. (2012)

Formation & Filtration of Nanoparticles

Structures at t_{cl} vs Pe



Void conical structure

Filtration of Nanoparticles: Evolution of Cake Structure and Pressure-Drop, *J. Aerosol Sci.* **40,** 965–81 (2009)

Conclusions

- The polydispersity of primary particles opens the structure of their agglomerates while, in contrast, sintering forms more compact aggregates.

- The primary particle diameter, d_{va}, can be obtained online by mass - mobility measurements by

$$\boxed{d_{va} = \left(\frac{\pi k_a}{6v} \left(d_m \right)^{2D_\alpha} \right)^{1/(2D_\alpha - 3)}}$$

regardless of material composition or sintering rate, in agreement with *ex-situ* N_2 adsorption & microscopy.

- Aggregates are distinguished from agglomerates.

Hike to Creux du Van, Neuchatel, August 22, 2011