Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Particle Technology Laboratory

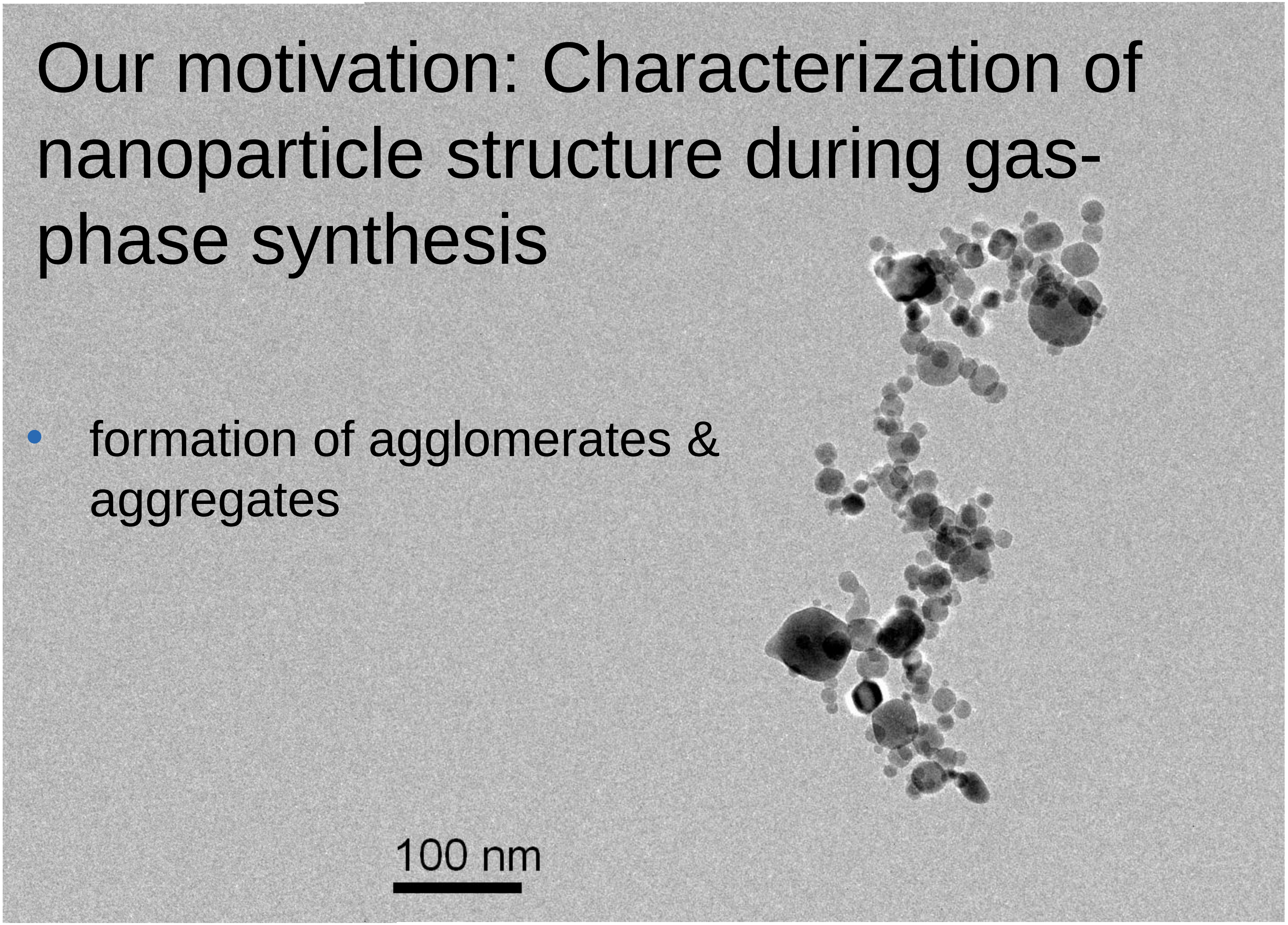
Dynamics of Fractal-like Aerosols during Sintering: Characterization

Max L. Eggersdorfer and Sotiris E. Pratsinis
Particle Technology Laboratory, ETH Zürich

Freitag, 18. Mai 2012

meggers@ptl.mavt.ethz.ch

Our motivation: Characterization of nanoparticle structure during gas-phase synthesis

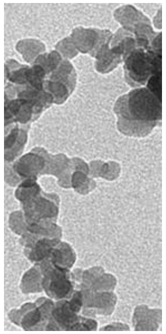


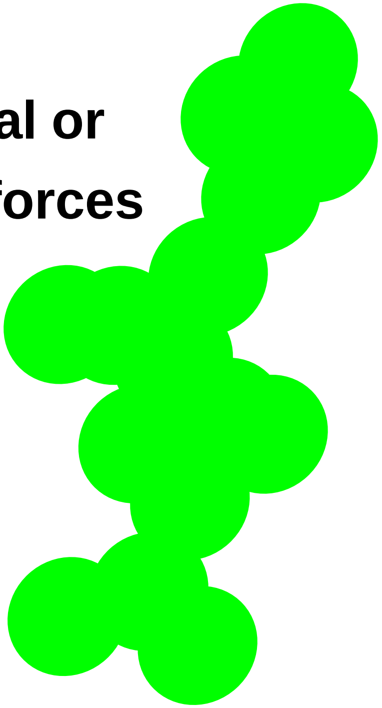
- formation of agglomerates & aggregates

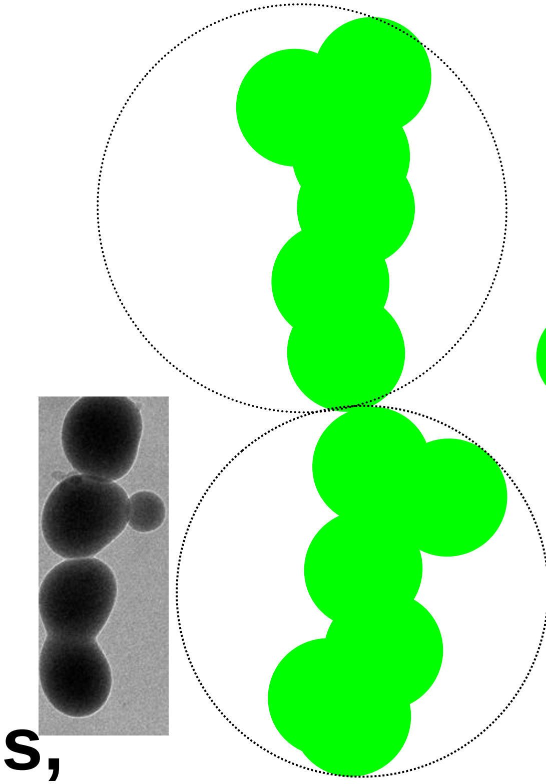
Aggregates and Agglomerates

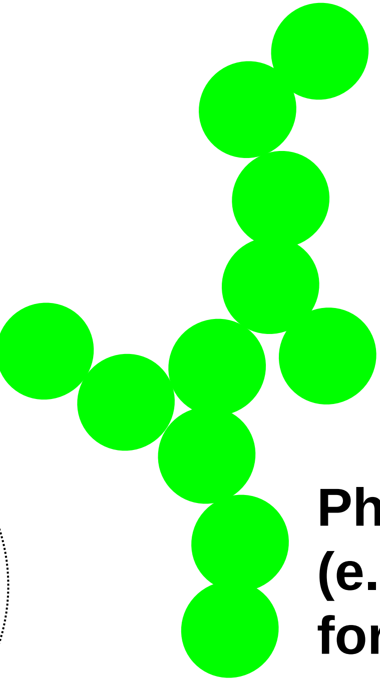
Chemical or

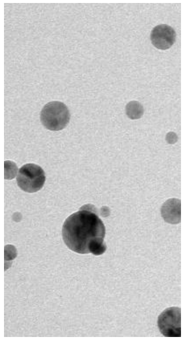
Sinter-forces











Physical
(e.g.vdW)
forces

Catalysts, lightguides, devices

Nanocomposites, paints

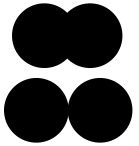
Less toxic?

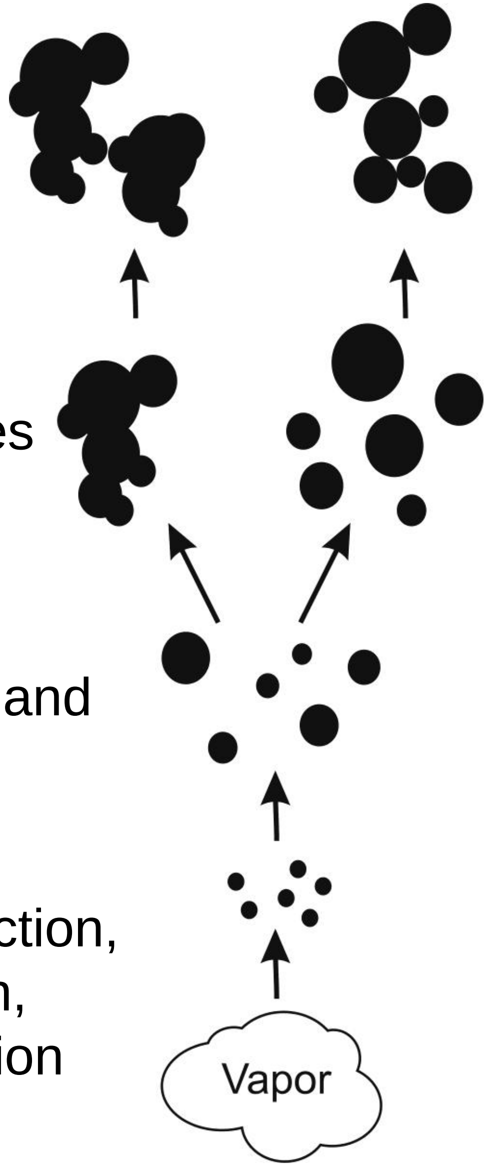
Potentially toxic?

Current aerosol instruments cannot distinguish them

S.E. Pratsinis in *"Aerosol Science and Technology: History and Reviews"*,
ed. D.S. Ensor & K.N. Lohr, RTI Press (2011), Ch. 18, 475-507.

Particle Generation in the Gas-Phase





Agglomerates

Aggregates

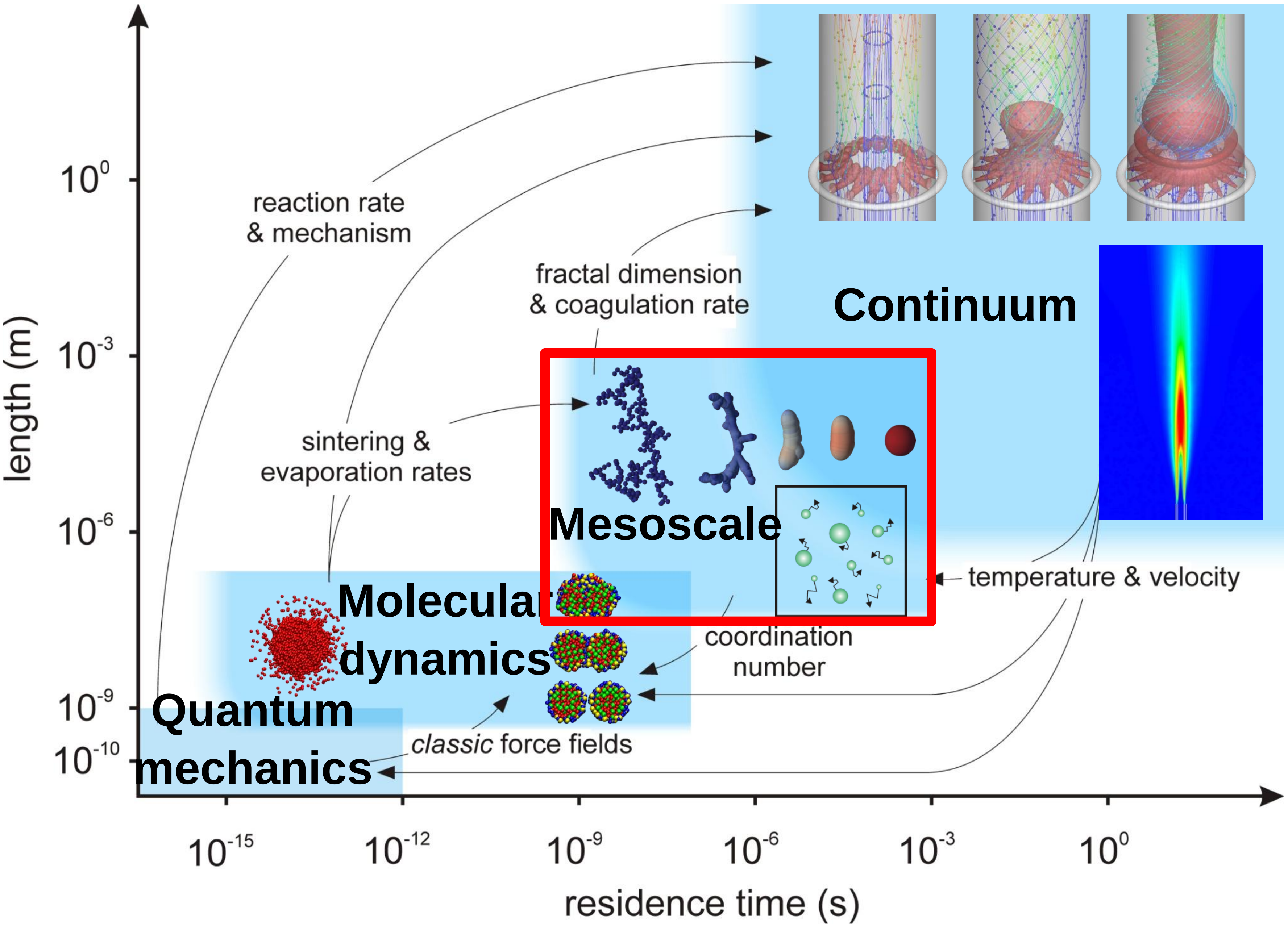
Individual primary particles

Coagulation and Sintering

Chemical reaction, nucleation, condensation

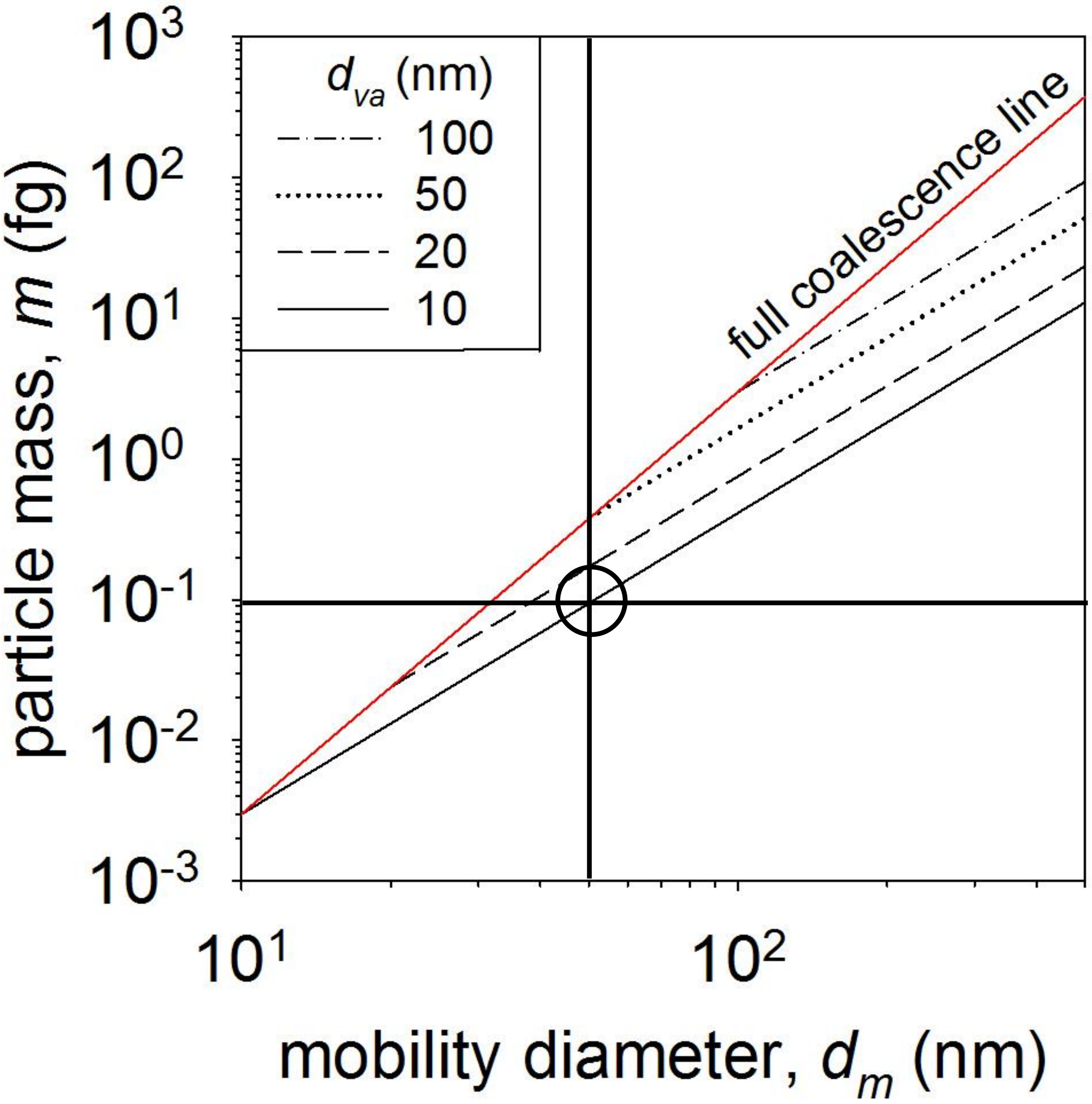
Primary particles

Molecules



B. Buesser & S.E. Pratsinis, *Annual Rev. Chem. Biomol. Eng.*, **3** (2012) 103–127.

Relation between mass, mobility and primary diameter



measure:

d_m = 50 nm

$m = 9 \cdot 10^{-2}$ fg

calculate:

d_{va} = 10 nm

ρ = 5720 kg/m^3

Outline

Part 1: Numerical

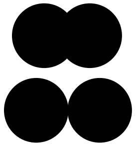
- characterization of agglomerate structure
- formation of aggregates by sintering

