17th ETH-Conference on Combustion Generated Nanoparticles
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Extended Abstract

On-line Diagnostics for Growth and Monitoring of Combustion Aerosols

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Real-time aerosol characterization is not only important for airborne pollutants but also for monitoring of continuous aerosol processes, such as the production of engineered nanoparticles. For instance, the primary particle and agglomerate sizes often govern particle properties and must be controlled in a narrow range in order to achieve certain product performance. Flame aerosol reactors that dominate the field in terms of throughput, cost and versatility have production rates up to 1 ton per hour. Here, real-time online diagnostics for particle size can assist process control, assuring production quality and resulting in significant cost savings.

Sampling these production streams, however, is all but trivial. Particle concentrations are as high as 10^{18} #/kg_{gas}, requiring an enormous dilution of the aerosol to quench particle growth processes. The probe has to withstand temperatures up ~1500 K and possibly corrosive environments. For this reason, mostly ex-situ methods have been used to determine particle size and morphology.

Here, an in-situ method for real-time determination of average agglomerate mass, volume, mobility and structure along with the constituent primary particle size is presented. It is performance-tested in continuous lab- and pilot-scale production lines for nanoparticles made by flame spray pyrolysis (FSP; Mädler et al., 2002).

A sampling probe for continuous extraction of the hot and highly concentrated aerosol was designed and constructed. Immediate dilution with adjustable cooling air flow rate allows effective suppression of coagulation. This enables in addition to continuous and real-time process monitoring direct measurement of the primary and agglomerate particle growth dynamics.

Online characterization of the fractal-like particles is achieved by combining a differential mobility analyzer (DMA) either directly with a condensation particle counter (CPC) or by passing the sample through an aerosol particle mass analyzer (APM), first (Figure 1). Thereby, the agglomerate size distribution as well as the average primary particle size is derived by applying a power-law correlation as proposed by Eggersdorfer et al. (2012). Results are compared against off-line particle size characterization by nitrogen adsorption and thermophoretic sampling/transmission electron microscopy (TEM).

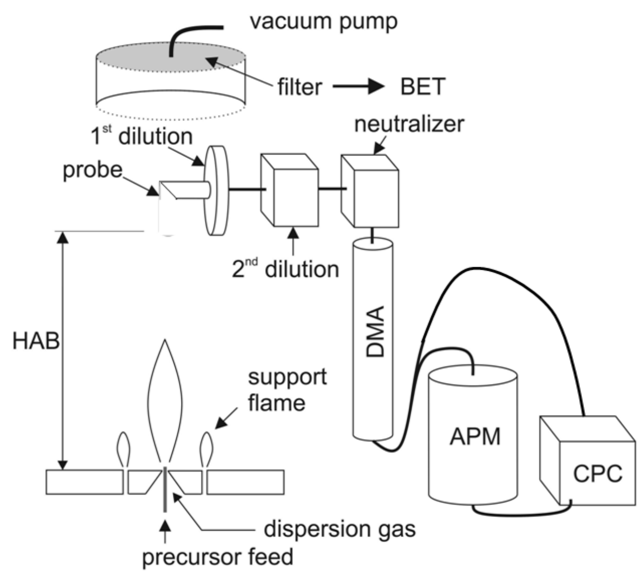

Figure 1: Experimental set-up with flame spray pyrolysis reactor producing zirconia nano-particles, product filter, sampling probe with primary diluter positioned at 75-300 mm height above burner (HAB), secondary diluter and aerosol instrumentation. Following size classification with a DMA, the aerosol sample is either passed directly to a condensation particle counter (CPC) or via an aerosol particle mass analyzer (APM). This allows to obtain the primary as well as the agglomerate particle size and structure (Eggersdorfer et al., 2012).

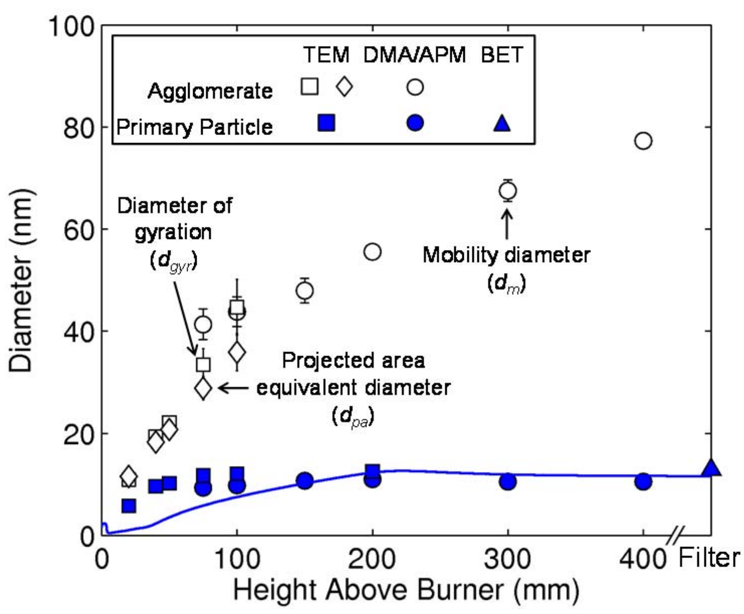

Figure 2: Growth of primary (filled symbols) and agglomerate (open symbols) particle Sauter mean diameters along the reactor centerline as measured by thermophoretic and aerosol (circles) sampling. The diameter of gyration (squares) and projected area equivalent diameter (diamonds) are obtained from TEM micrographs. Fair agreement with the BET-measured primary particle size (triangle) is attained for both methods. After HAB ~100 mm the primary particle diameter stays rather constant while the mean agglomerate size increases throughout the reactor. A process model (line) by Gröhn et al. (2012) correctly predicts the product primary particle size but underpredicts early growth.

Primary zirconia particle growth was shown to be completed at 100 mm above burner as a constant primary particle diameter was observed for downstream axial positions (Figure 2). At this height, average line-of-sight flame temperatures around 1400K were measured by infrared spectroscopy (Gröhn et al., 2012), indicating that sintering of zirconia nanoparticles ceases at this temperature. Figure 2 further shows how process simulations (line, Gröhn et al., 2012) correctly predict the product particle size but underpredict early particle growth.

Similar-sized primary particles were also observed at all radial positions at 100 mm HAB and downstream. Such homogeneity indicates well mixed conditions in the high temperature region of the flame where sintering takes place. As expected, the average agglomerate size was found to increase with axial distance from the burner (Figure 2). However, larger agglomerates were observed at the fringes of the aerosol plume attributed to prolonged residence time due to lower gas velocity there.

References:

Eggersdorfer, M.L., Gröhn, A.J., Sorensen, C.M., McMurry, P.H. and Pratsinis, S.E. (2012), *J. Colloid. Interface Sci.* **387**, 12 - 23.

Gröhn, A.J., Pratsinis, S.E., and Wegner, K. (2012), *Chem. Eng. J.* **191**, 491 - 502.

Mädler, L., Kammler, H.K., Mueller, R. and Pratsinis, S.E. (2002), *J. Aerosol Sci.* **33**, 369 - 389.