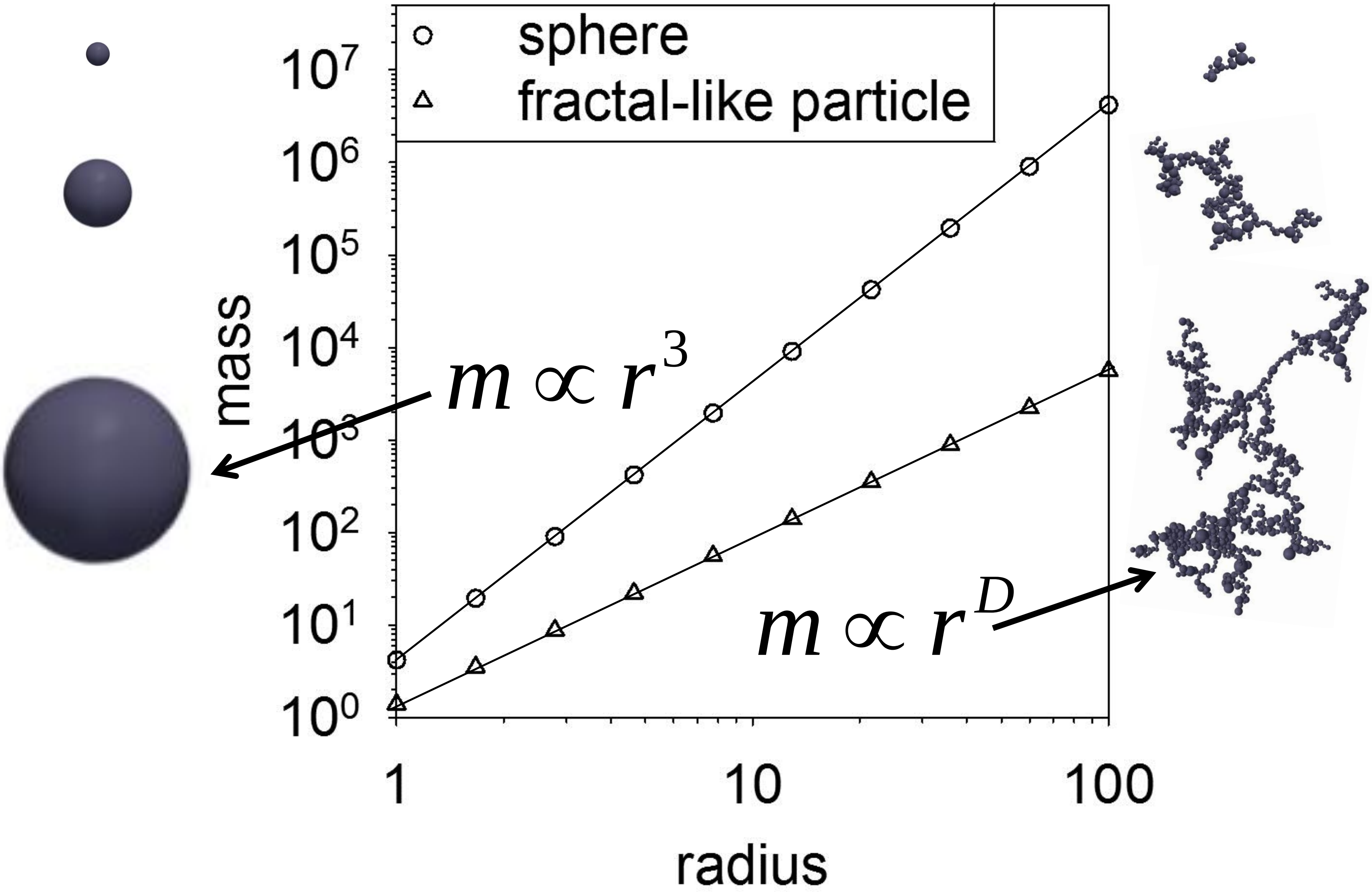
➡ **mass – mobility relation**

Part 2: Experimental

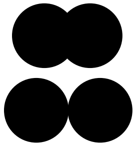
- mass-mobility characterization of ZrO_2

Scaling of Agglomerate Structure





Characteristic Agglomerate Radius



Mass fractal dimension[1], D_f

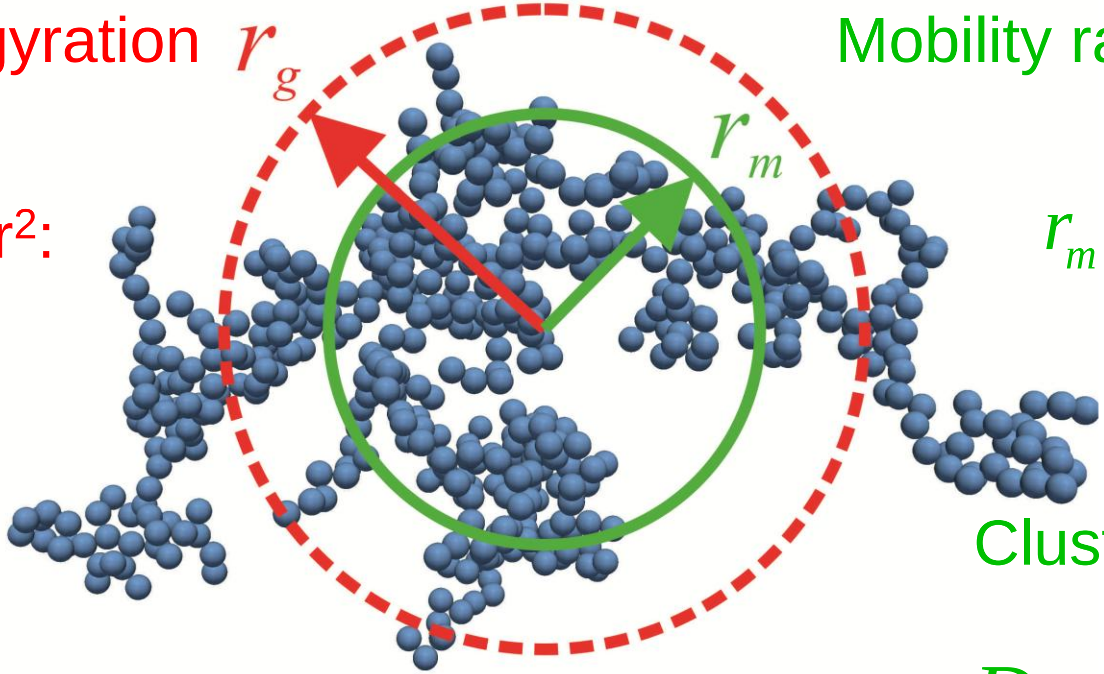
$$\frac{m}{m_p} = k_n \left(\frac{r_g}{r_p} \right)^{D_f}$$

Mass-mobility exponent[3], D_{fm}

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

Radius of gyration

Mobility radius



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

Cluster-cluster[2]:

$$D_f \approx 1.8$$

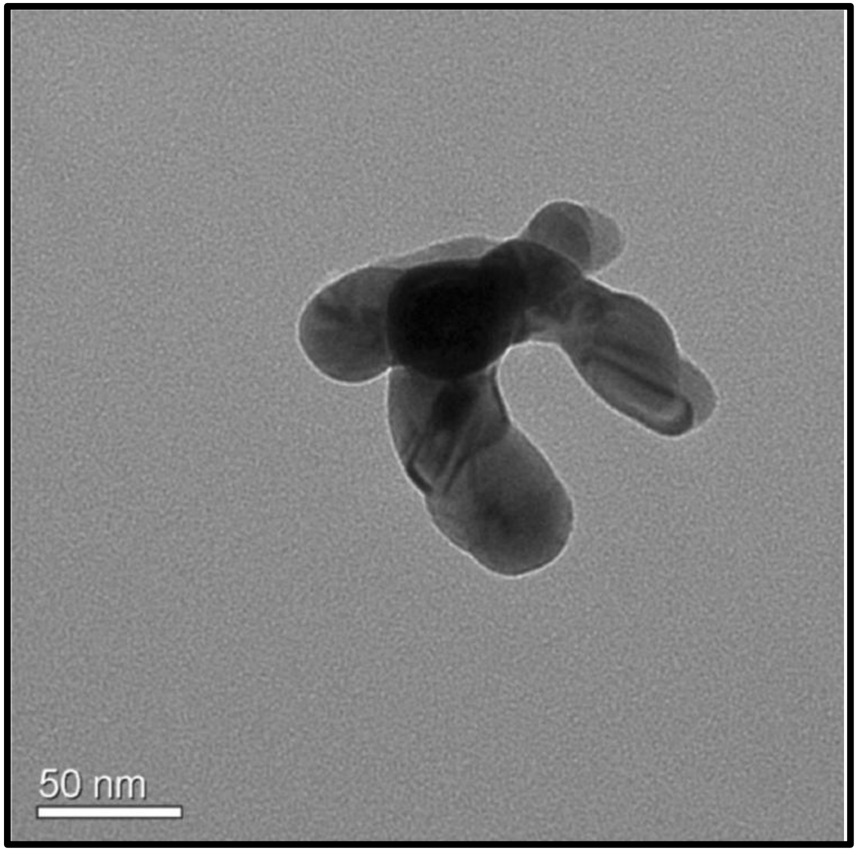
Cluster-cluster[2]:

$$D_{fm} \approx 2.15$$

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.

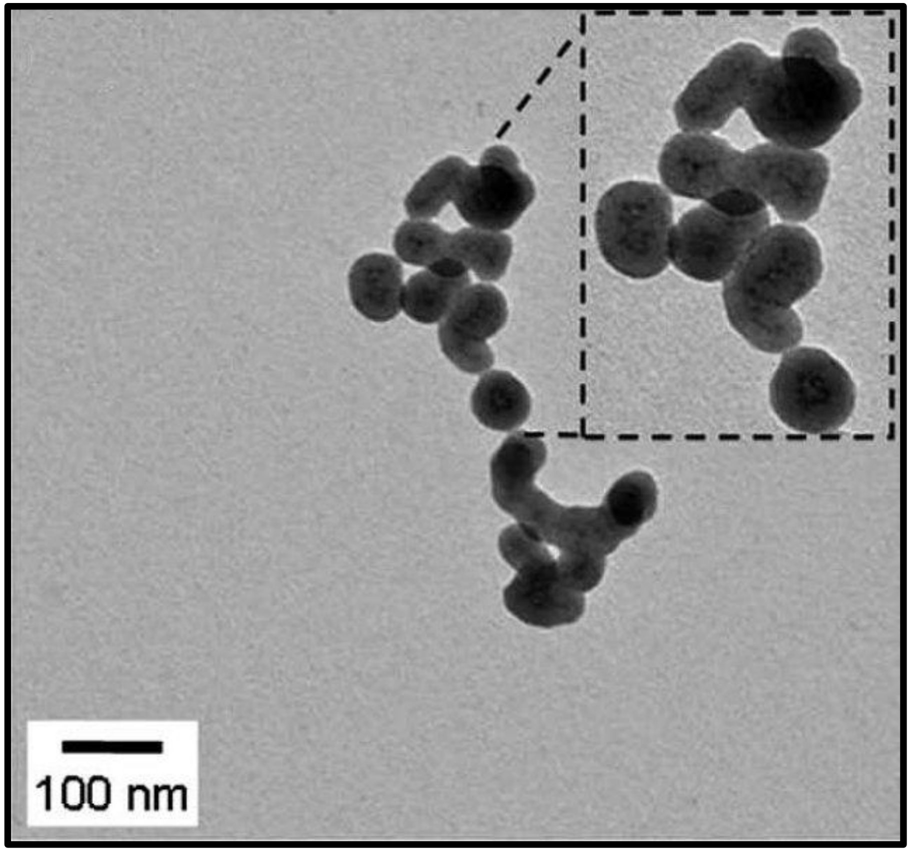
Formation of Aggregates by Sintering

Ag: grain boundary diffusion



S.C. Kim, J. Wang, M.S. Emery, W.G. Shin, G.W. Mulholland & D.Y.H. Pui, *J. Aerosol Sci.* **43** (2009) 344-355.

SiO_2: viscous flow sintering



J.C. Park, D.A. Gilbert, K. Liu & A.Y. Louie, *J. Mater. Chem.* **22** (2012) 8449-8454.

Simulation Method: Viscous Flow Sintering

Geometric Model

Constant strain rate ε in particle

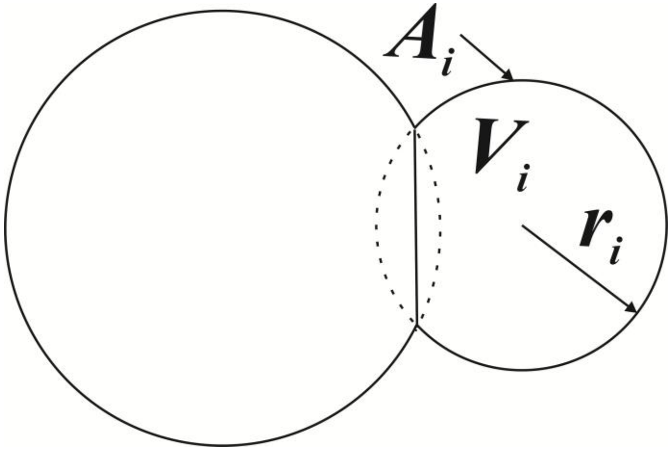
1. Energy balance[1]

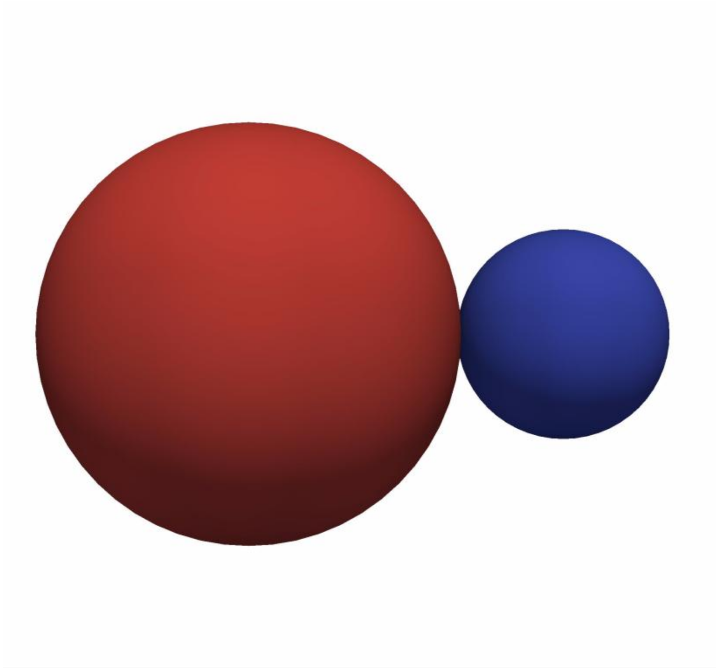
$$\underbrace{\gamma \frac{dA_i}{dt}}_{\text{Change in surface energy}} = \underbrace{\iiint 3\eta\dot{\varepsilon}^2 dV_i}_{\text{viscous dissipation}} = 3\eta\dot{\varepsilon}^2 V_i$$

Change in surface energy = viscous dissipation

2. Mass balance[2]

$$\frac{dV_i}{dt} = 0$$

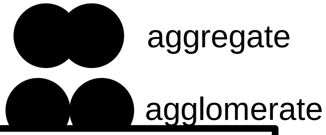


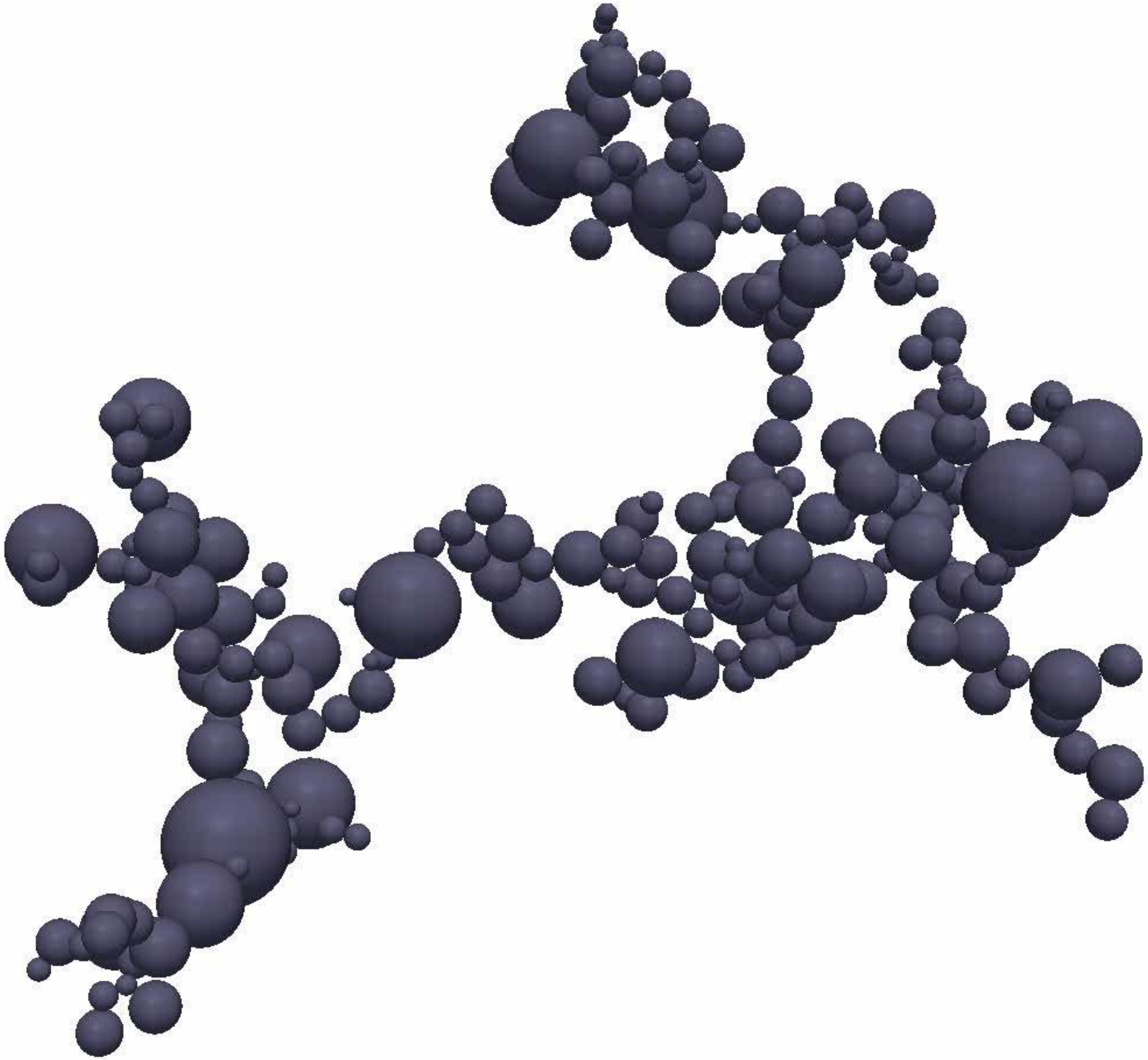


---

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.

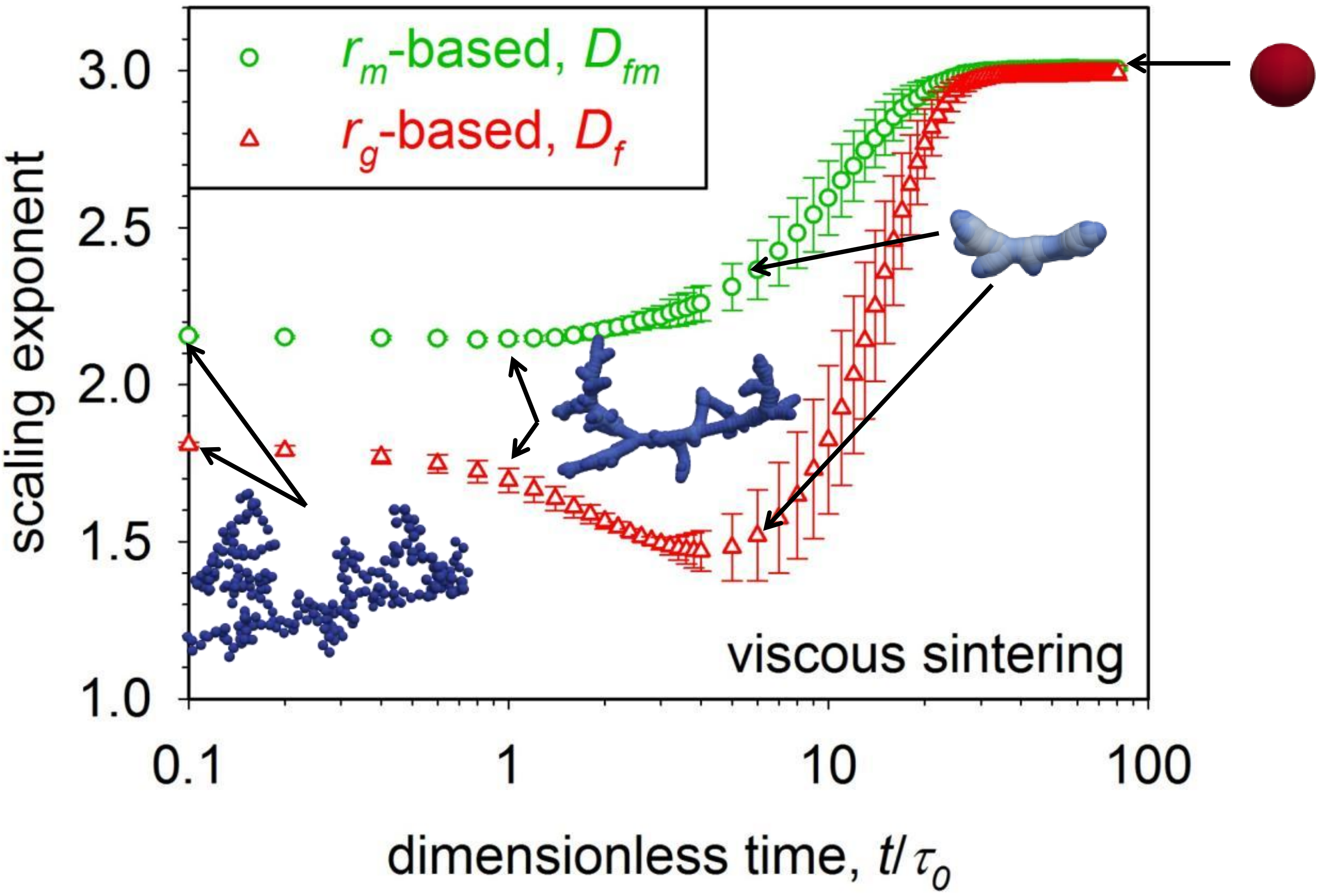
Formation of Aggregates by Sintering





Evolution of D_f & D_{fm}

Ensemble average over 200 clusters with 16-512 PPs

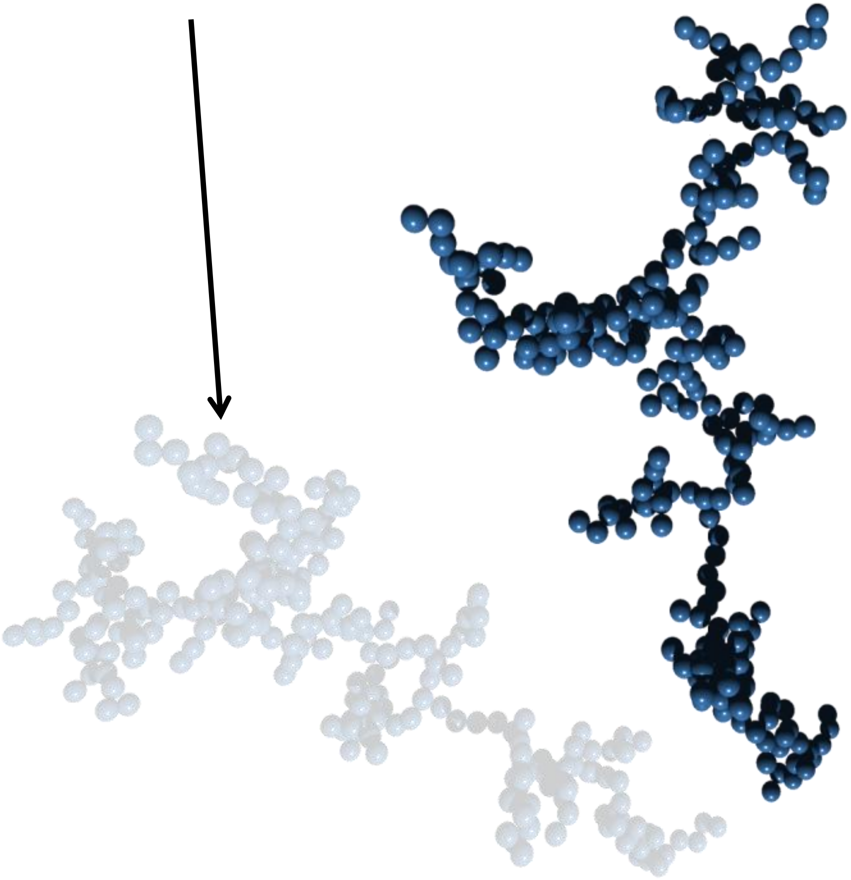


1. A. Camenzind, H. Schulz, A. Teleki, G. Beaucage, T. Narayanan & S.E. Pratsinis, *Eur. J. Inorg. Chem.* (2008) 911-918.

Scaling of Projected Aggregate[1] Area during Sintering

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

a_a: projected area



d_{va}: average PP diameter

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

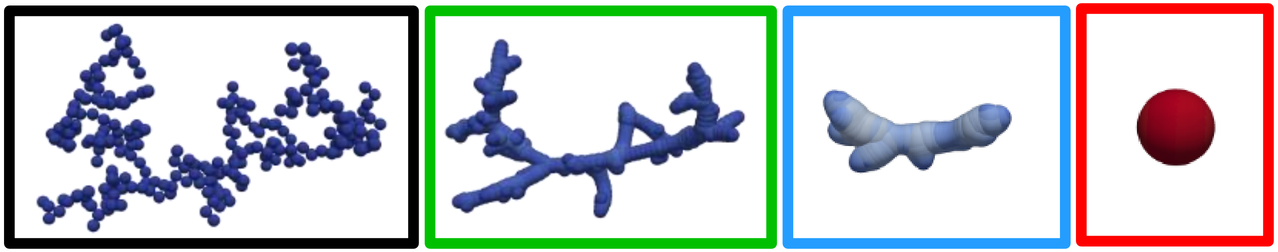
n_{va}: average number of PPs

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

---

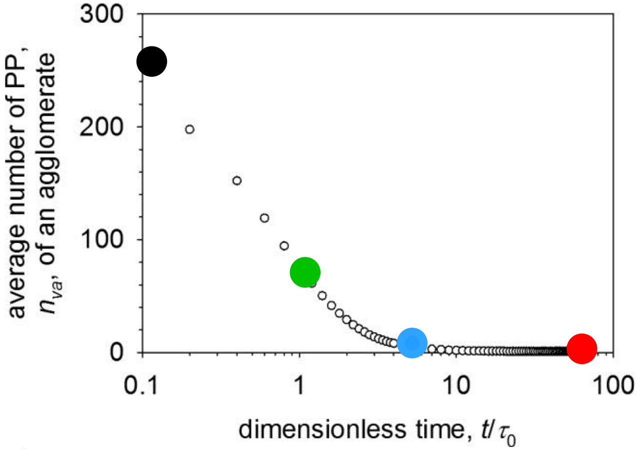
1. A.I. Medalia, *J. Colloid Interface Sci*. **24** (1967) 393-404.

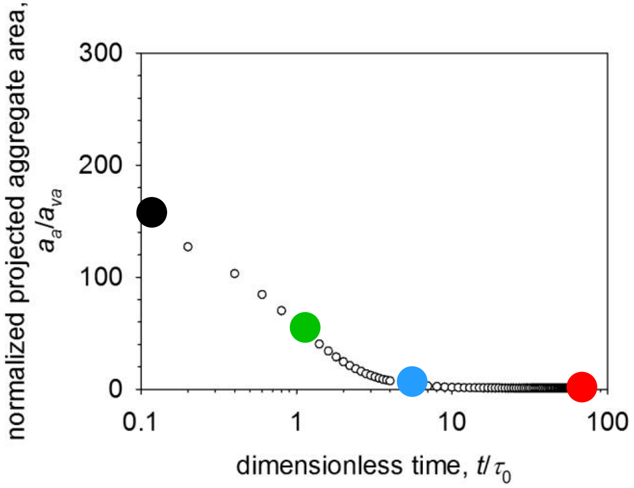
Scaling of Projected Aggregate[1] Area during Sintering

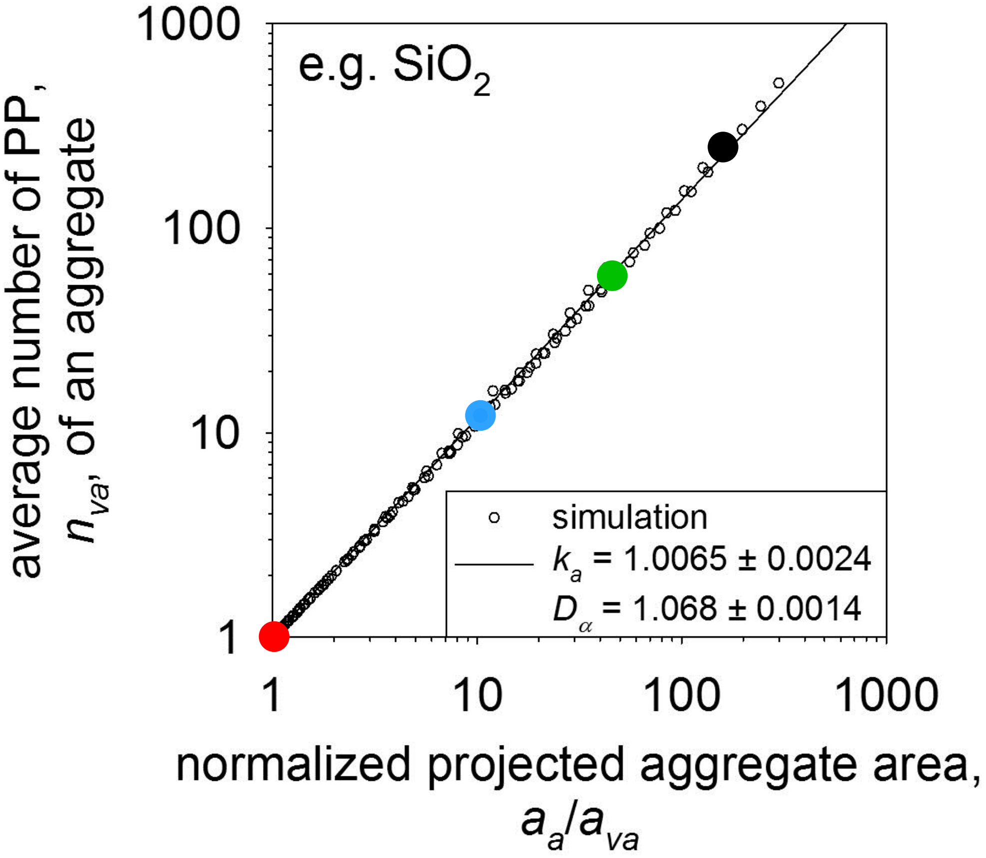


$$n_{va} = k_a \left(\frac{a_a}{a_{va}}\right)^{D_\alpha}$$

viscous flow sintering[2]







---

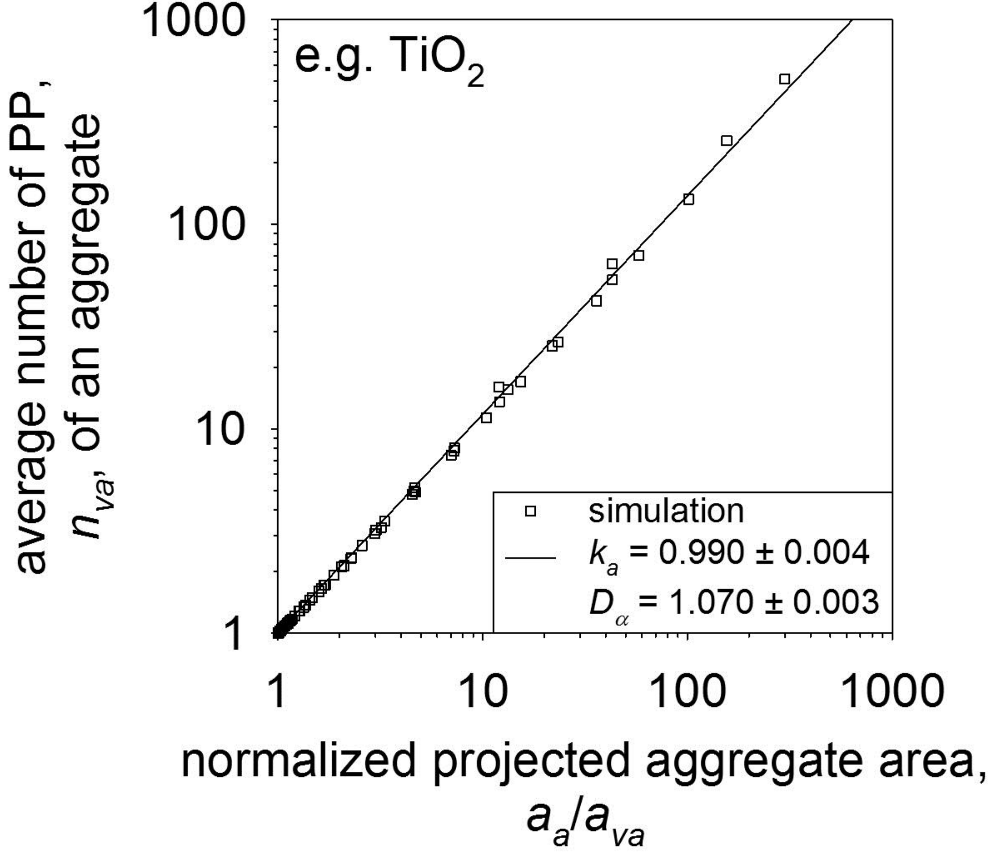
1. A.I. Medalia, *J. Colloid Interface Sci*. **24** (1967) 393-404.
2. M.L. Eggersdorfer, D. Kadau, H.J. Herrmann & S.E. Pratsinis, *Langmuir* **27** (2011) 6358-6367.

Scaling of Projected Aggregate[1] Area during Sintering

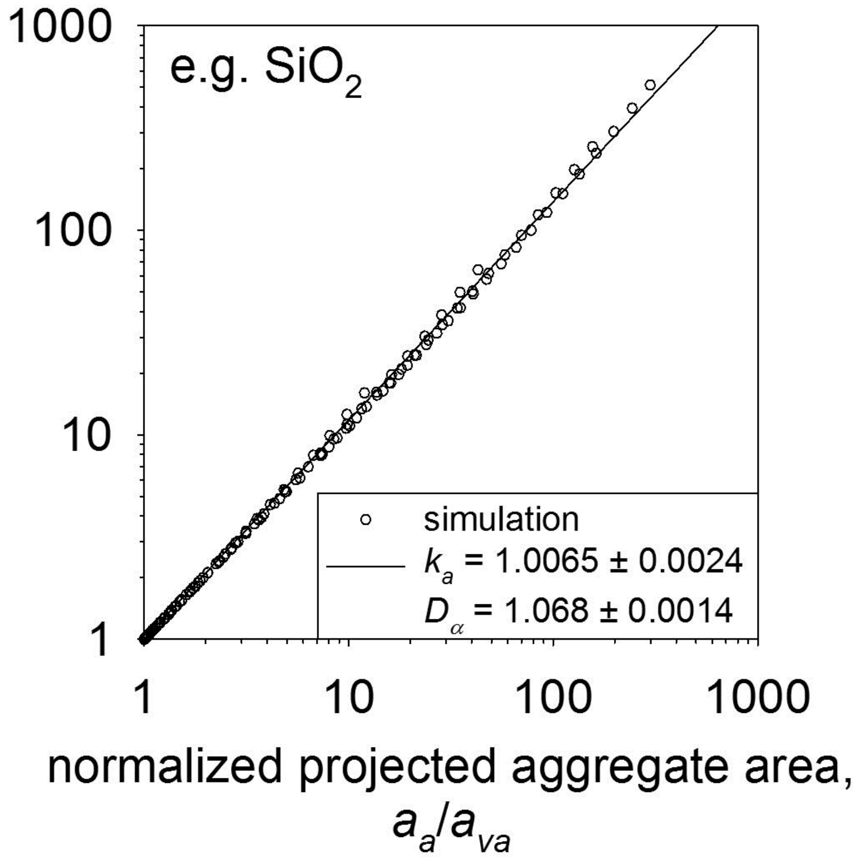
k_a = 1 & **D_α** = 1.07 are nearly independent of sintering mechanism

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

grain boundary diffusion[3]



viscous flow sintering[2]



1. A.I. Medalia, *J. Colloid Interface Sci*. **24** (1967) 393-404.
2. M.L. Eggersdorfer, D. Kadau, H.J. Herrmann & S.E. Pratsinis, *Langmuir* **27** (2011) 6358-6367.
3. M.L. Eggersdorfer, D. Kadau, H.J. Herrmann & S.E. Pratsinis, *J. Aerosol Sci*. **46** (2012) 7-19.

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

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

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.