On-line Diagnostics for Growth and Monitoring of Combustion Aerosols

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Environment

Climate

Smog

Acid Rain

Ozone Hole

Energy

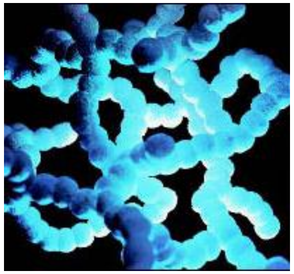
Fuel Injection Engines

Coal Combustion

Turbine Combustion

Flue Gas Cleaning

Aerosols



Health

Allergies

Smoking

Asbestosis

Medicine

Materials

Batteries, Fuel Cells

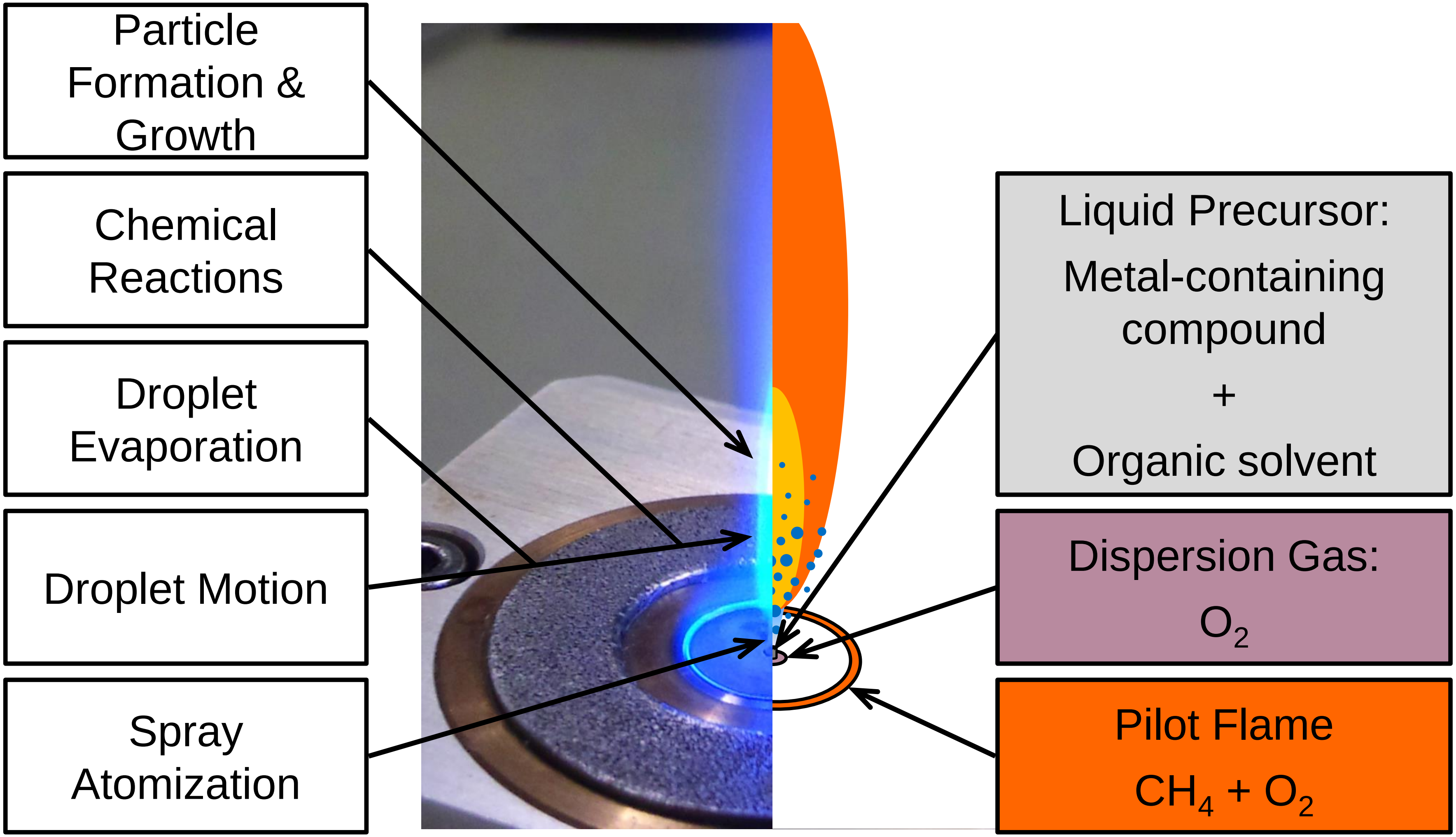
Ceramics, Pigments

Catalysts

Polymers

Food Additives

Flame Spray Synthesis of Nanoparticles



Process model: Gröhn, Pratsinis, Wegner (2012), *Chem. Eng. J.* **191**, 491.

Scale-up toward Industrial Production

Lab-Scale

25 g/h ZrO_2

× 200?

Same particle properties

Continuous process

Pilot-Scale

5000 g/h ZrO_2

Financial Support by the European FP7 Research Project "Advance-FSP" is kindly acknowledged

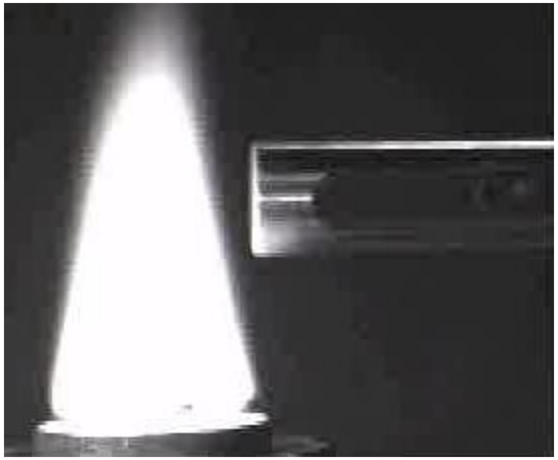
Off-line Particle Characterization

Nitrogen adsorption

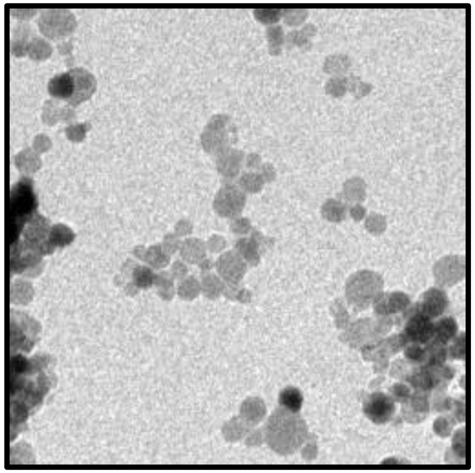
Analysis of collected product powder.

Specific surface area and BET-equivalent primary particle diameter.

Thermophoretic sampling



TEM →

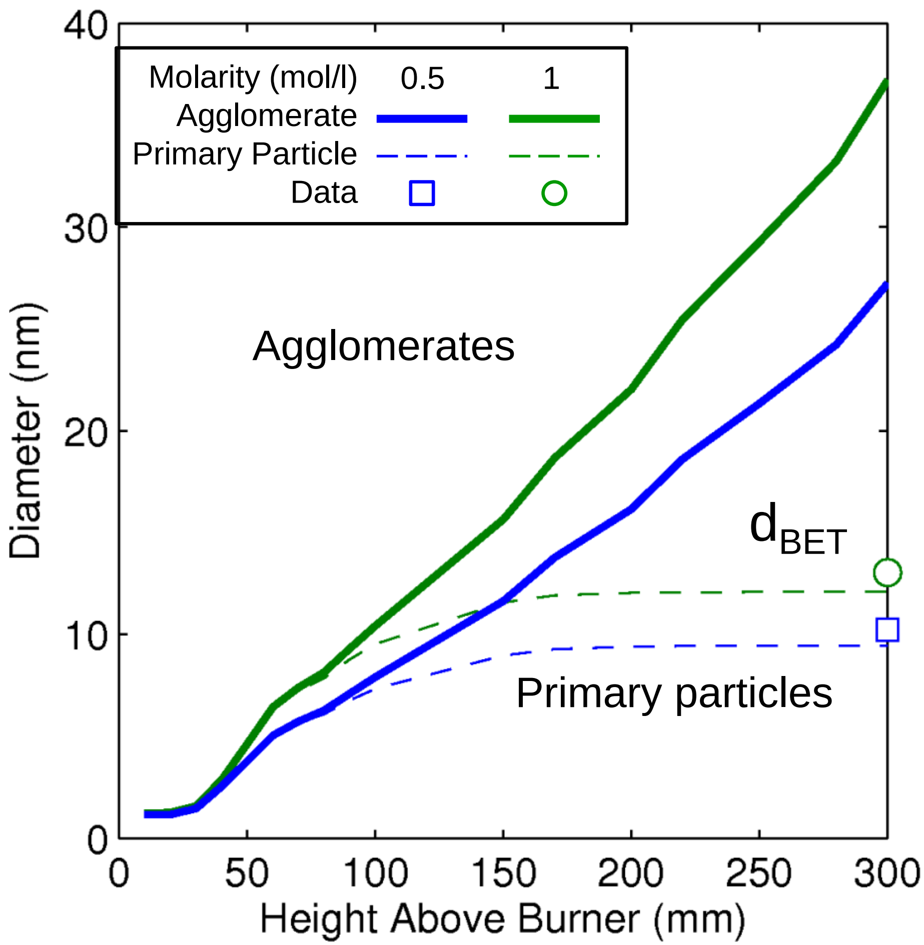


- Primary particle diameter
- Diameter of gyration
- Projected area equivalent diameter

→ Need for *on-line* and *real-time* diagnostics.

Required: On-line Diagnostics for Particle Size

A) Process model validation:

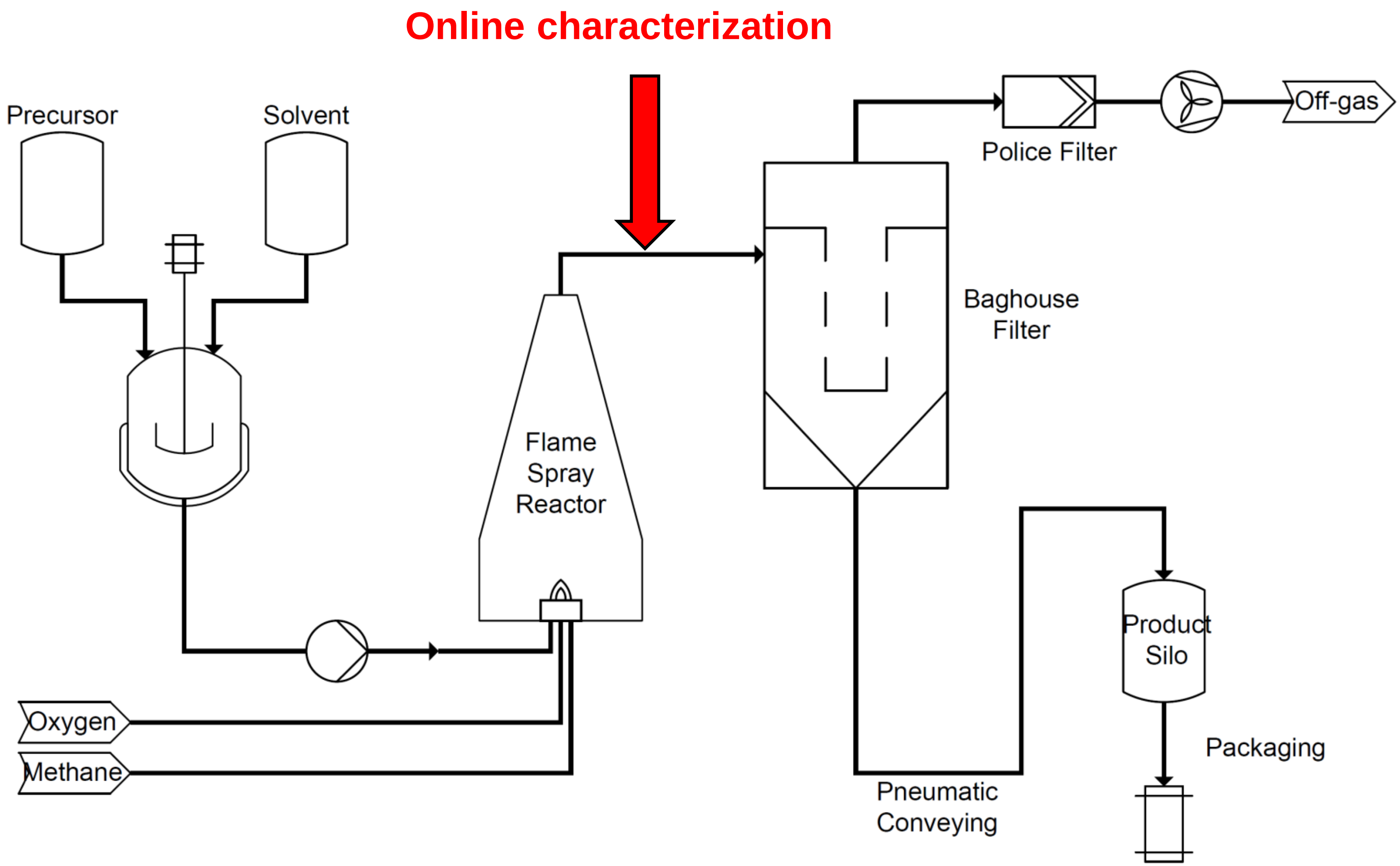


Model prediction of primary and agglomerate particle growth during flame synthesis of zirconia

Gröhn, Pratsinis, Wegner (2012), *Chem. Eng. J.* **191**, 491.

Required: On-line Diagnostics for Particle Size

B) Process and quality control:



Wegner , Schimmoeller, Thiebaut, Fernandez, Rao (2011), *KONA Powder and Particle* **29**, 251.

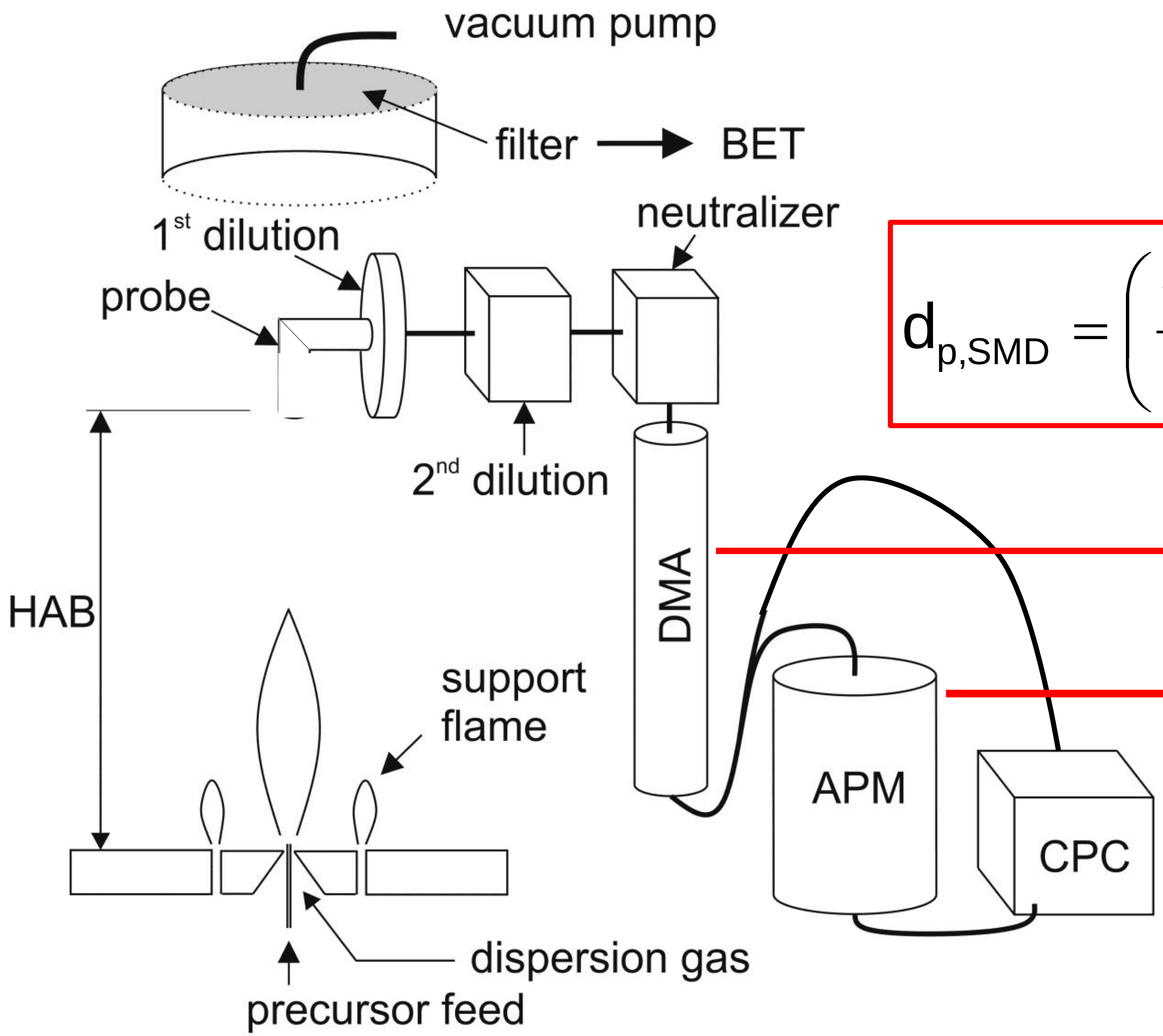
Previous Work

- In-situ light scattering, e.g.
  Sorensen, Cai, Lu (1992), *Appl. Opt.* **31**, 6547.
  Xing, Koylu, Rosner (1999), *Appl. Opt.* **38**, 2686.
  Optical properties of particles, rather dilute concentrations

- In-situ small-angle X-ray spectroscopy, e.g.
  Mueller, Kammler, Pratsinis, Vital, Beaucage, Burtscher (2004), *Powder Technol.* **140**, 40.
  Synchrotron radiation, challenging theory

- DMA/APM, e.g.
  Park, Cao, Kittelson, McMurry (2003), *Environ. Sci. Technol.* **37**, 577.
  Wang, Shin, Mertler, Sachweh, Fissan, Pui (2010),*Aerosol Sci. Tech.* **44**,97.
  Eggersdorfer, Gröhn, Sorensen, McMurry, Pratsinis (2012), *J. Colloid Interface Sci.* **387**, 12.

Aerosol Diagnostics Set-up



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

Agglomerates:
k_a = 1.1
D_α = 1.08
(Medalia, 1967)