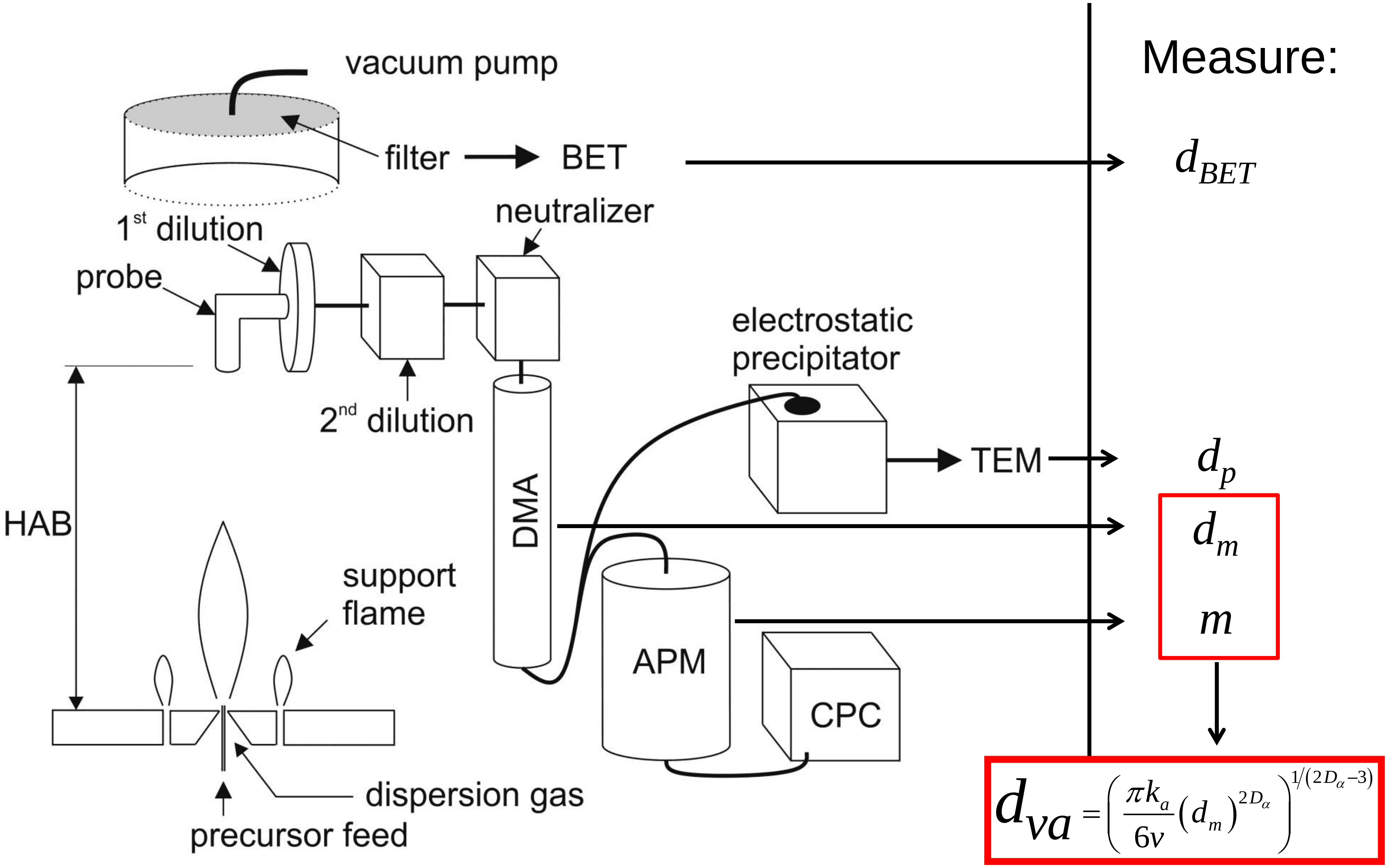
Summary & Conclusions

- Mass-mobility relation in free molecular and transition regime:

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

- independent of time, material or sintering mechanism, with $k_a = 1.0$ & $D_\alpha = 1.07$

Reality Check: Characterization of ZrO_2 Nanoparticles



Measure:

d_{BET}

d_p

d_m

m

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

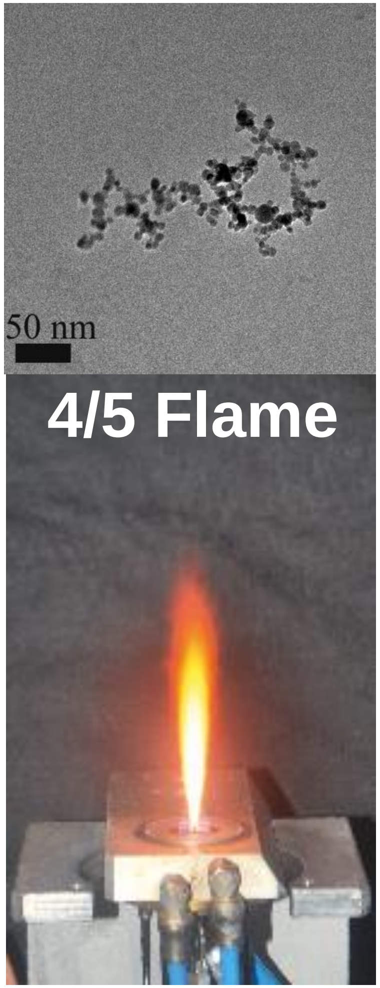
Effect of Liquid Precursor Feed Rate X

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]



4/5 Flame

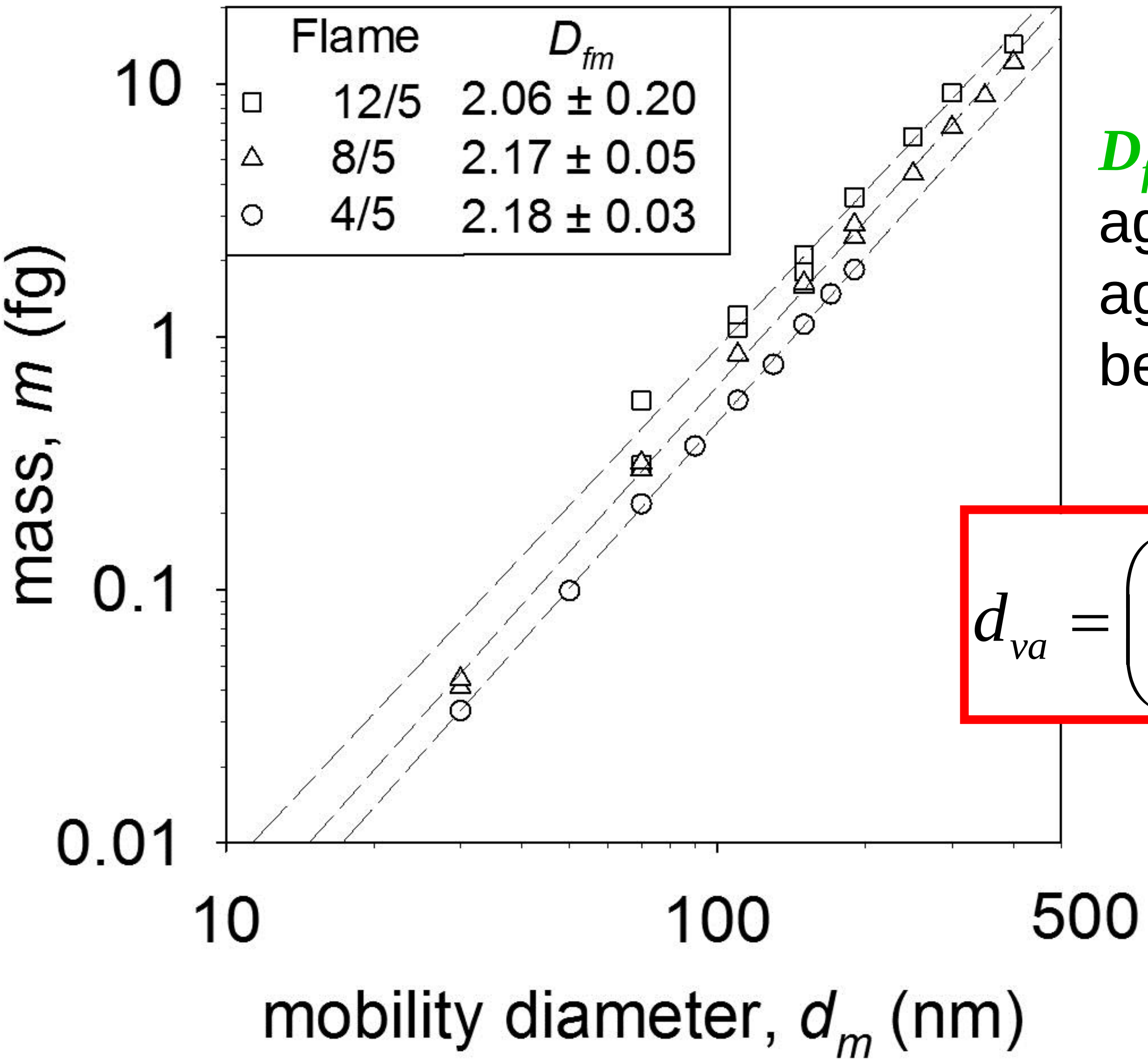
8/5 Flame

12/5 Flame

---

1. S.E. Pratsinis, W.H. Zhu & S. Vemury, Powder Technol. 86 (1996) 87-93.

Effect of Precursor Feed Rate: Mass-Mobility

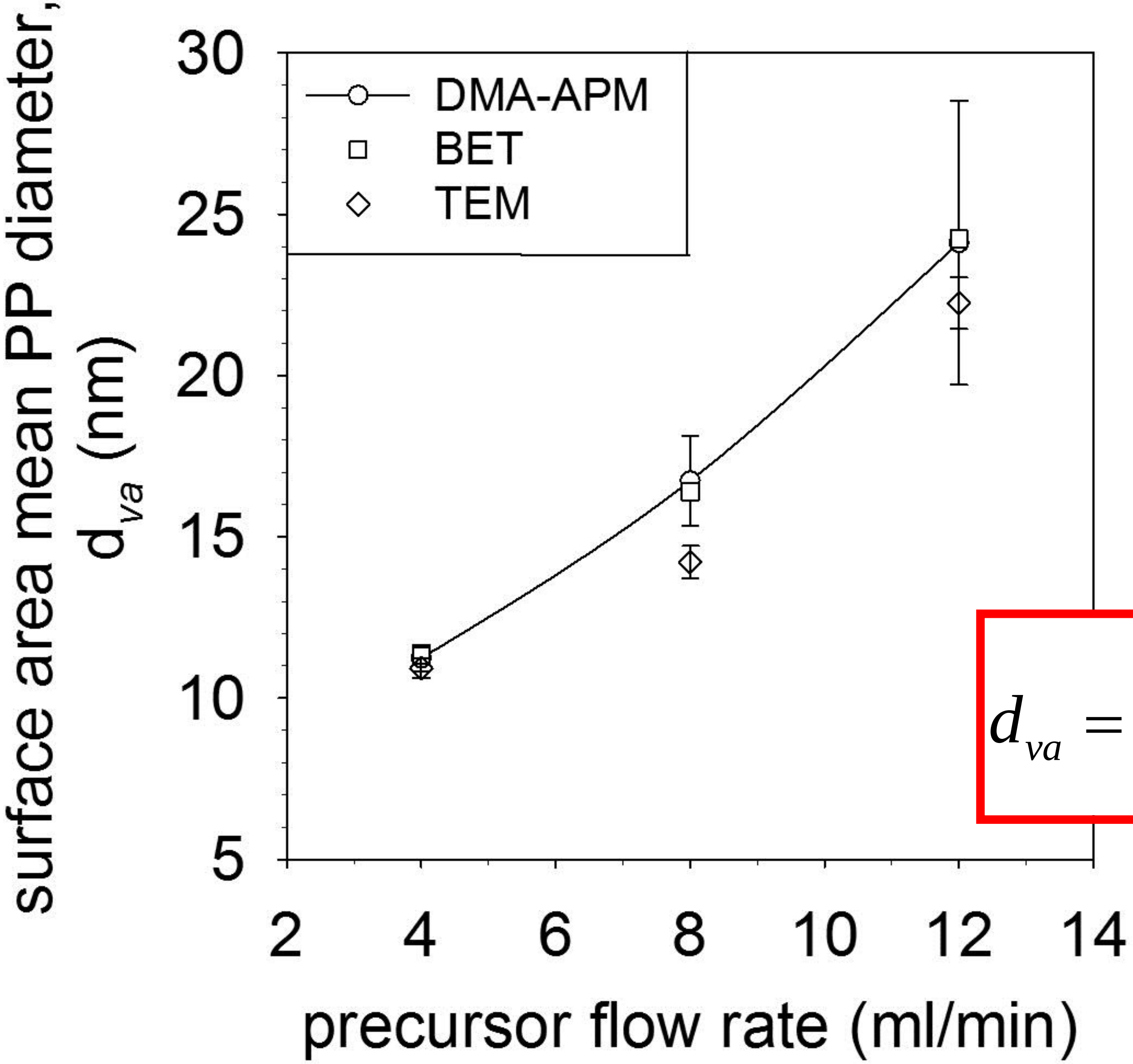


$D_{fm} \approx 2.15$: agglomerates or aggregates at beginning of sintering

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

M.L. Eggersdorfer, A.J. Gröhn, C.M. Sorensen, P.H. McMurry & S.E. Pratsinis (2012) in review.

Effect of Liquid Precursor Feed Rate: d_{va}

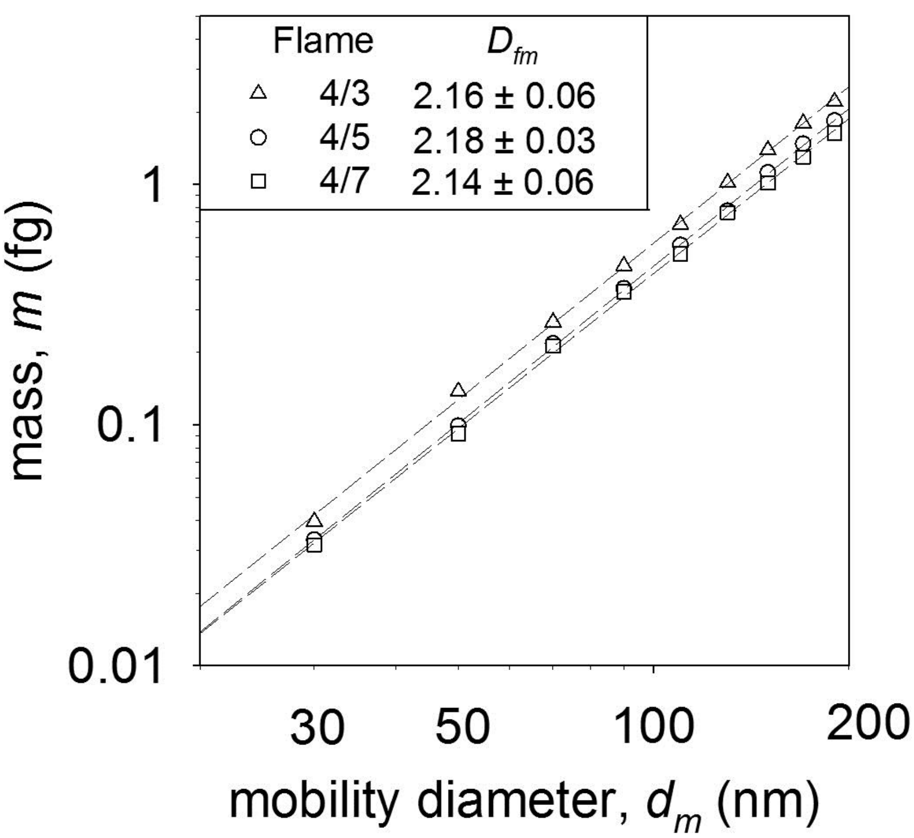


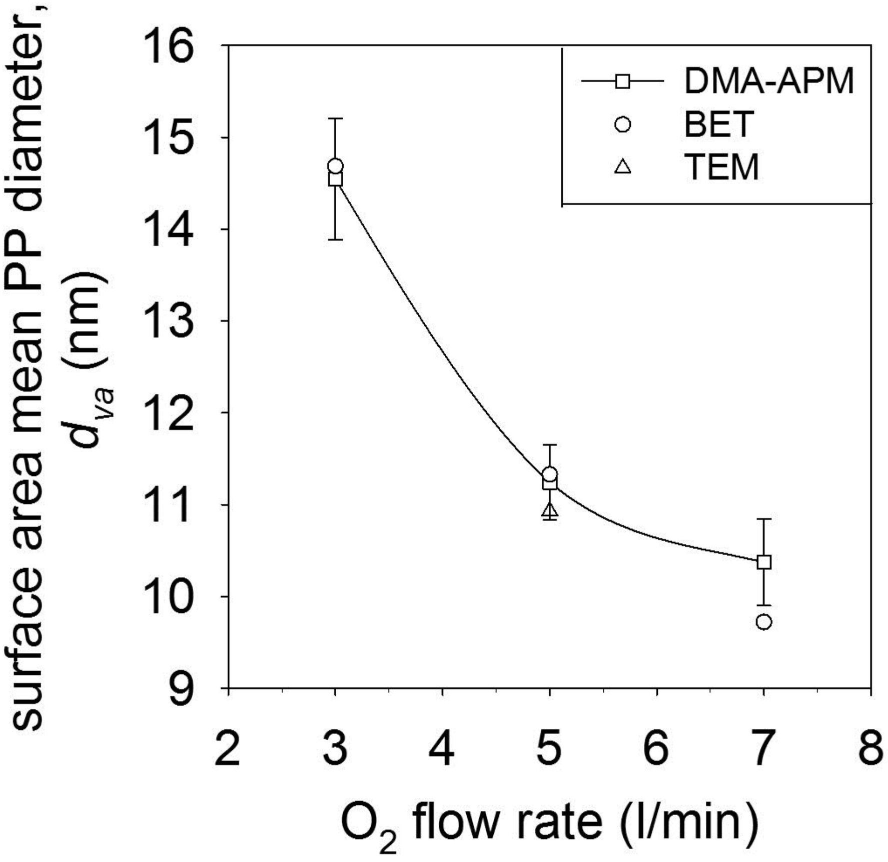
d_{va} can be rapidly determined during nanoparticle production by DMA-APM measurements with material density and

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

M.L. Eggersdorfer, A.J. Gröhn, C.M. Sorensen, P.H. McMurry & S.E. Pratsinis, Mass-Mobility Characterization of Flame-made ZrO2 Aerosols: the Primary Particle Diameter & extent of Aggregation , in review. (2012)

Effect of Oxygen Dispersion Flow Rate





Increasing O_2 flow rate results in a shorter residence time at high temperatures[1]

[1] S.E. Pratsinis, W.H. Zhu & S. Vemury, Powder Technol. 86 (1996) 87-93.

Summary & Conclusions

- Mass-mobility relation in free molecular and transition regime:

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

- independent of time, material or sintering mechanism, with $k_a = 1.0$ & $D_\alpha = 1.07$

- The d_{va} by online mass-mobility measurements is in good agreement with ex-situ BET & TEM measurements.

Creux du Van, Neuchatel, August 22, 2011

Acknowledgments:

Prof. Peter H. McMurry, University of Minnesota

Prof. Christopher M. Sorensen, Kansas State University

Prof. Hans J. Herrmann, ETH Zürich

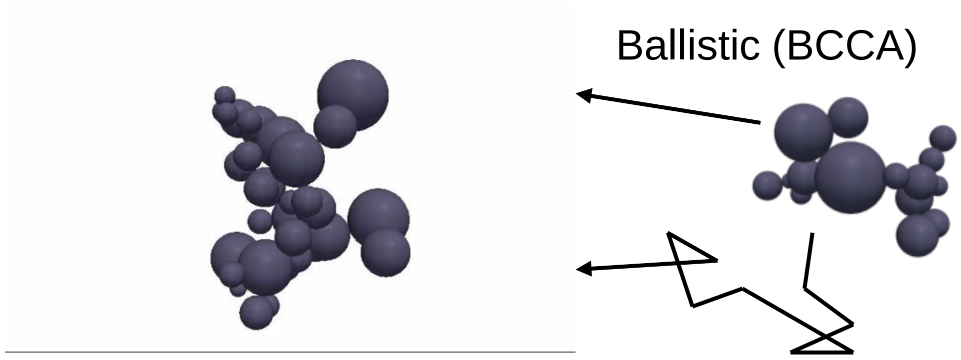
Arto Gröhn, ETH Zürich

Dr. Dirk Kadau, Wärtsilä Schweiz AG

Dr. Frank Krumeich, ETH Zürich

Agglomerates of Polydisperse Primary Particles (PP)

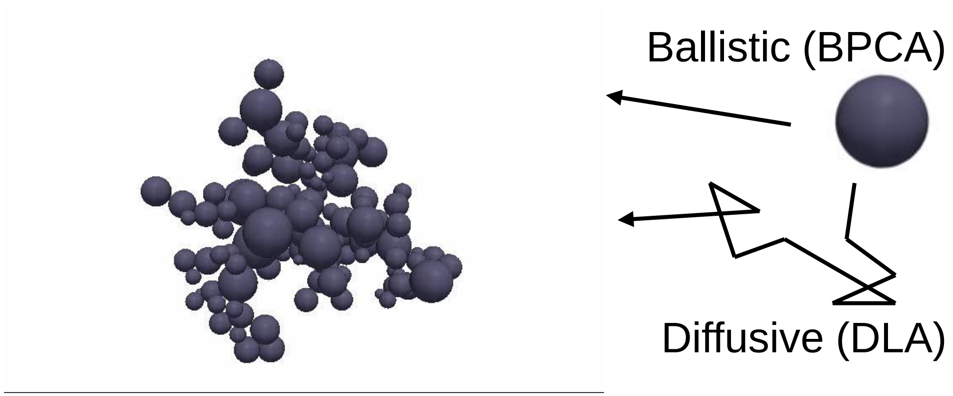
by cluster-cluster agglomeration[1]:



Ballistic (BCCA)

Diffusive (DLCA)

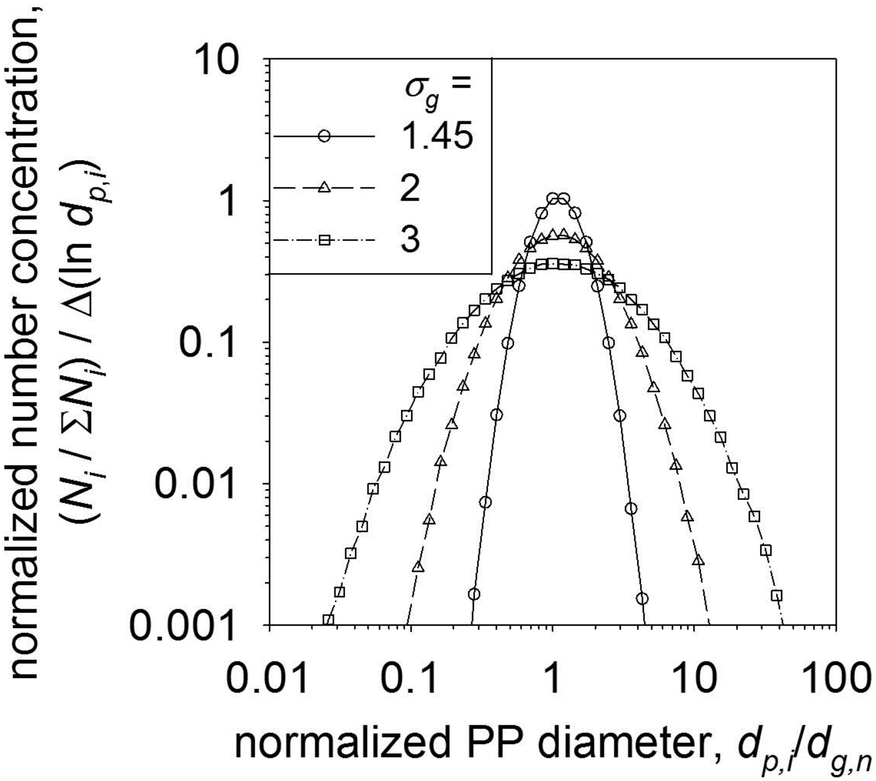
by particle-cluster agglomeration[2]:



Ballistic (BPCA)

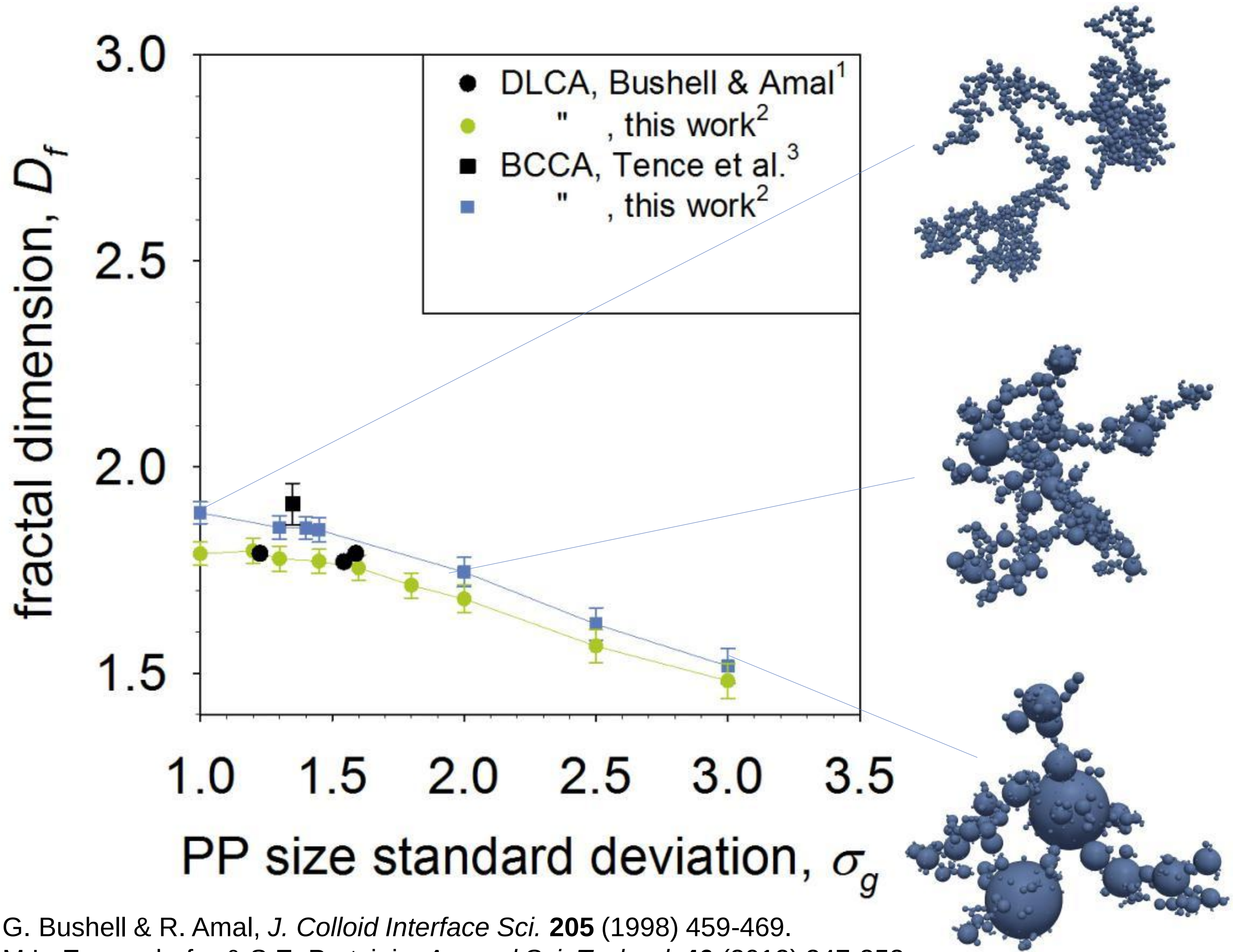
Diffusive (DLA)

Log-normal PP distribution



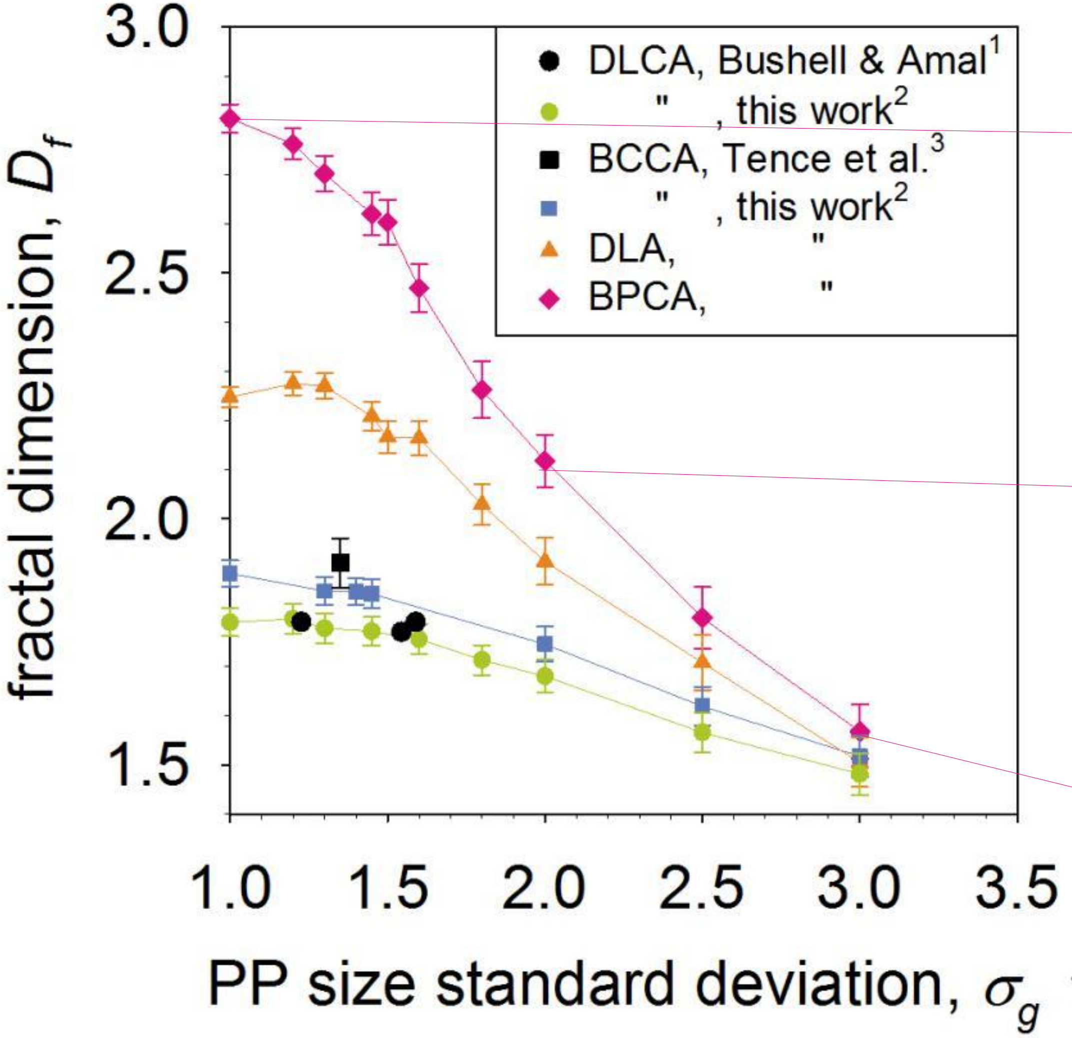
1. R. Botet, R. Jullien & M. Kolb, *J. Phys. A: Math. Gen.* **17** (1984) L75-L79.
2. T.A. Witten & L.M. Sander, *Phys. Rev. Lett.* **47** (1981) 1400-1403.

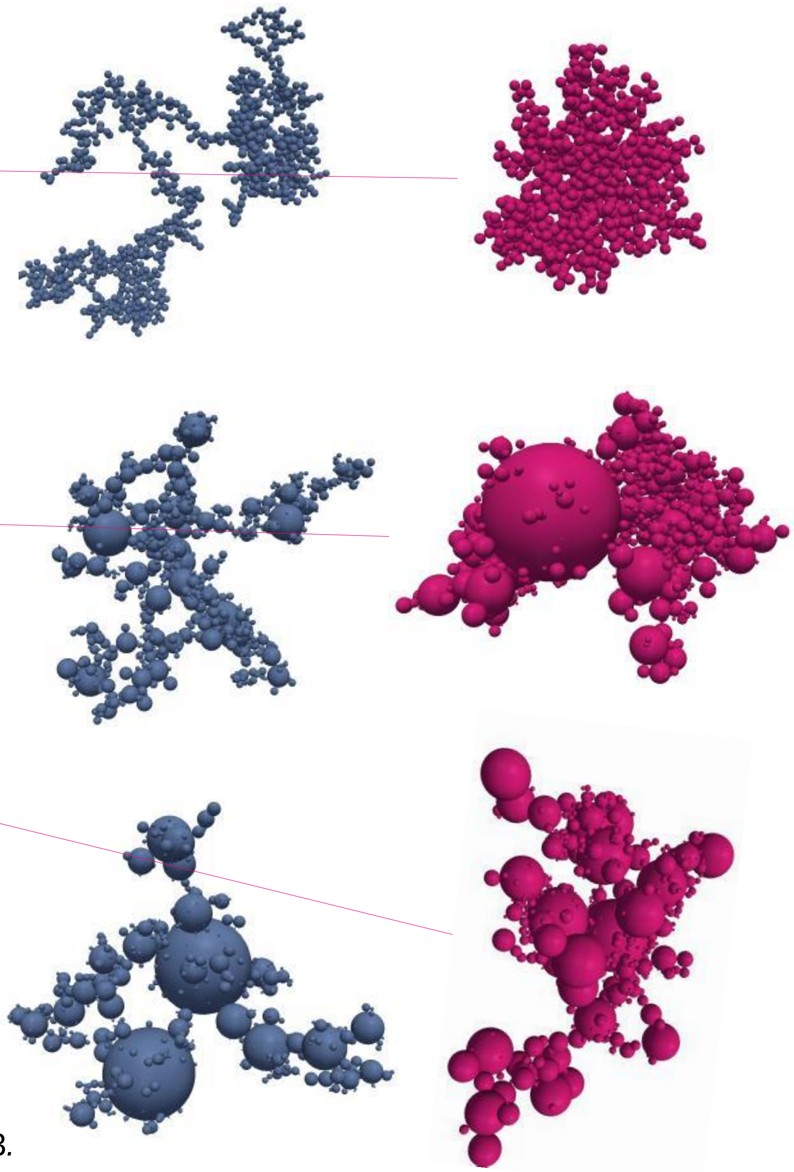
Effect of PP Polydispersity on D_f



1. G. Bushell & R. Amal, *J. Colloid Interface Sci.* **205** (1998) 459-469.
2. M.L. Eggersdorfer & S.E. Pratsinis, *Aerosol Sci. Technol.* **46** (2012) 347-353.
3. M. Tence, J.P. Chevalier & R. Jullien, *J. Phys.* **47** (1986) 1989-1998.

Effect of PP Polydispersity on D_f



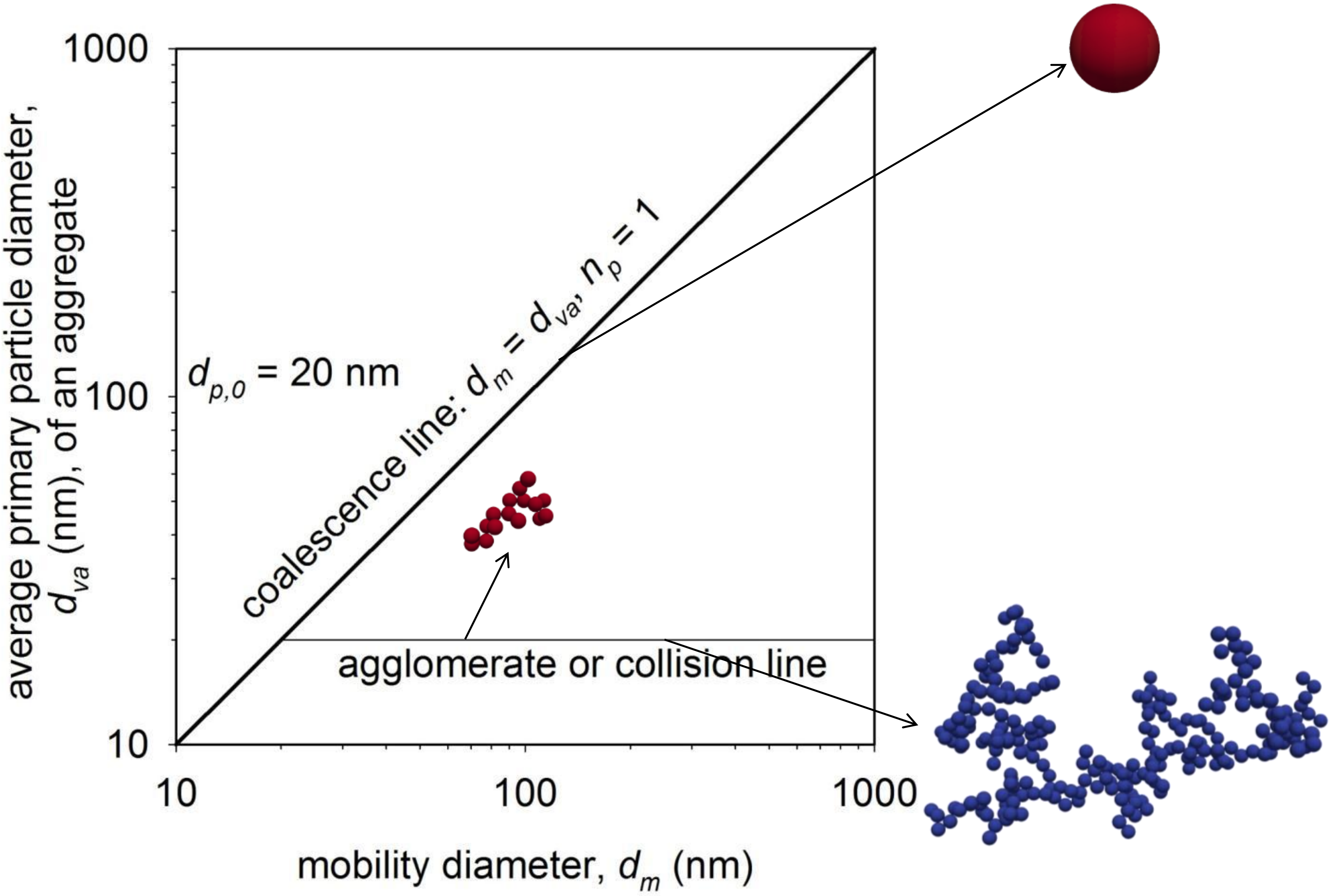


1. G. Bushell & R. Amal, *J. Colloid Interface Sci.* **205** (1998) 459-469.
2. M.L. Eggersdorfer & S.E. Pratsinis, *Aerosol Sci. Technol.* **46** (2012) 347-353.
3. M. Tence, J.P. Chevalier & R. Jullien, *J. Phys.* **47** (1986) 1989-1998.