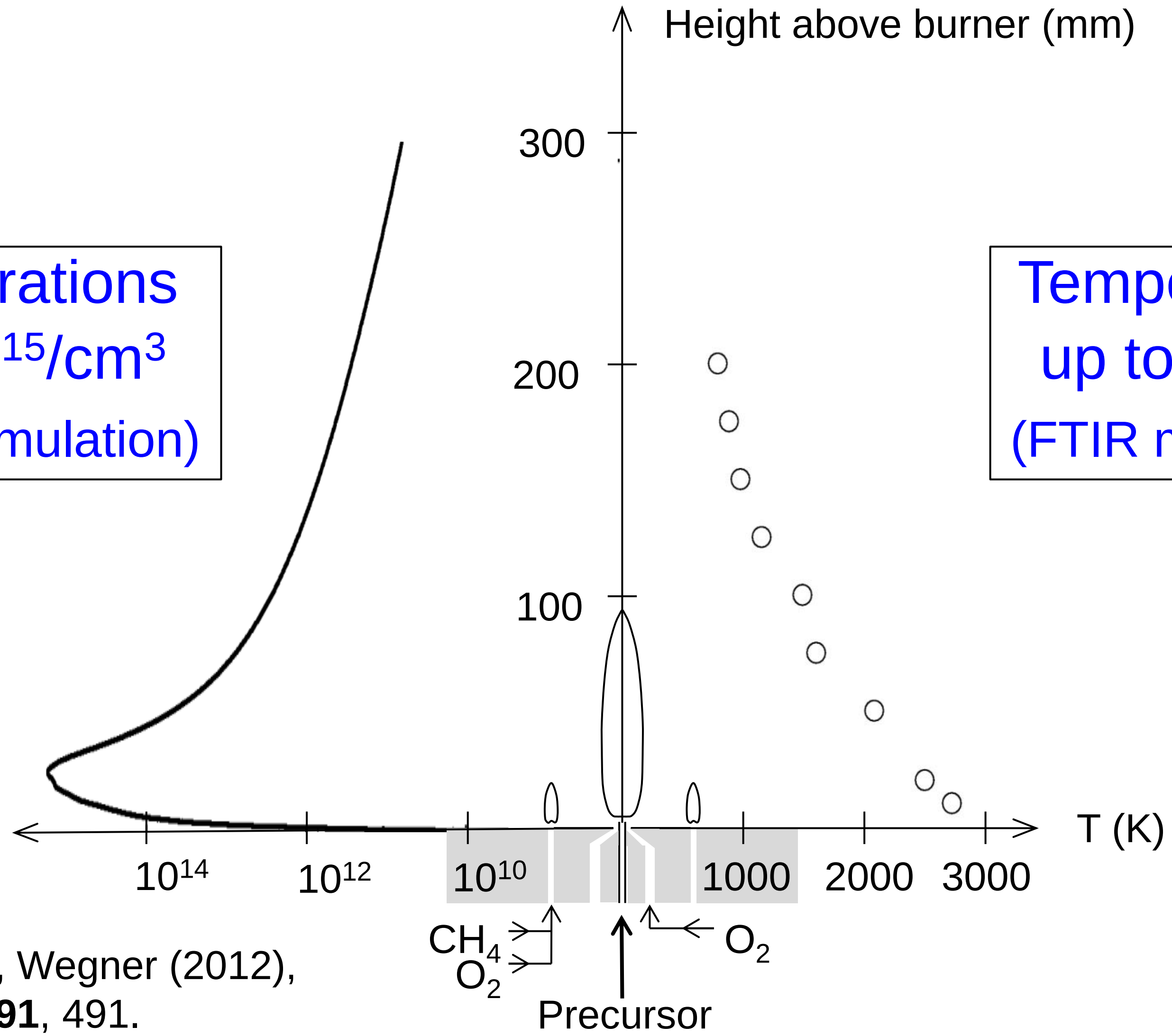
Eggersdorfer, Gröhn, Sorensen, McMurry, Pratsinis, (2012), *J. Colloid Interface Sci.* **387**, 12.

Medalia (1967), *J. Colloid Interface Sci*. **24,** 393.

Particle Concentration and Temperature Profiles at the Centerline

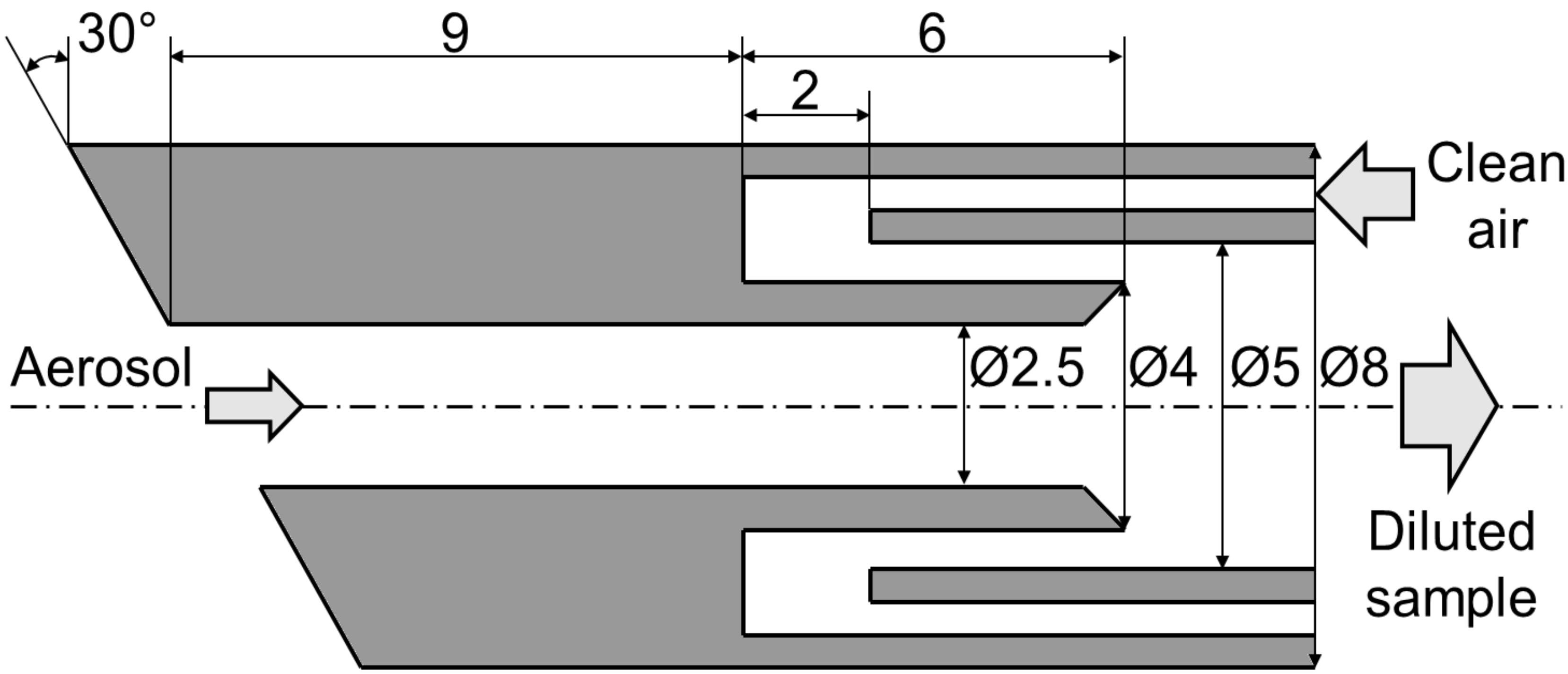
Concentrations up to 10^{15}/cm^3 (process simulation)

Temperatures up to 3000K (FTIR measured)



Gröhn, Pratsinis, Wegner (2012), *Chem. Eng. J.* **191**, 491.