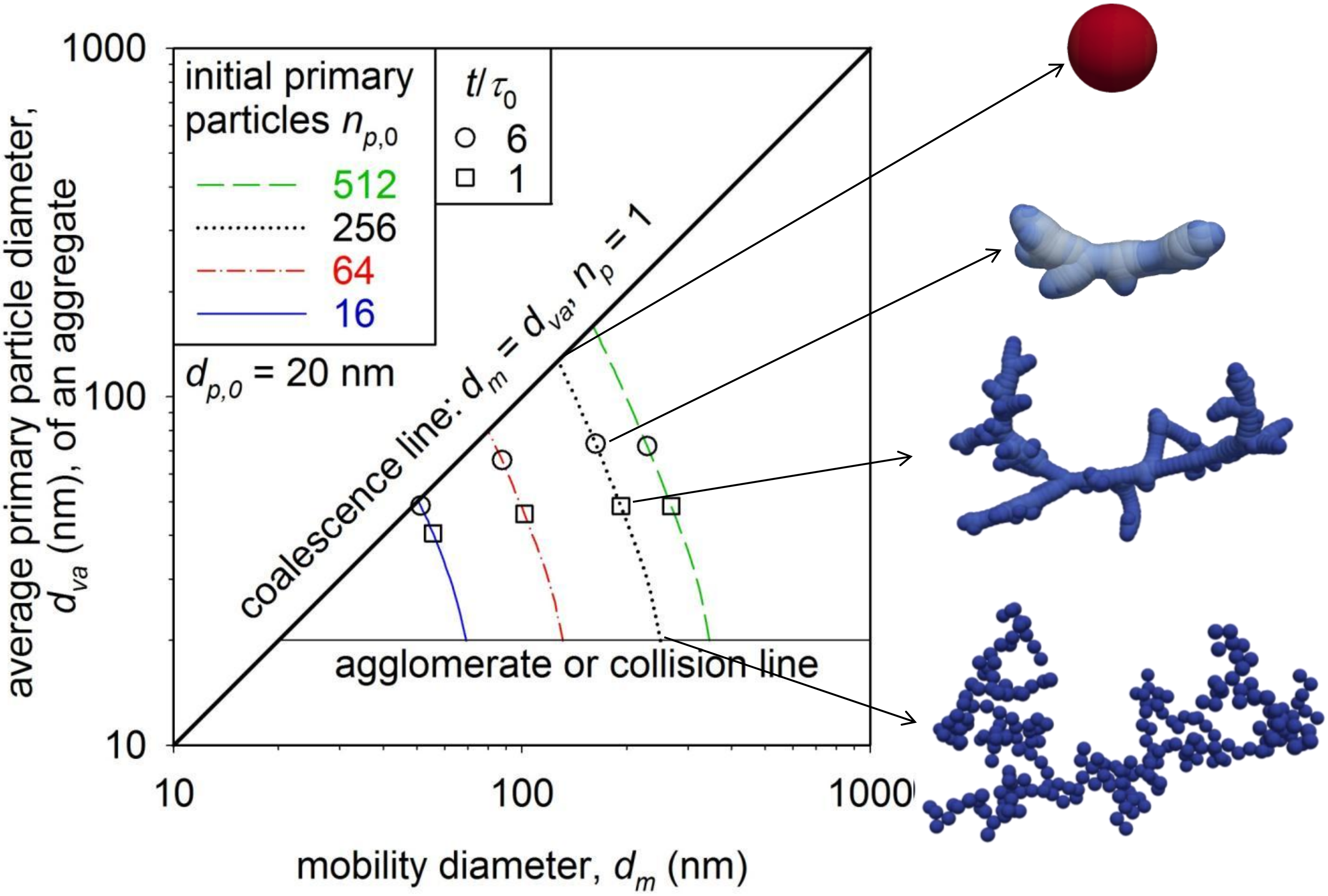
Summary & Conclusions

- PP Polydispersity reduces D_f & D_{fm} and determines agglomerate structure for large σ_g (> 2.5)

Mobility d_m & Primary Particle Diameter d_{va} during Sintering



Mobility d_m & Primary Particle Diameter d_{va} during Sintering



Application to Silver Nanoparticle Sintering[1]

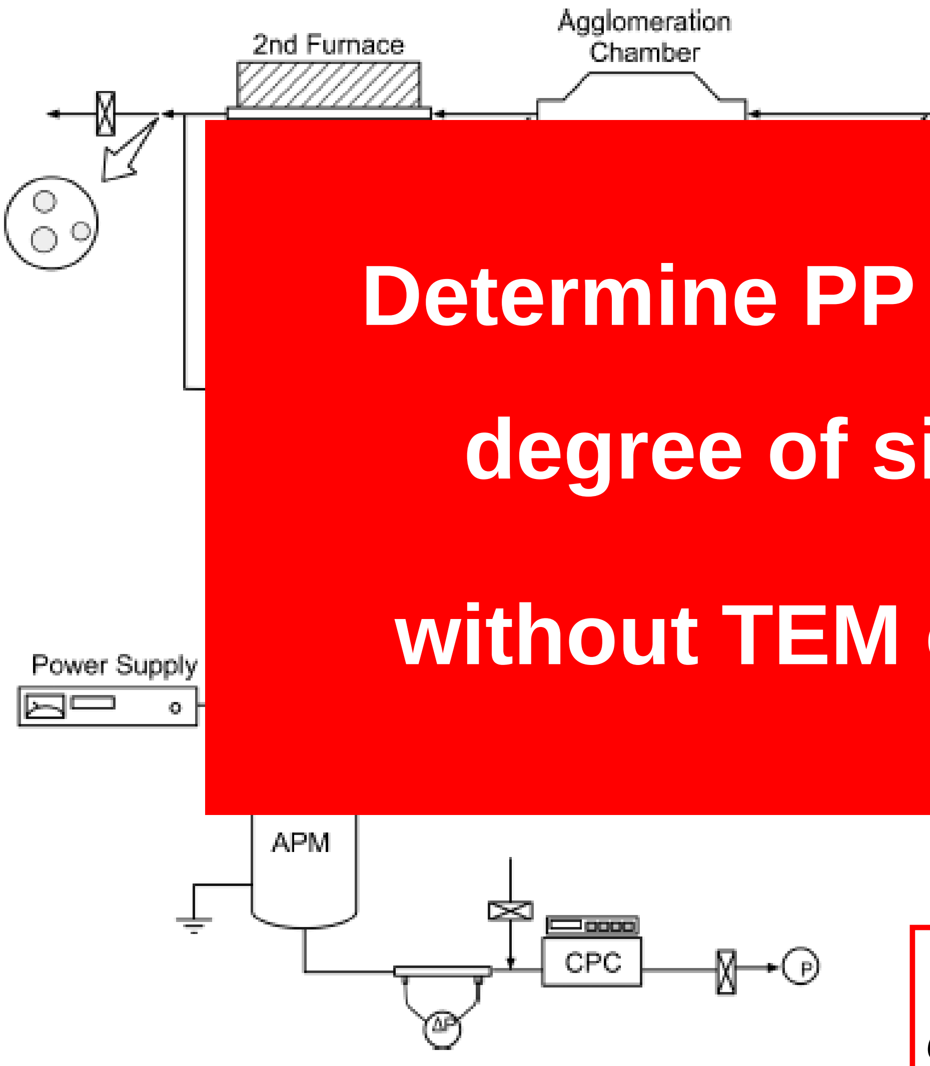
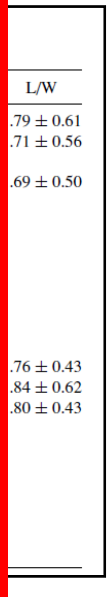


FIG. 4. DMA-APM system for NP agglomerates mobility diameter

Determine PP diameter d_{va} and degree of sintering ONLINE without TEM or sintering rate



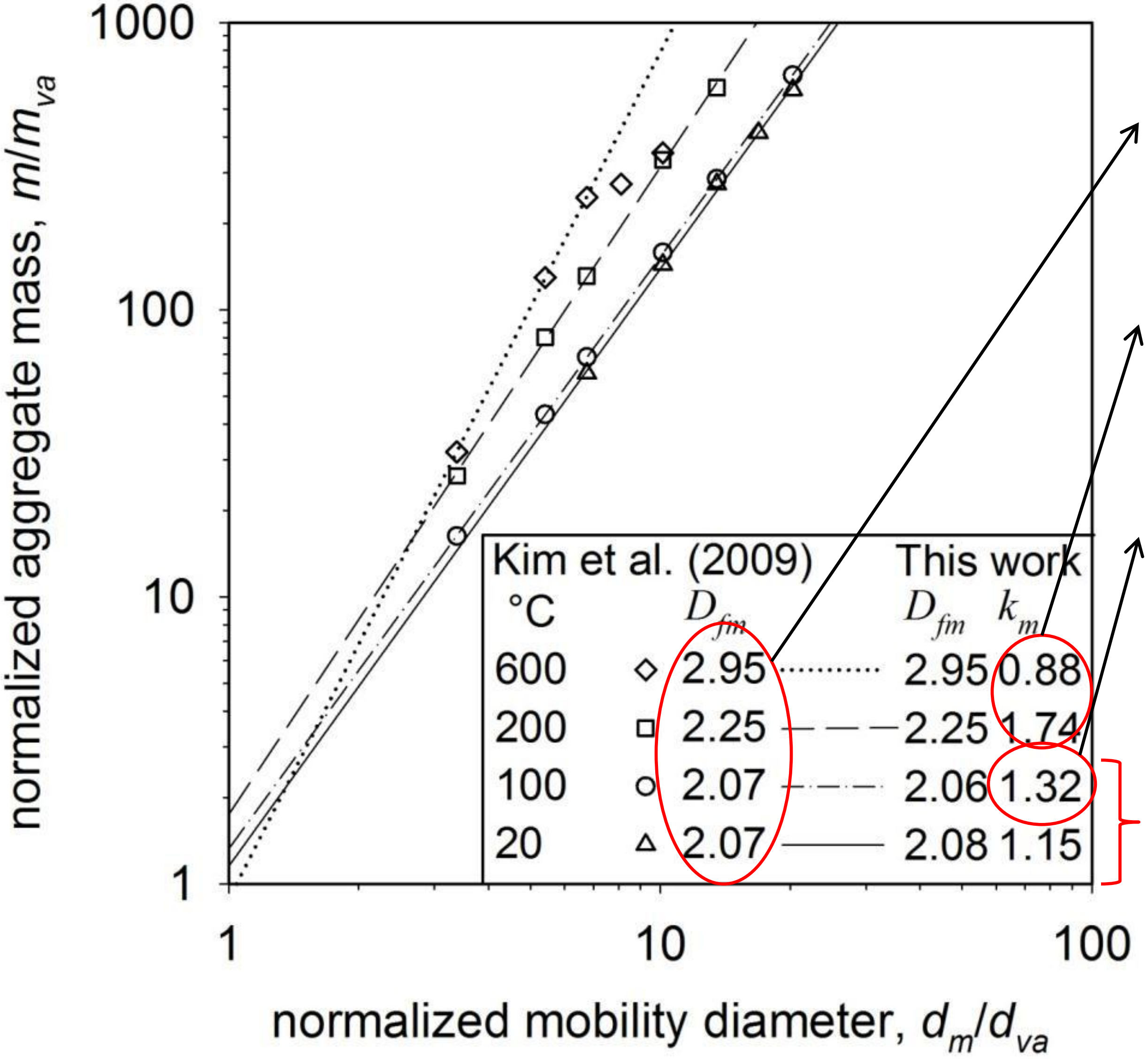
L/W
.79 ± 0.61
.71 ± 0.56
.69 ± 0.50
.76 ± 0.43
.84 ± 0.62
.80 ± 0.43

ρ = 10500 kg/m^3

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

[1] S.C. Kim, J. Wang, M.S. Emery, W.G. Shin, G.W. Mulholland & D.Y.H. Pui, *J. Aerosol Sci.* **43** (2009) 344-355.

Comparison to Experiments[1]: Sintering of Ag – Nanoparticle Aggregates



Monotonic increase in D_{fm}

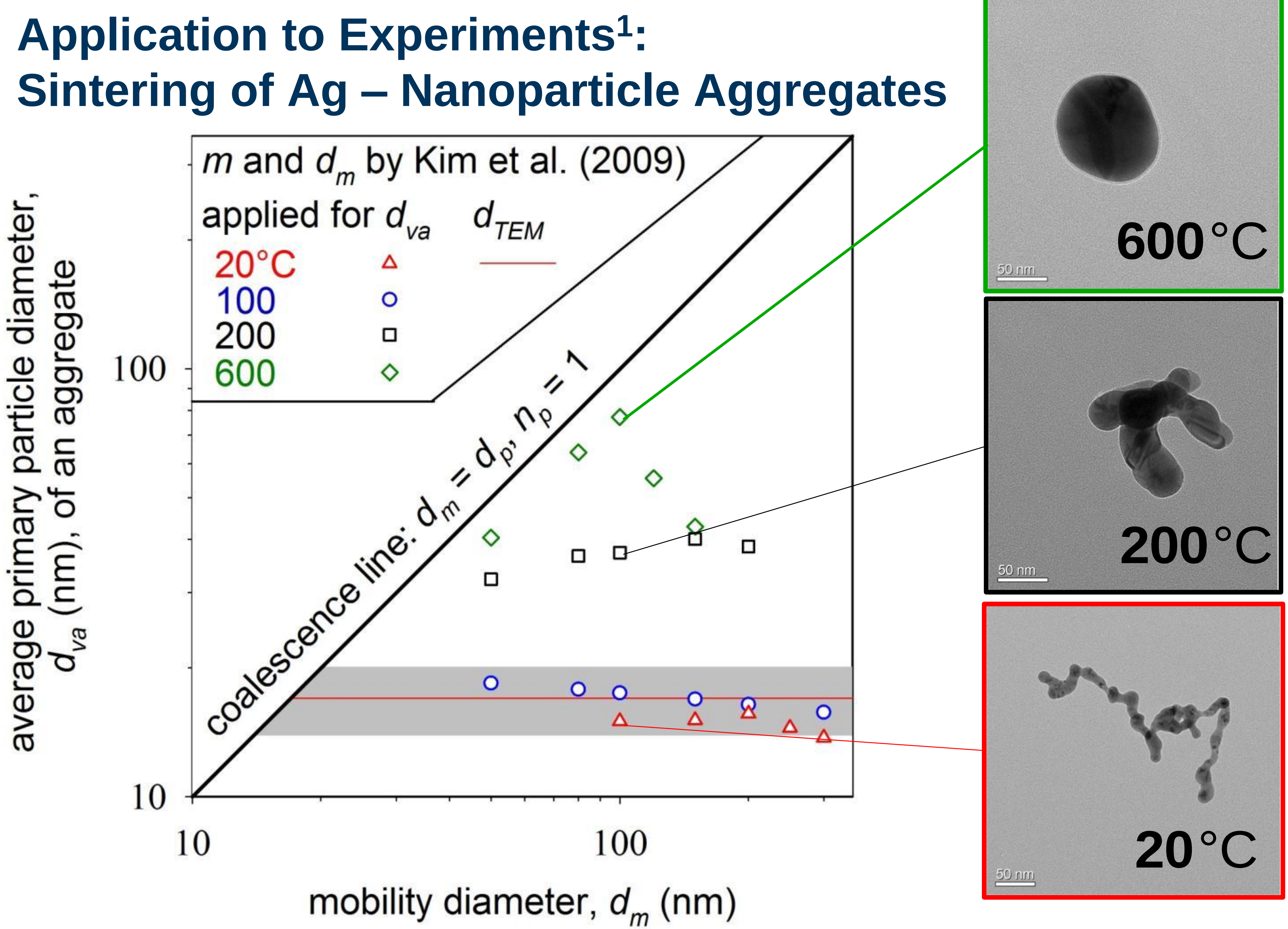
A maximum in k_m is reached

Increase in prefactor k_m is indication for sinter neck formation

Close to theoretical value of D_{fm} = 2.15 for DLCA[2]

1. S.C. Kim, J. Wang, M.S. Emery, W.G. Shin, G.W. Mulholland & D.Y.H. Pui, *J. Aerosol Sci.* **43** (2009) 344-355.
2. C.M. Sorensen, *Aerosol Sci. Technol.* **45** (2011) 755-769.