Sampling probe

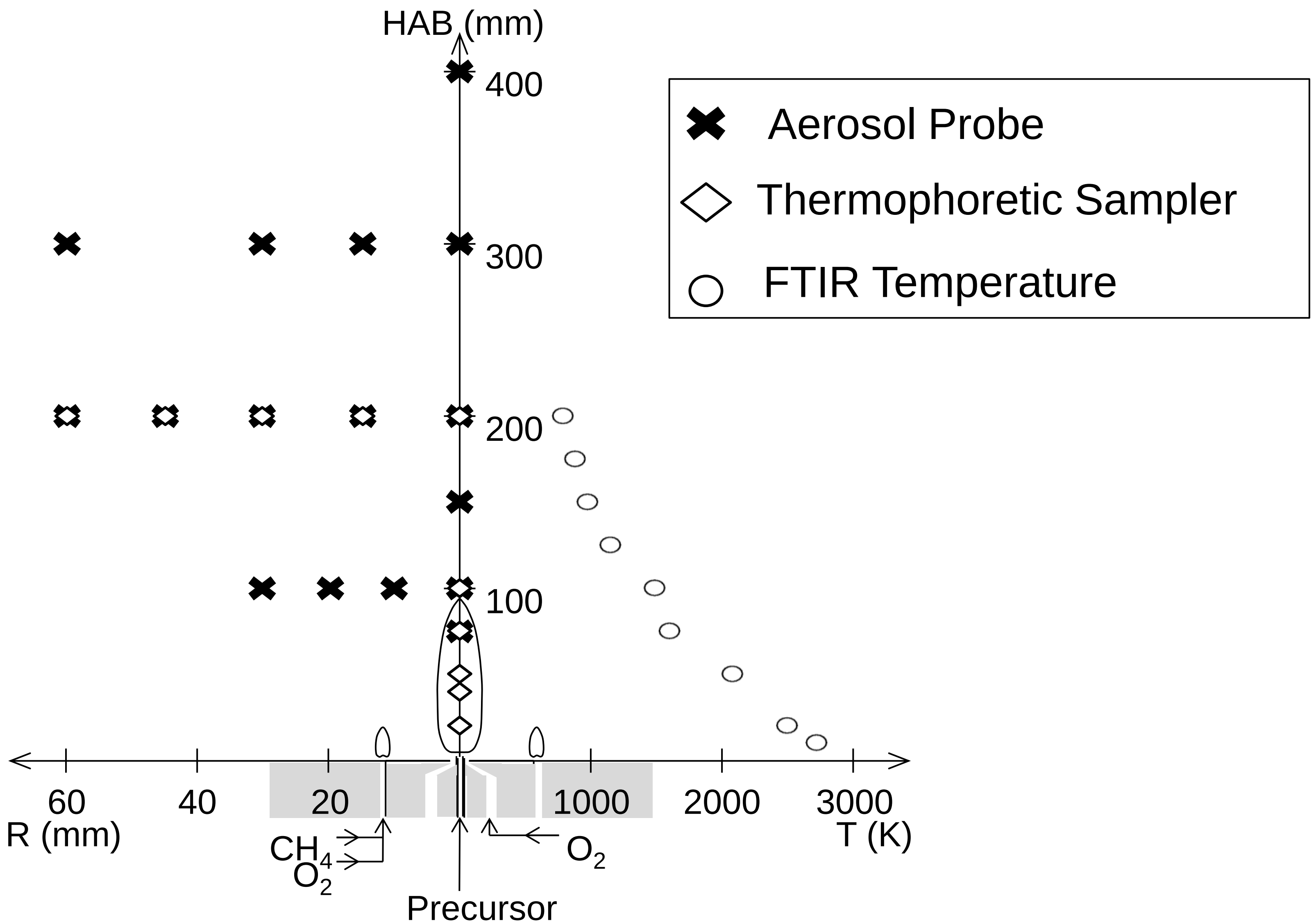


Dimensions in mm

Dilution factors up to 10^4

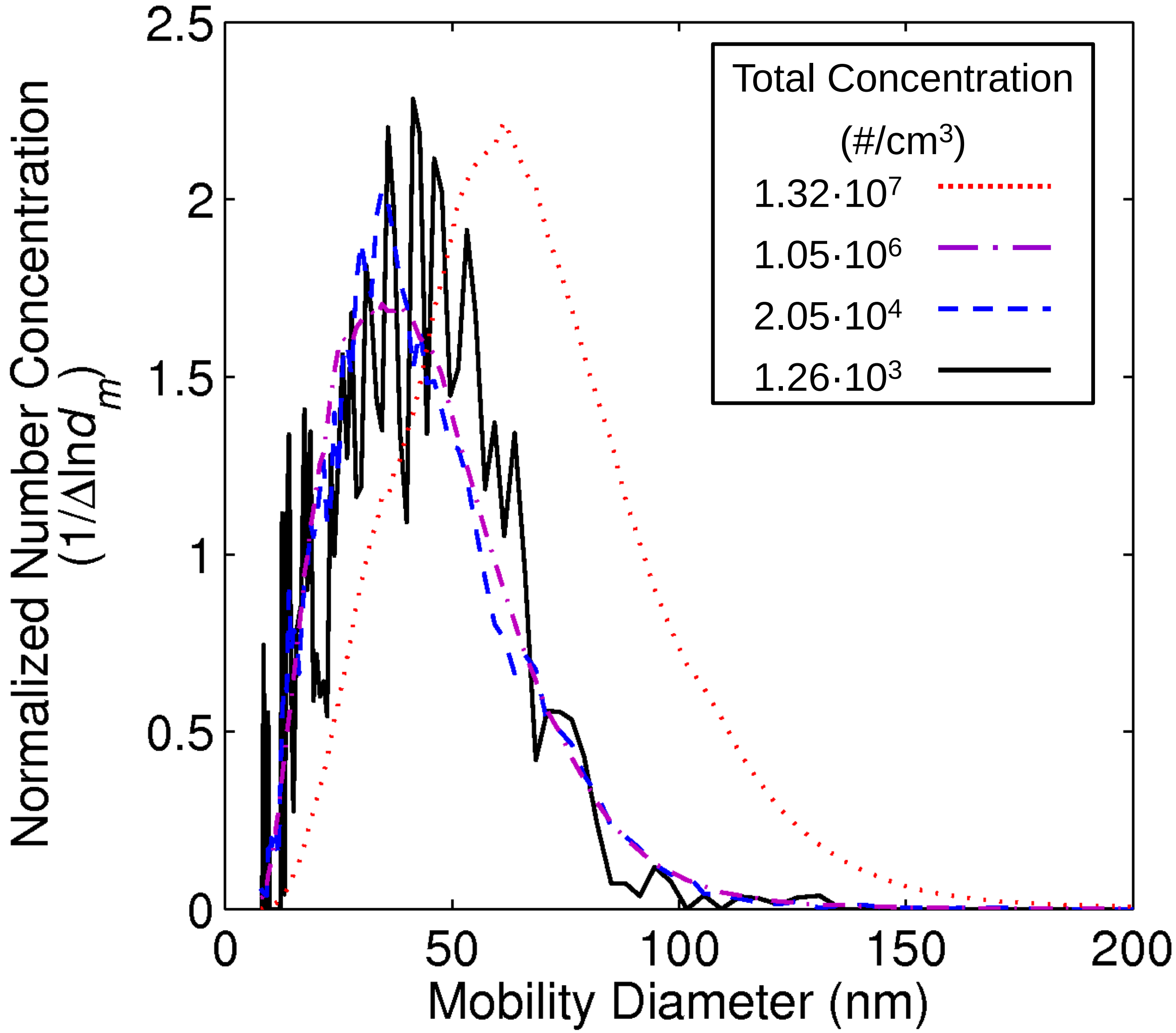
Goertz, Korp, Al-Hasan, Giglmaier, Nirschl (2011), *Chem. Eng. Proc.* **50**, 836.
Ulrich, Milnes, Subramanian (1976), *Combust, Sci. Technol.* **14**, 243.