Application to Experiments[1]: Sintering of Ag – Nanoparticle Aggregates

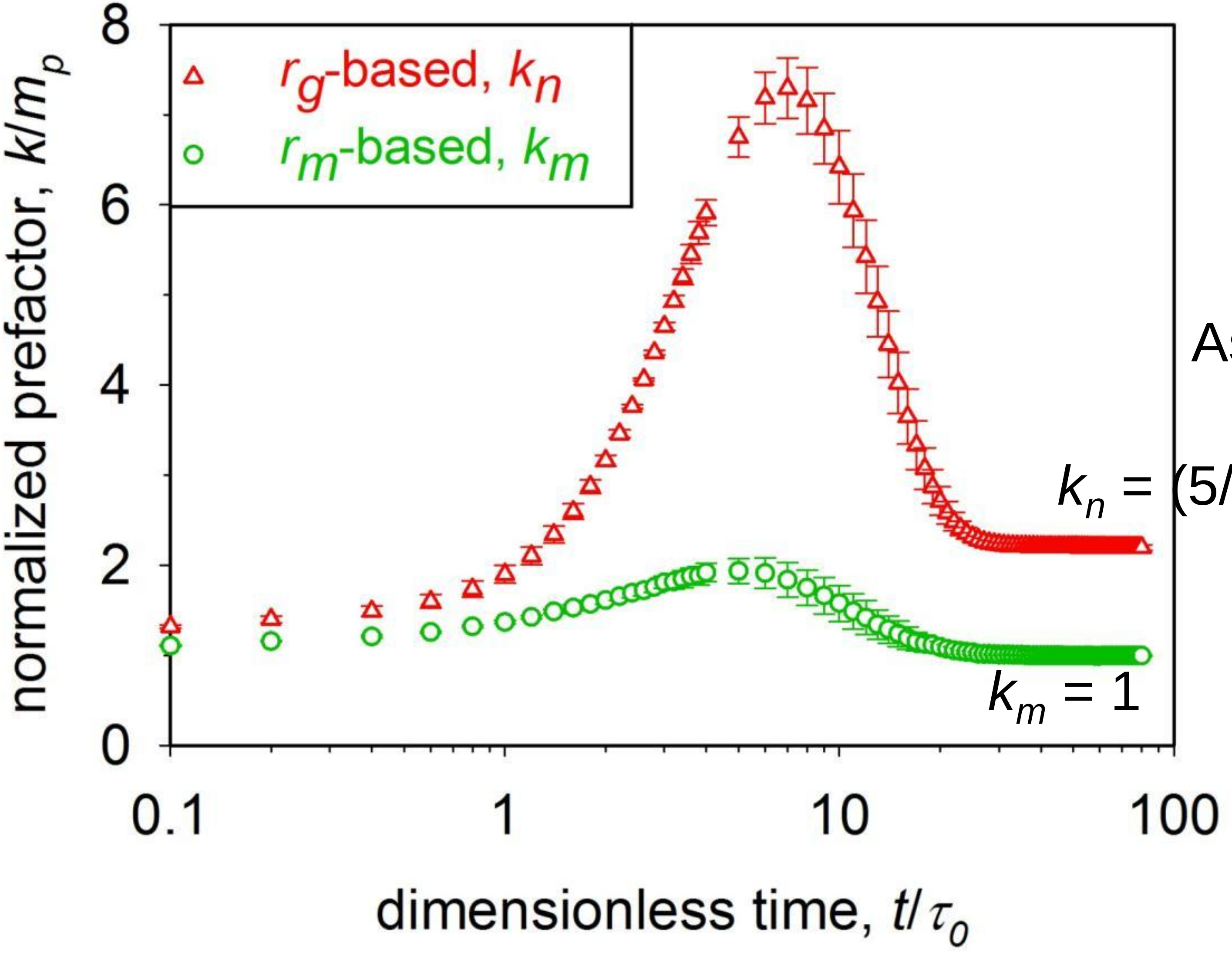


1. S.C. Kim, J. Wang, M.S. Emery, W.G. Shin, G.W. Mulholland & D.Y.H. Pui, *J. Aerosol Sci.* **43** (2009) 344-355.

Evolution of Prefactors k_n & k_m

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

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



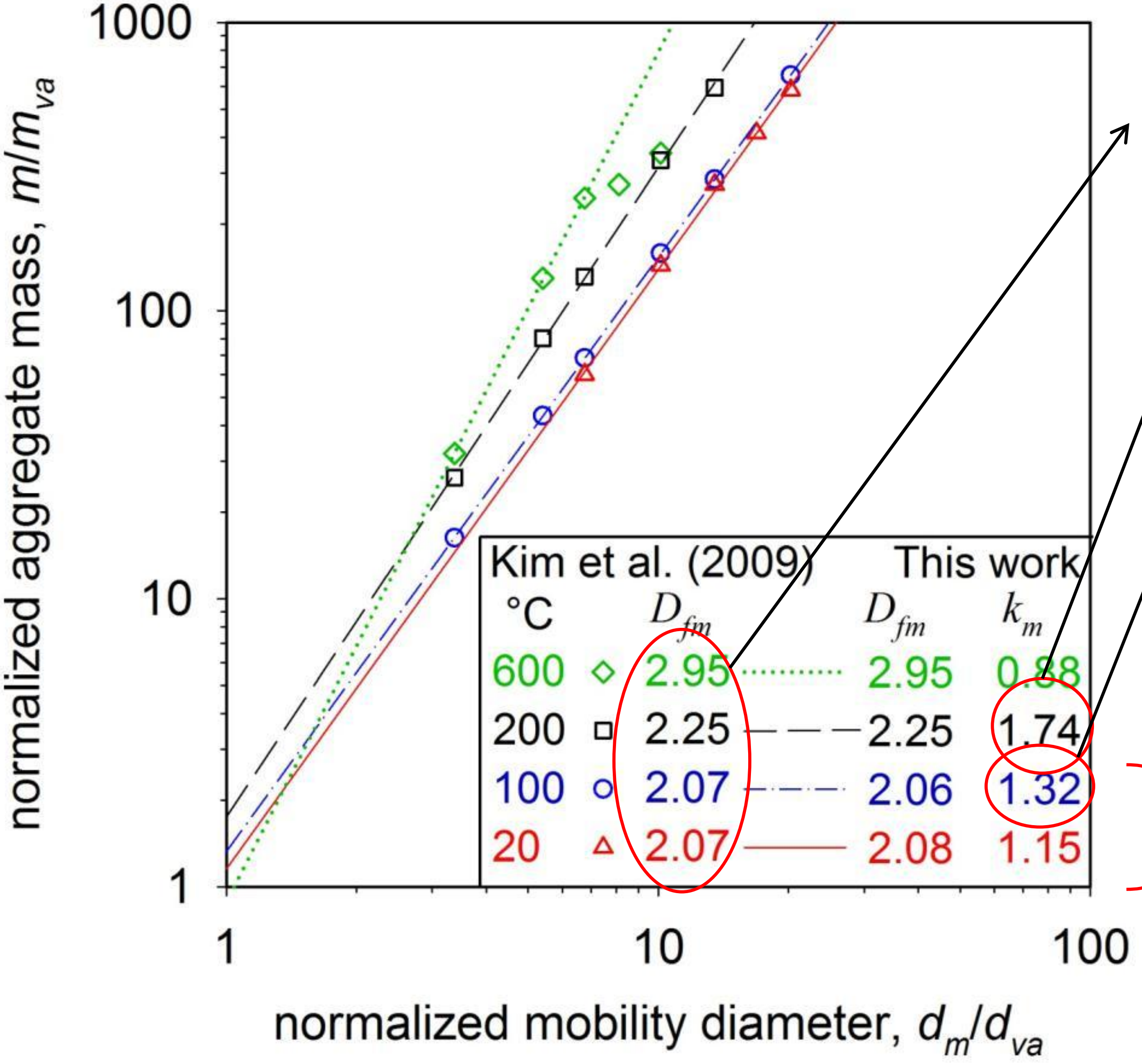
Asymptotic values

$k_n = (5/3)^{3/2} = 2.15$

$k_m = 1$

Both k_n and k_m reach a maximum

Comparison to Experiments[1]: Sintering of Ag – Nanoparticle Aggregates



Monotonic increase in D_{fm}

A maximum in k_m is reached

Increase in prefactor k_m is indication for sinter neck formation

Close to theoretical value of D_{fm} = 2.15 for DLCA[2]

---

1. S.C. Kim, J. Wang, M.S. Emery, W.G. Shin, G.W. Mulholland & D.Y.H. Pui, *J. Aerosol Sci.* **43** (2009) 344-355.
2. C.M. Sorensen, *Aerosol Sci. Technol.* **45** (2011) 755-769.

Summary and Conclusions I

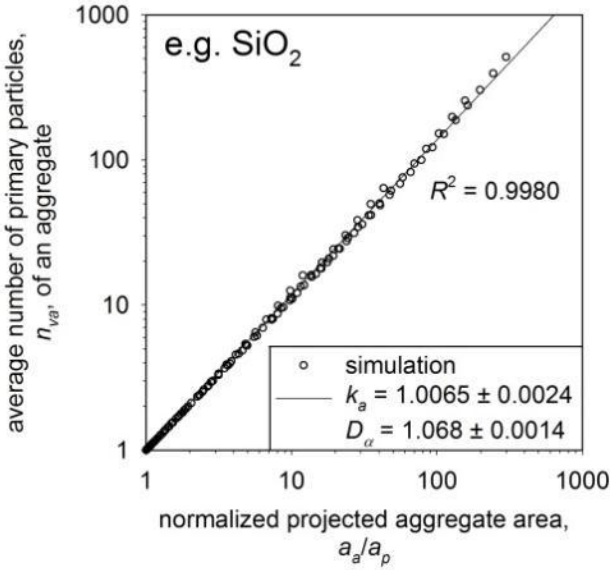
1. We propose a formula to calculate d_{va} for nanoparticle agglomerates/aggregates/spheres.

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

2. Viscous flow[1] and grain boundary diffusion sintering simulations show that

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

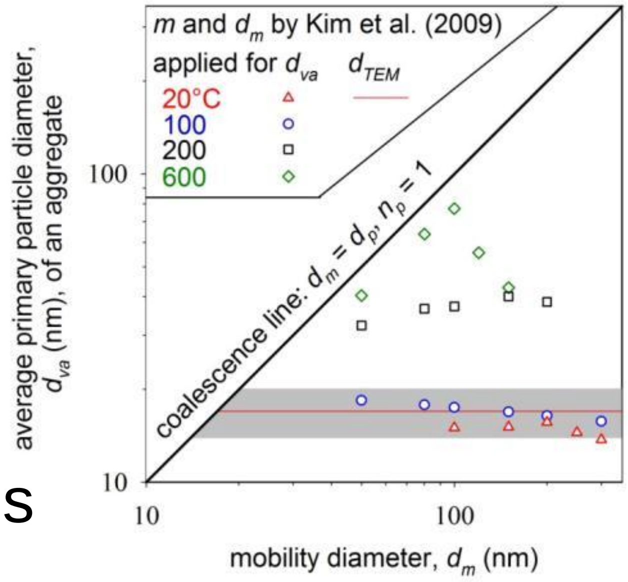
is valid during sintering → D_α & k_a.



---

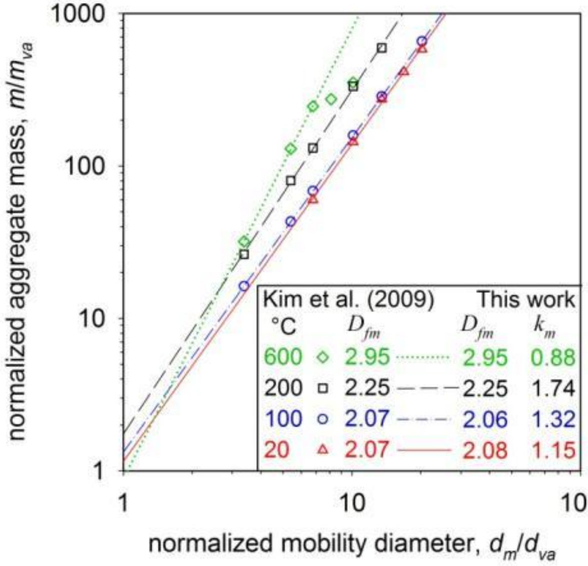
[1] M.L. Eggersdorfer, D. Kadau, H.J. Herrmann & S.E. Pratsinis, *Langmuir* **27** (2011) 6358-6367.

Summary and Conclusions II



3. d_{va} & n_{va} can be determined by realtime mass-mobility (e.g. DMA-APM) measurements using D_α & k_a from simulations.

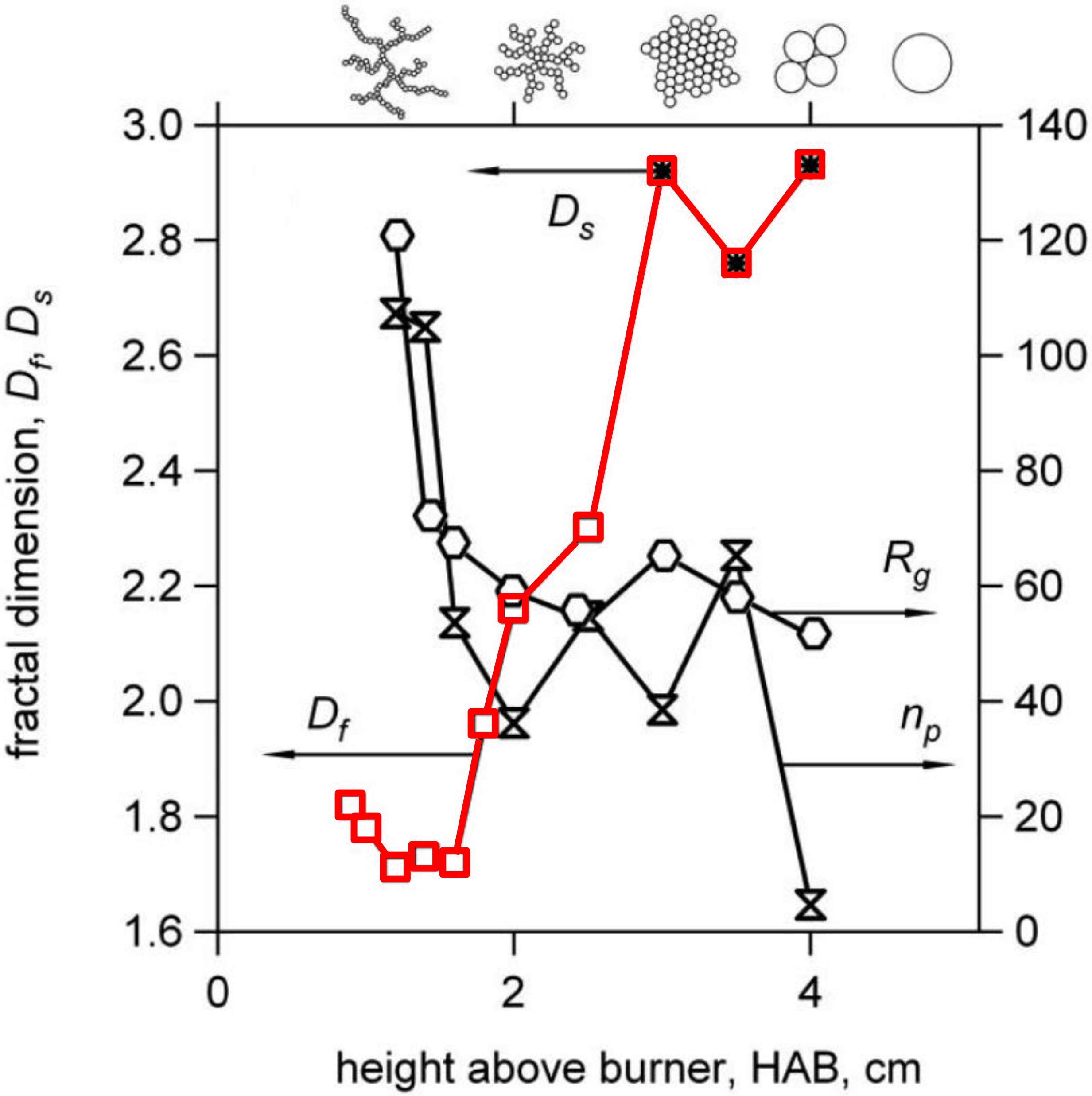
4. Good agreement between d_{va} and d_{TEM} is found.

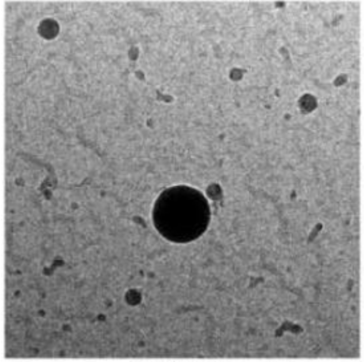


5. The extent of sintering is best described by mass-mobility exponent D_{fm} (monotonic increase).

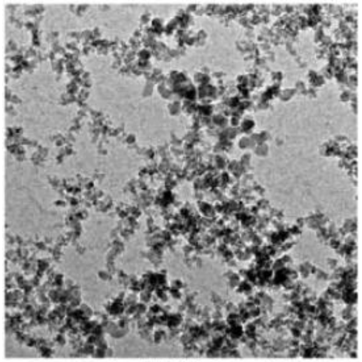
6. Increase in prefactor k_m is an indication for sinter neck formation.