Sampling Locations



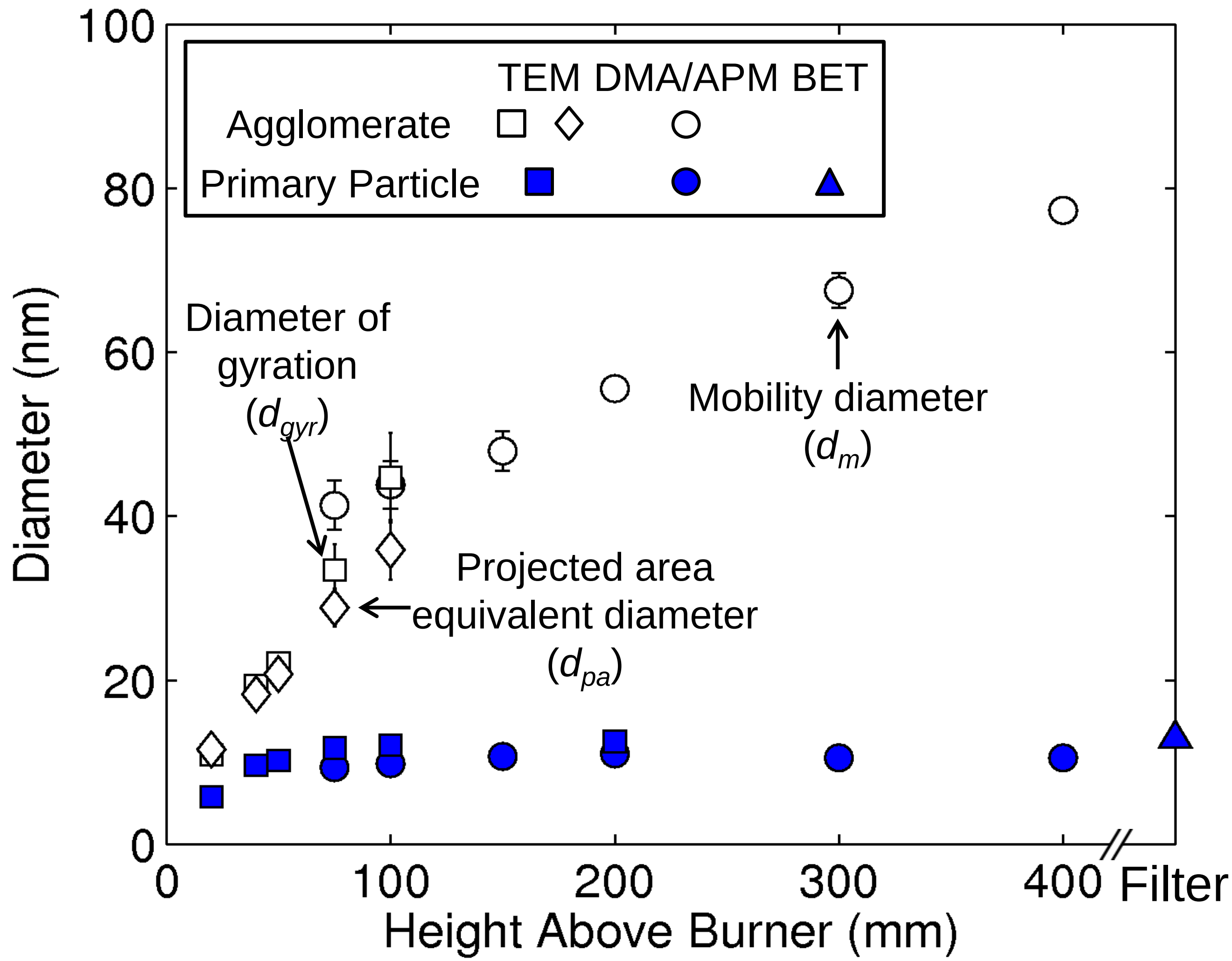
Effect of Dilution on Coagulation

Position: Centerline at 200 mm HAB



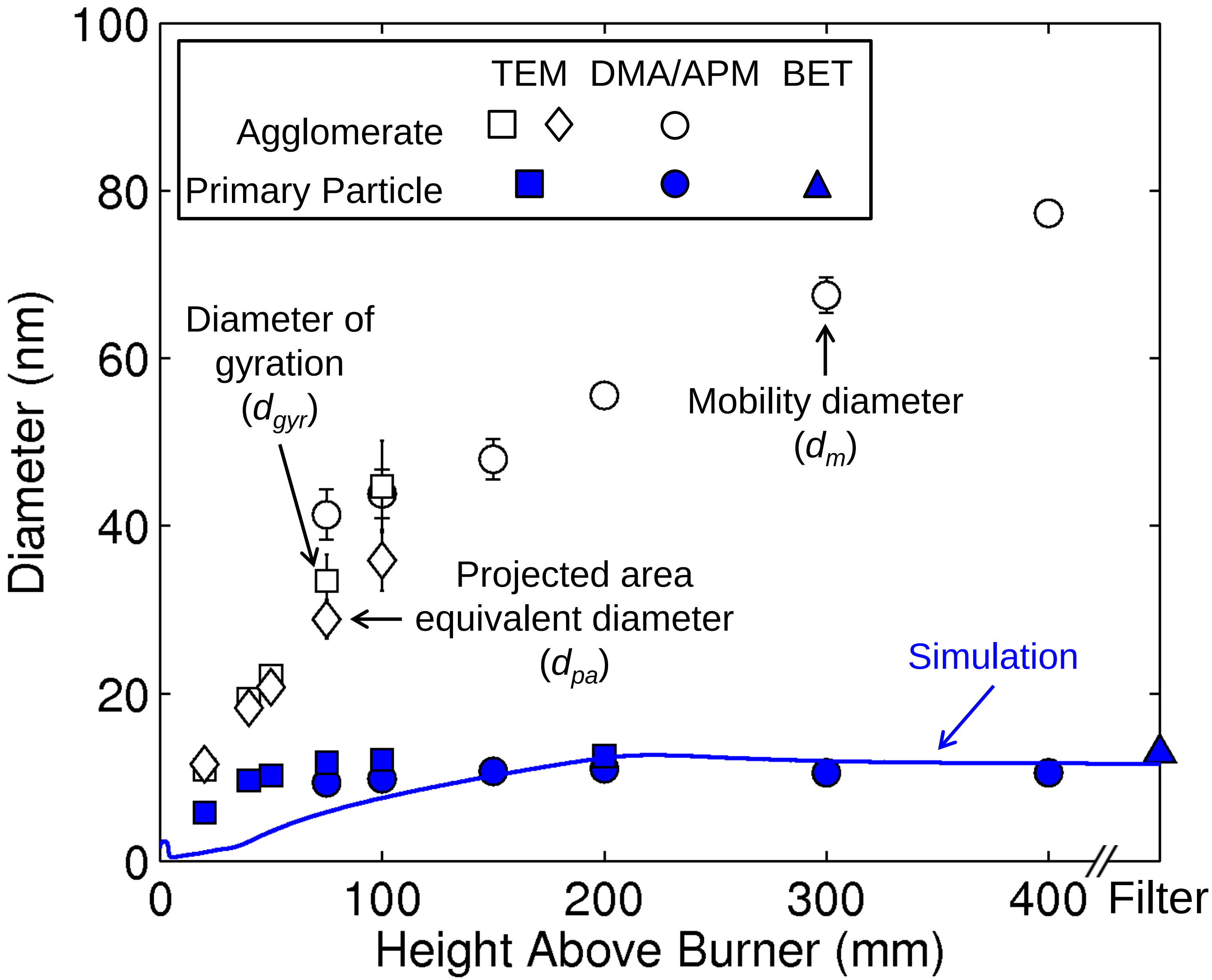
Centerline Evolution of Particle Size

Sauter mean diameters

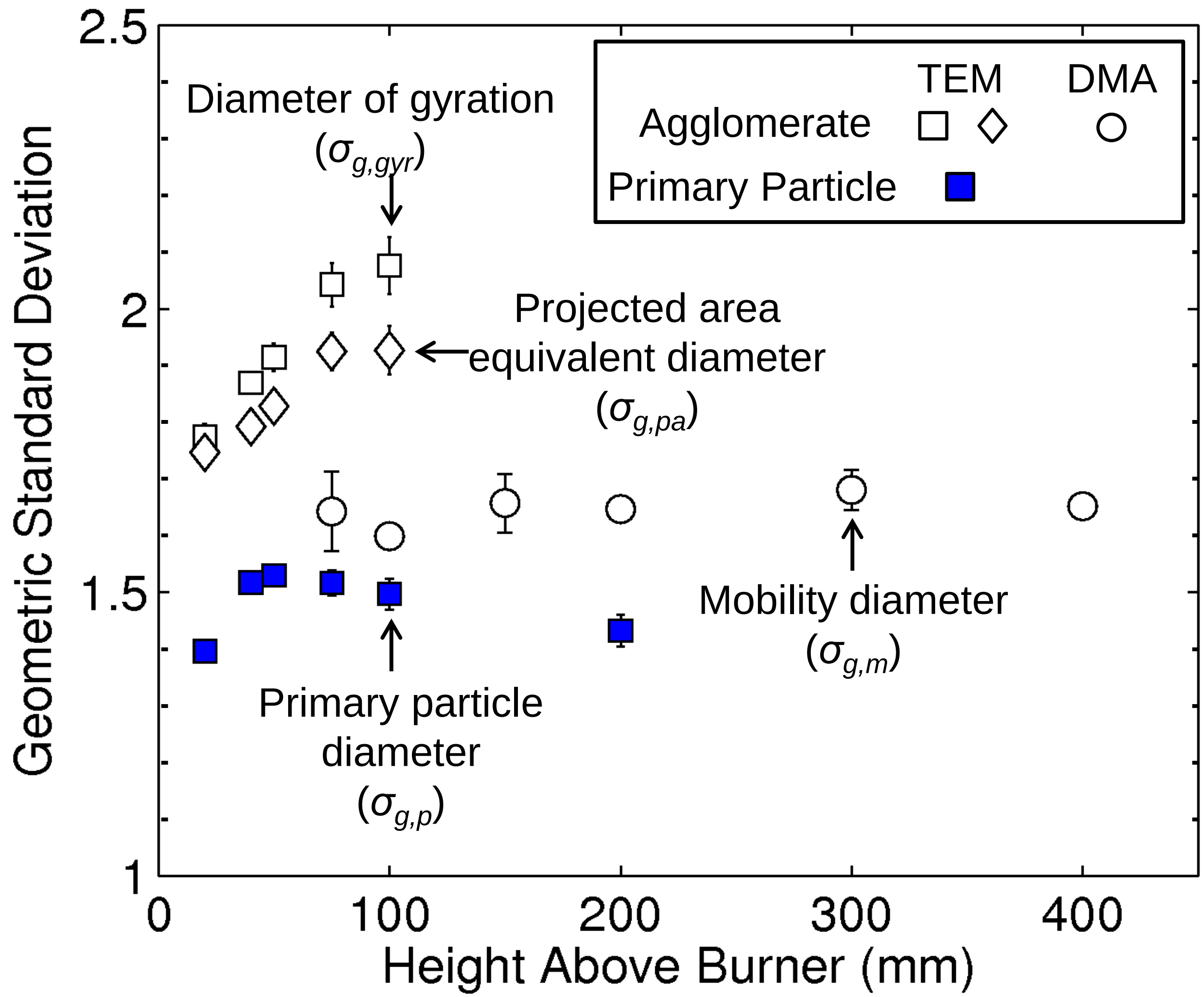


Well known: $d_m \approx d_{pa}$ (e.g. Sorensen (2011), *Aerosol Sci. Technol.* **45**, 765.)

Comparison with Model Results



Centerline Evolution of the Distribution Width



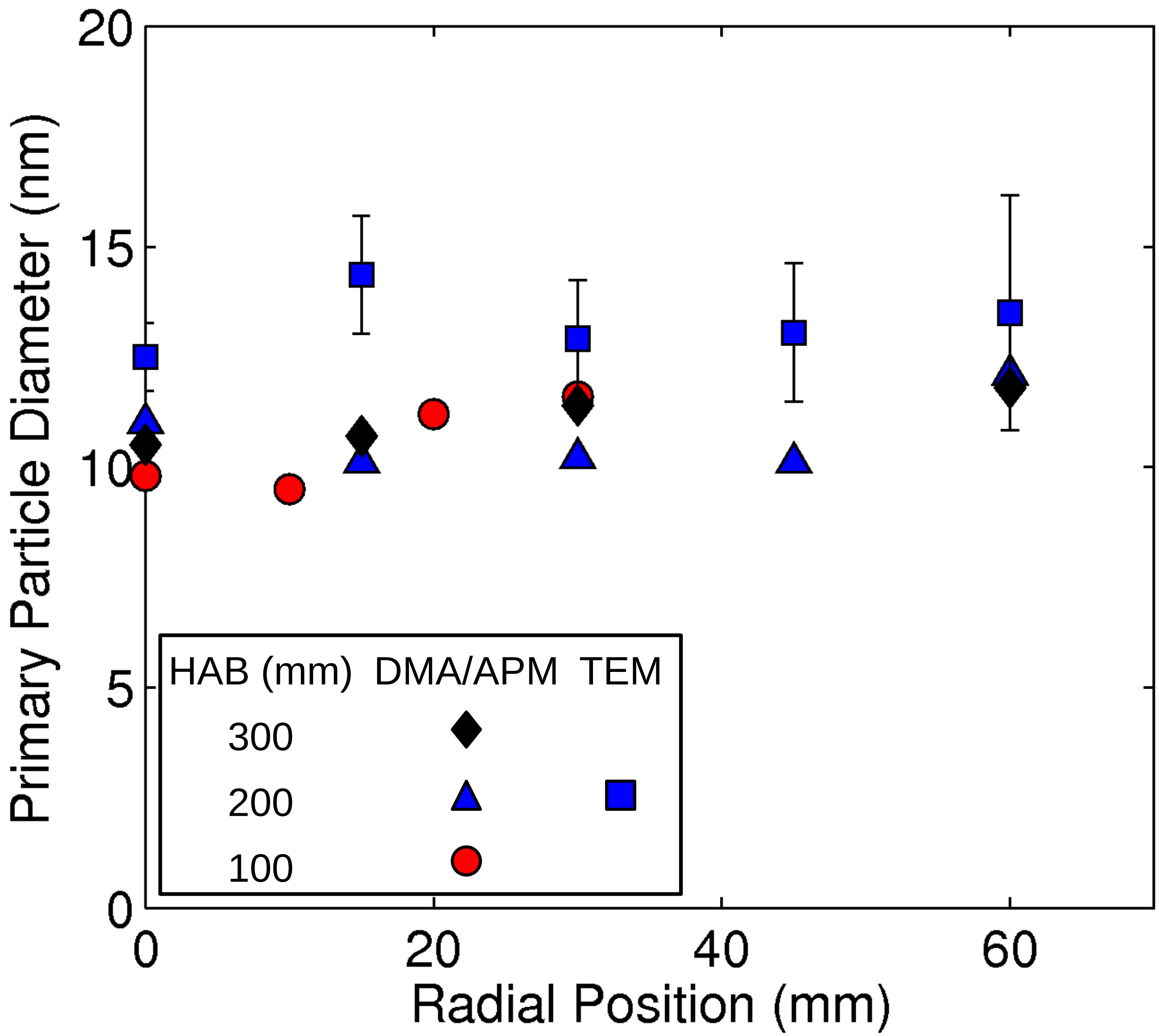
Self-preserving size distribution (free molecular regime)

$\sigma_{g,gyr} \approx 2.2$

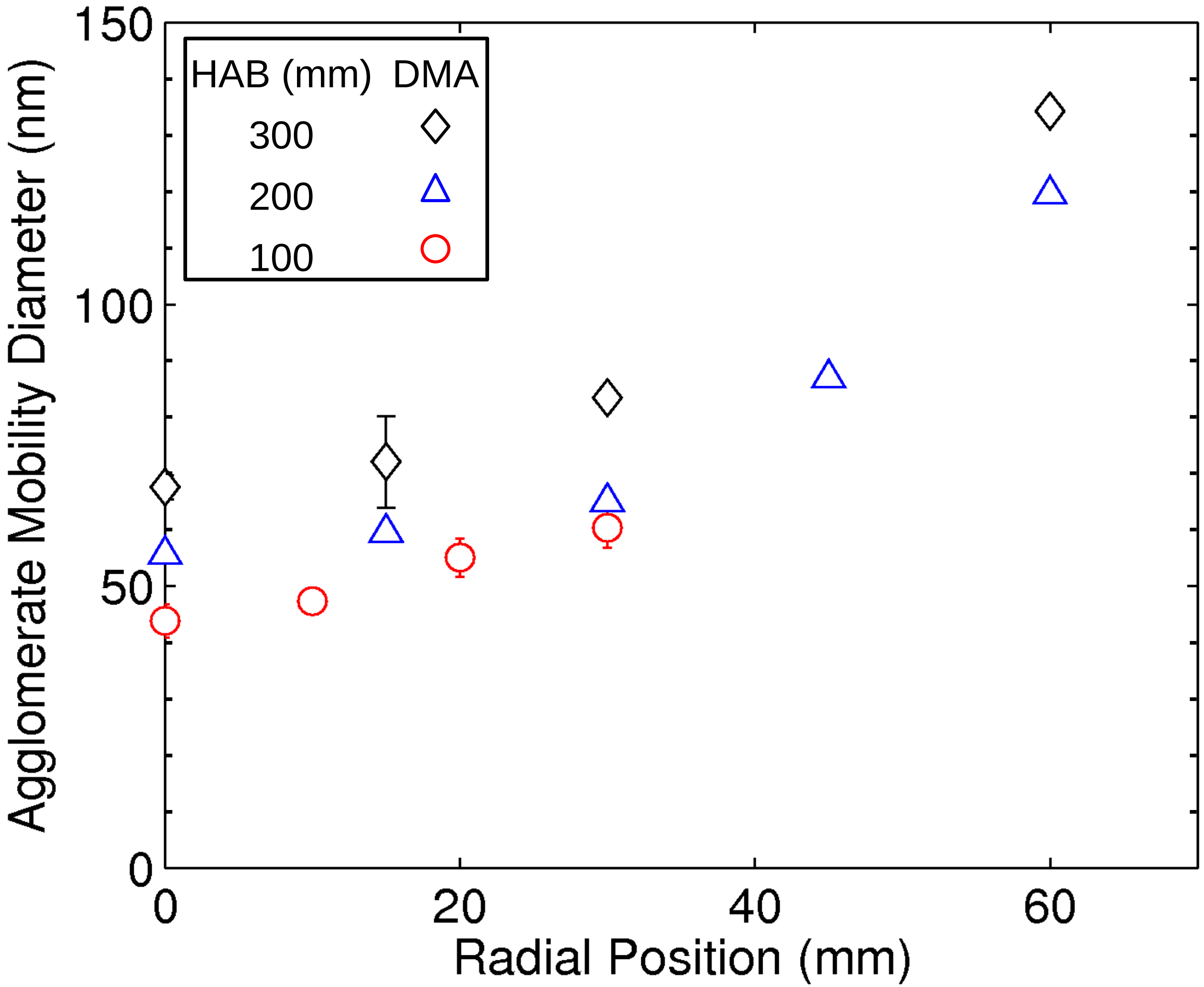
$\sigma_{g,pa} \approx \sigma_{g,m} \approx 2.0$

$\sigma_{g,p} \approx 1.46$ (D_f=3)

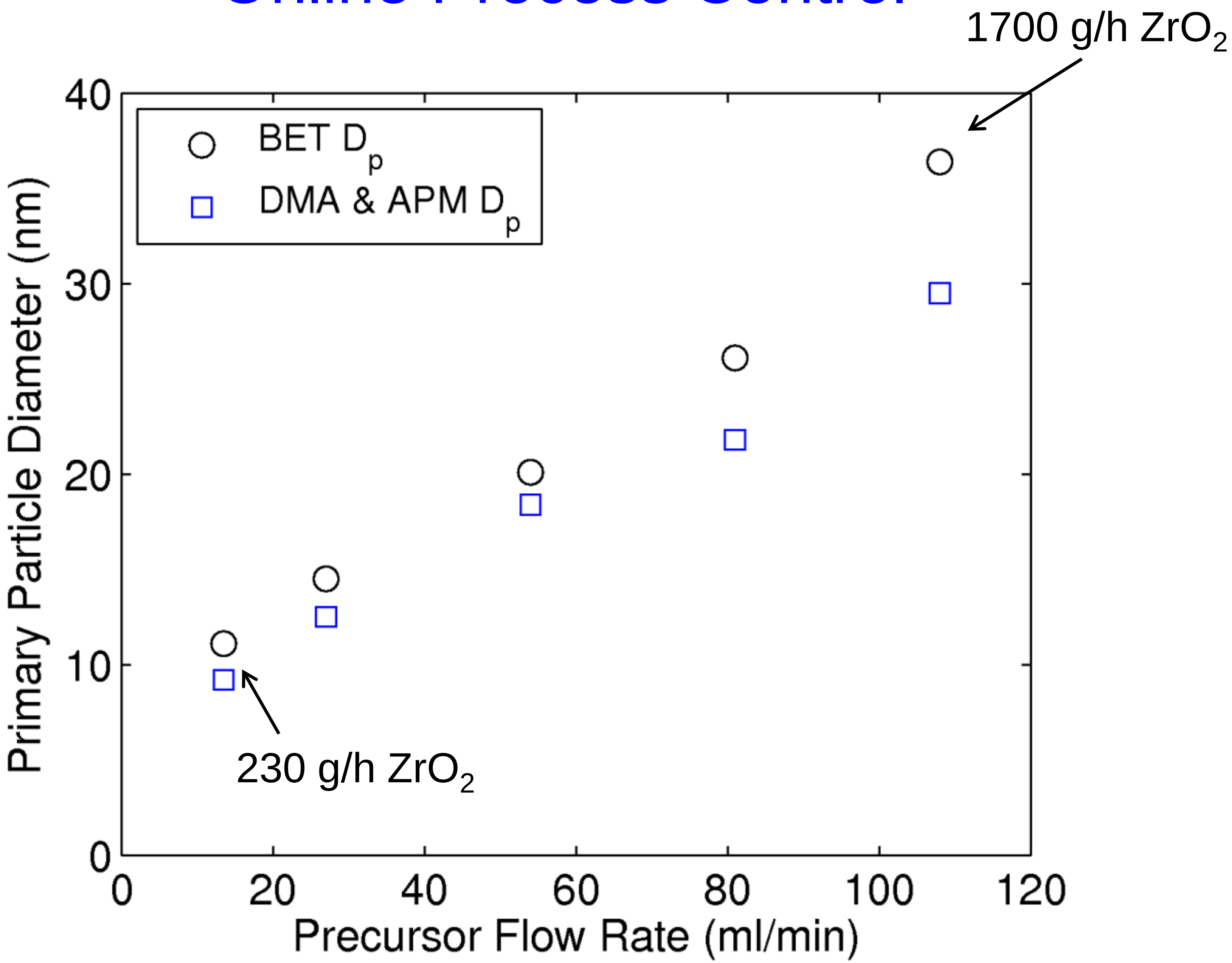
Radial Profiles of Primary Particle Size