meggers@ptl.mavt.ethz.ch

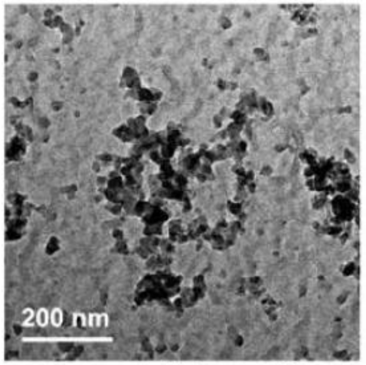




HAB = 5 cm



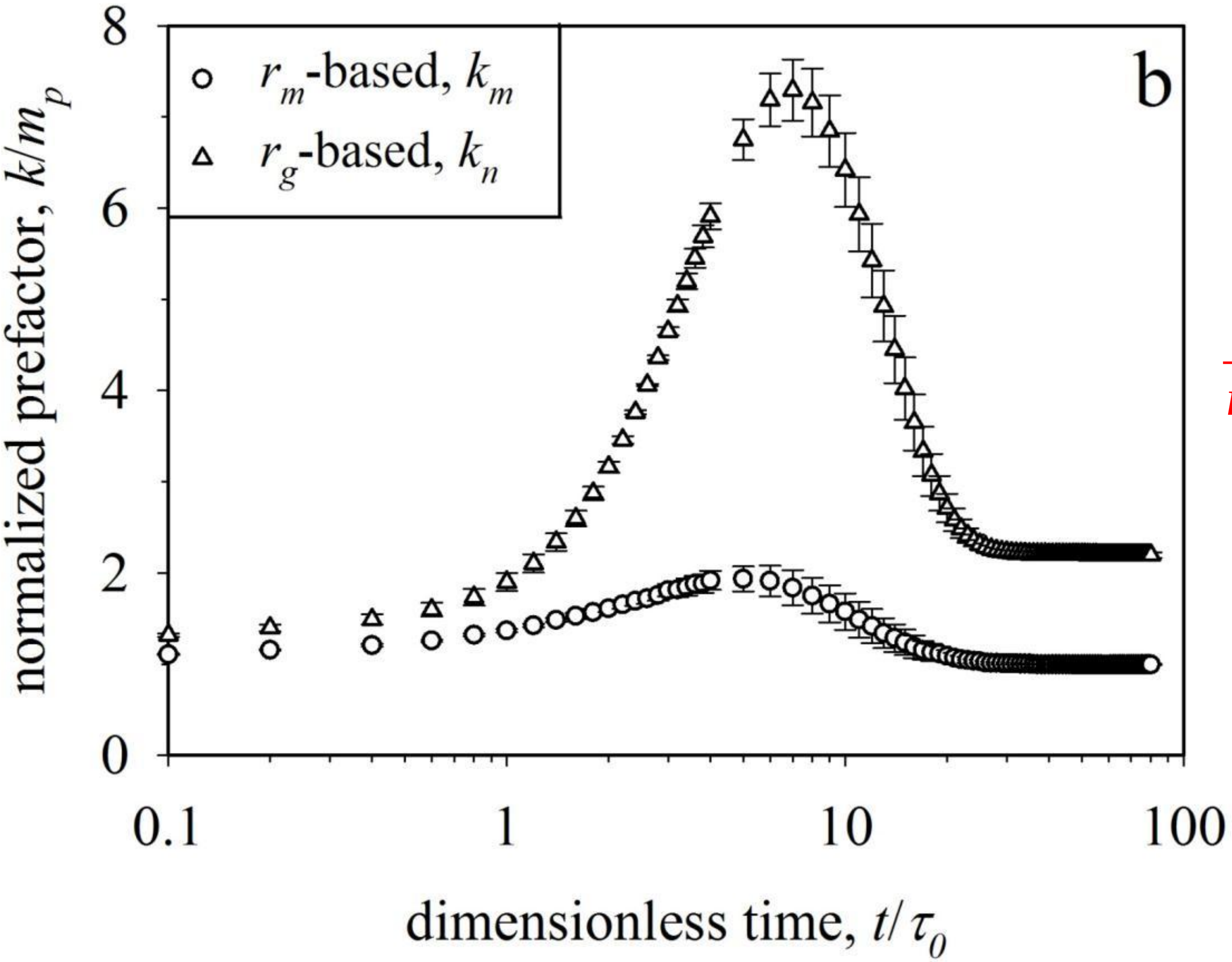
HAB = 3 cm



HAB = 1 cm

A. Camenzind, H. Schulz, A. Teleki, G. Beaucage, T. Narayanan & S.E. Pratsinis, *Eur. J. Inorg. Chem.* (2008) 911-918.

Evolution of Prefactor k_n and k_m during Sintering

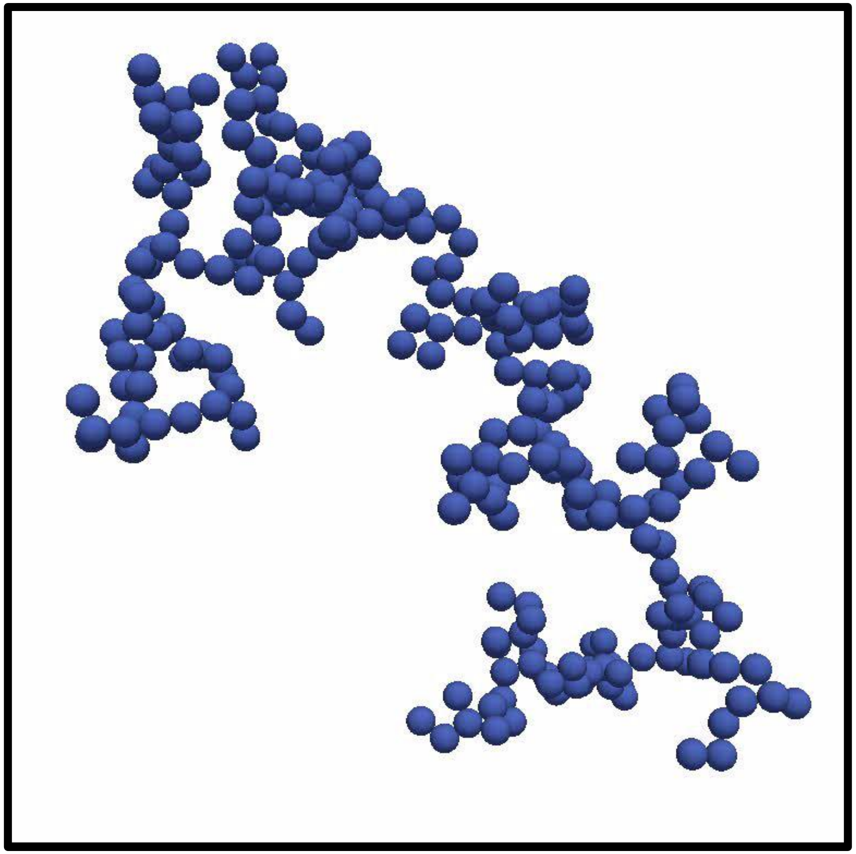


$$\frac{m}{m_p} = k_n \left(\frac{r_g}{r_p} \right)^{D_f}$$

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

M.L. Eggersdorfer, S.E. Pratsinis, *Aerosol Sci. Technol.*, accepted.

Simulation Method: Multi-Particle Sintering

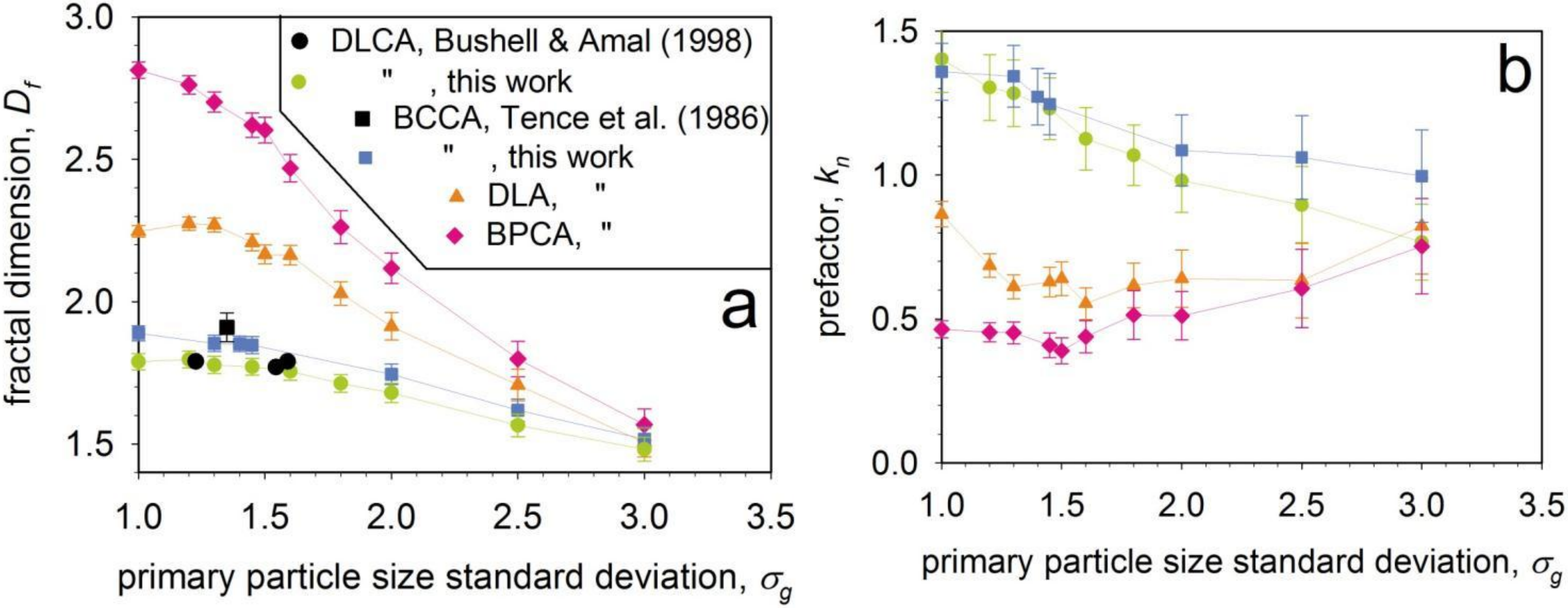


- Color: particle size based on curvature
- Vorlume[1] software to calculate particle volume, surface and neck area.
- SHAKE[2] algorithm to fulfill constraints for particle distances.
- Simulate viscous sintering of aggregates:
  - $N = 2 – 512$ primary particles
  - Average over 50 aggregates of each size (irregular structures)

---

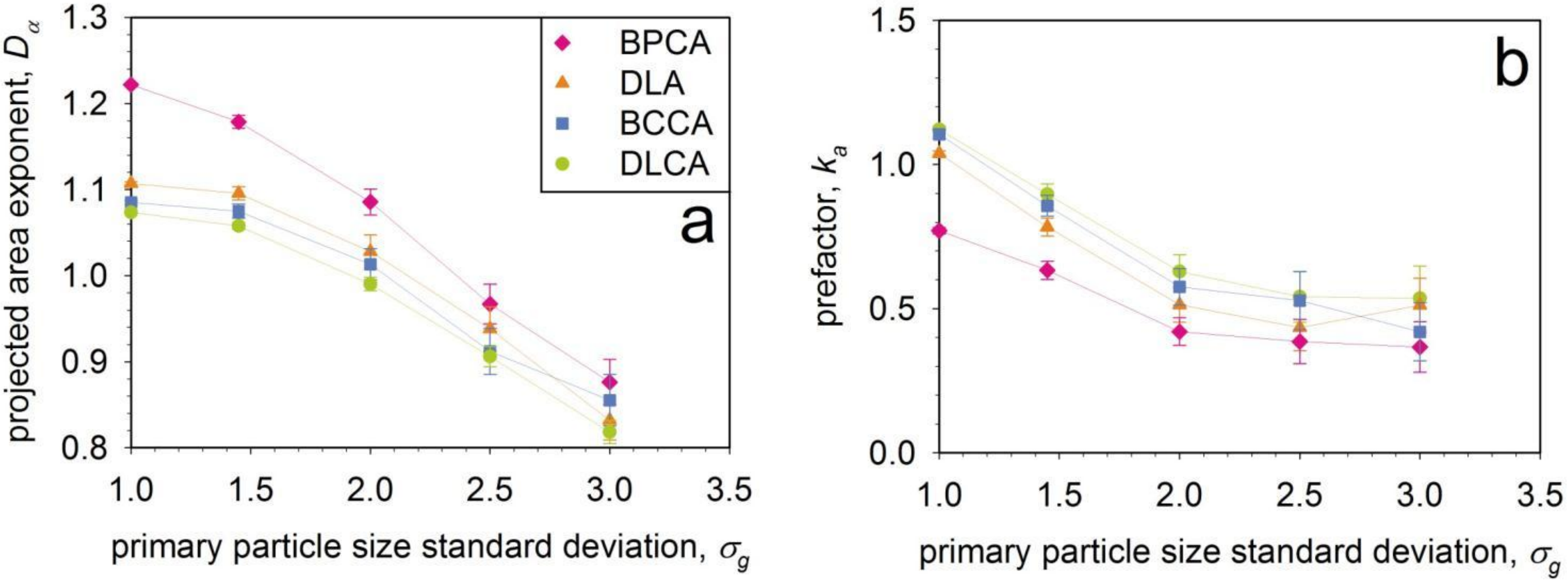
1. F. Cazals, H. Kanhere & S. Loriot, *INRIA Tech Report* No. 7013 (2009).
2. J.P. Ryckaert, G. Ciccotti & H.J.C. Berendsen, *J. Comp. Phys.* **23** (1977) 327-341.

Effect of Primary Particle Polydispersity on D_f and k_n



M.L. Eggersdorfer, S.E. Pratsinis, *Aerosol Sci. Technol.*, accepted.

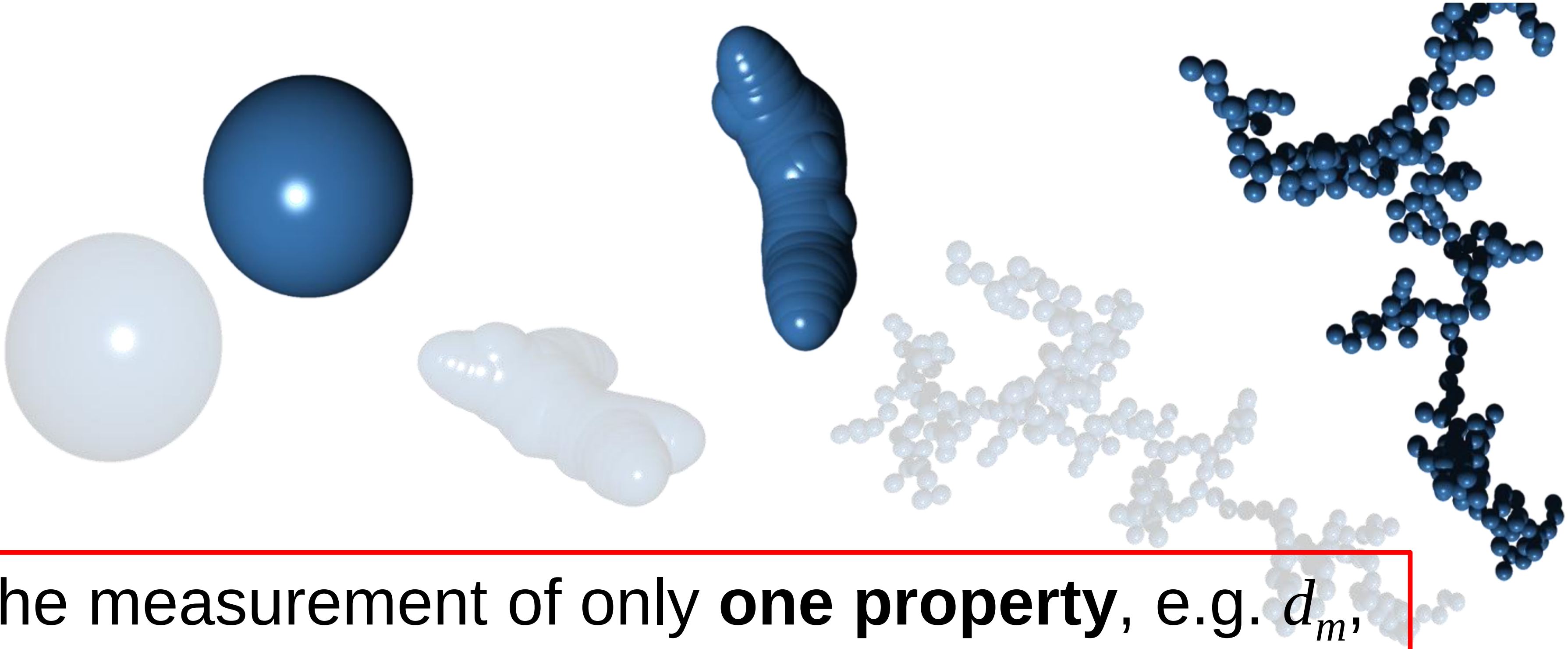
Effect of Primary Particle Polydispersity on D_α and k_a



M.L. Eggersdorfer, S.E. Pratsinis, *Aerosol Sci. Technol.*, accepted.

Goal: Online Characterization of Nanoparticle Morphology

Mobility size[1,2] d_m: $d_{m,1} = d_{m,2} = d_{m,3}$ → e.g. DMA
Mass m: $m_1 > m_2 > m_3$ → e.g. APM
Surface area a: $a_1 < a_2 < a_3$ → e.g. UNPA



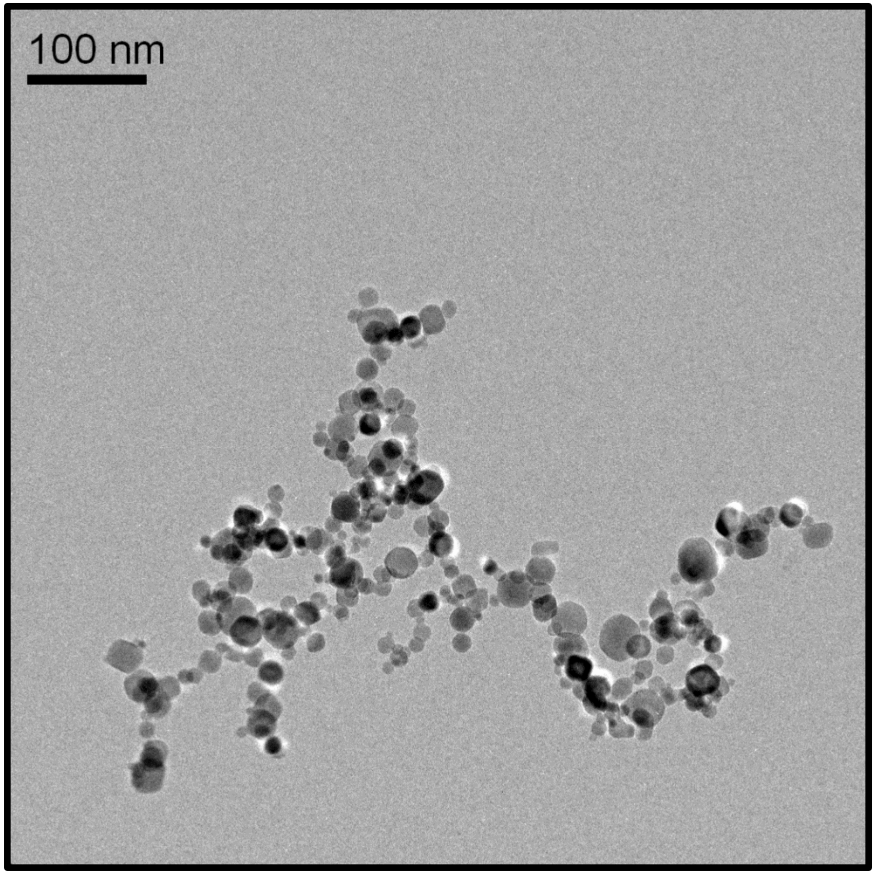
The measurement of only **one property**, e.g. d_m, is **not sufficient** to characterize aggregate/ agglomerate structure

1. P. Meakin, *Adv. Colloid Interface Sci.* **28** (1988) 249-331.
2. S.N. Rogak, R.C. Flagan & H.V. Nguyen, *Aerosol Sci. Technol.* **18** (1993) 25-47.

Nomenclature

agglomerate:

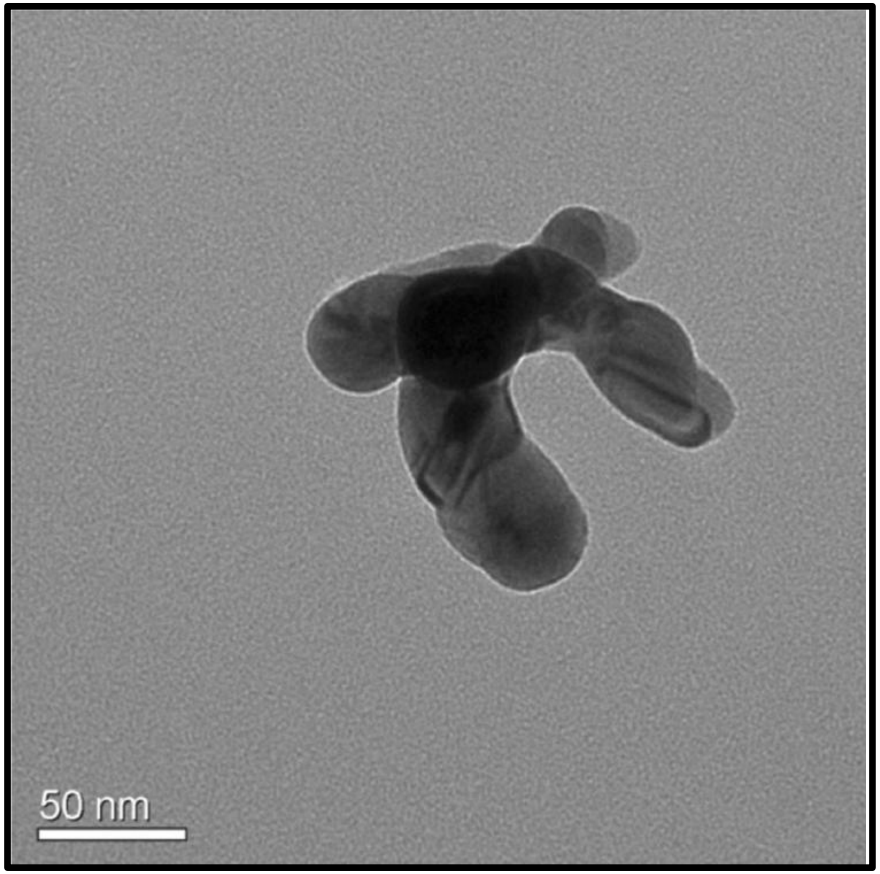
physically bonded



ZrO2 agglomerate generated by FSP @ PTL, ETH Zürich

aggregate:

chemically or sinter-bonded



S.C. Kim, J. Wang, M.S. Emery, W.G. Shin, G.W. Mulholland & D.Y.H. Pui, *J. Aerosol Sci.* **43** (2009) 344-355.