Radial Profiles of Agglomerate Size



Online Process Control



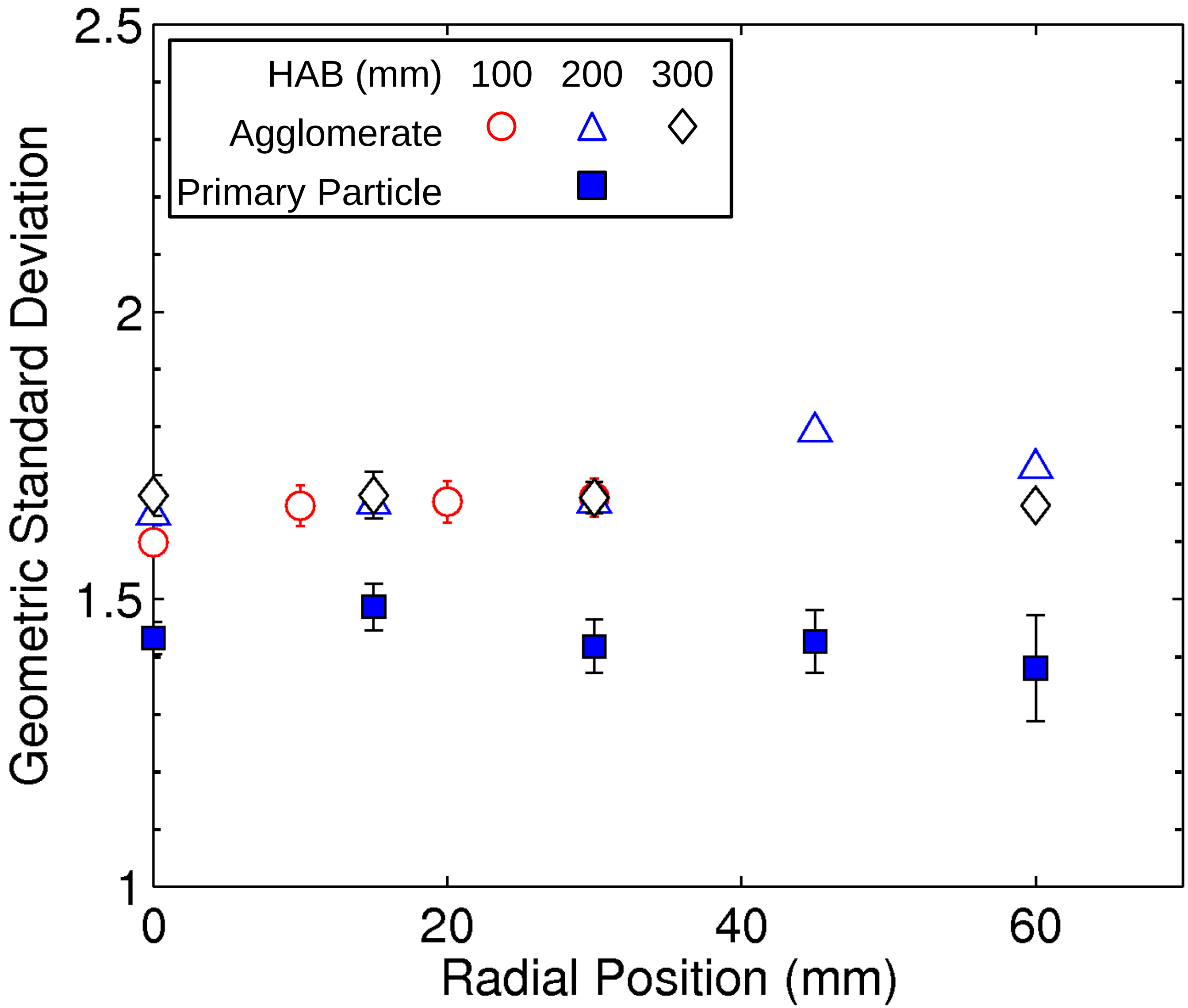
Conclusions

- Aerosol diagnostics can be applied to high-temperature nanoparticle manufacturing processes.
- On-line determination of primary particle and agglomerate size for understanding particle growth and process control.
- Primary ZrO_2 particle growth ceased at ~1400K (100 mm HAB). Computational model underpredicts initial growth.
- Self-preserving size distributions are attained for primary particles and agglomerates. Large agglomerates may align or restructure inside the DMA.
- Homogeneous primary particle size across the flame. Larger agglomerates are observed at the fringes.

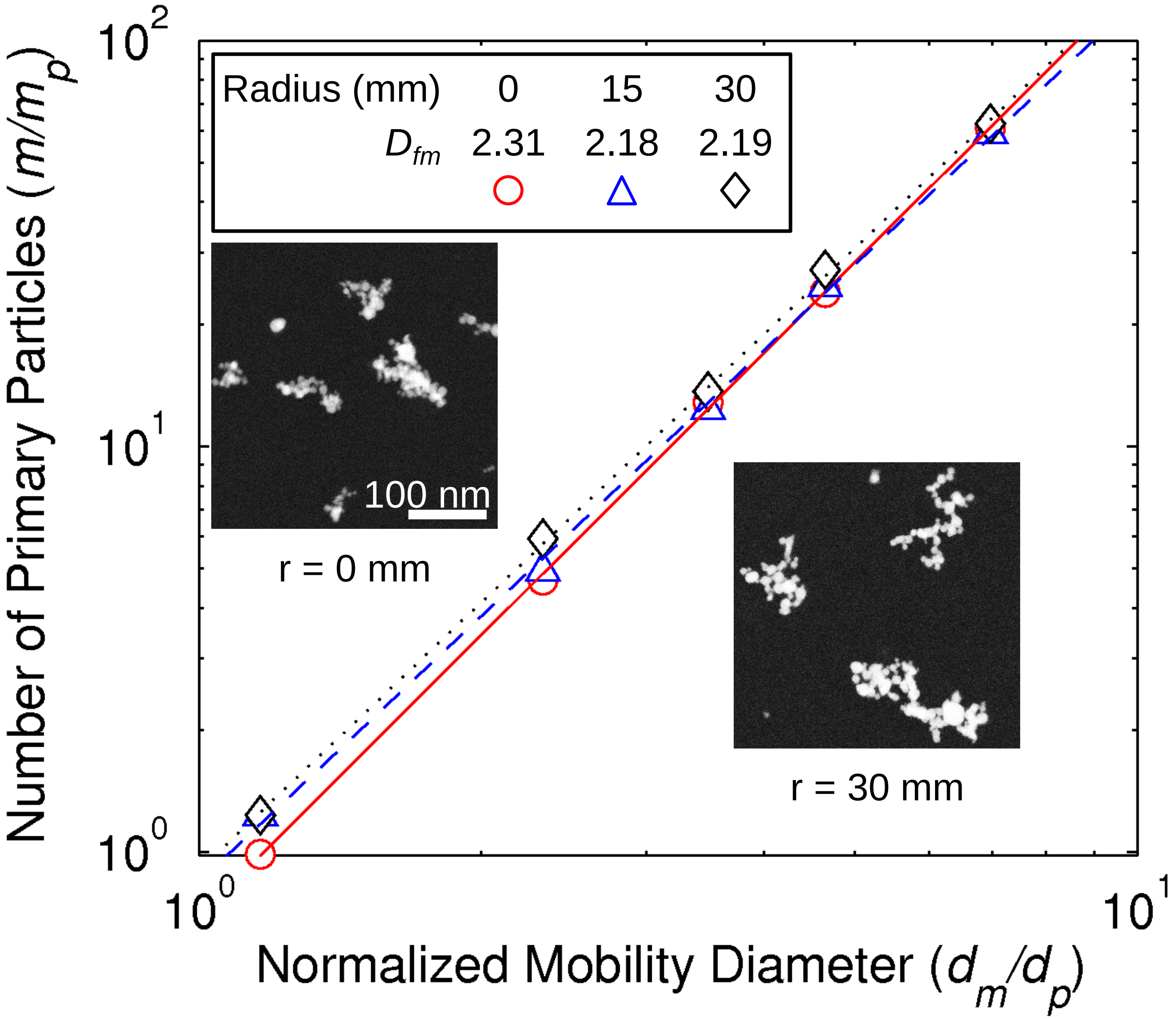
Thank you for your attention!

Nanoparticle Production Unit
at ARCI Hyderabad, India
Capacity: 20 t/year

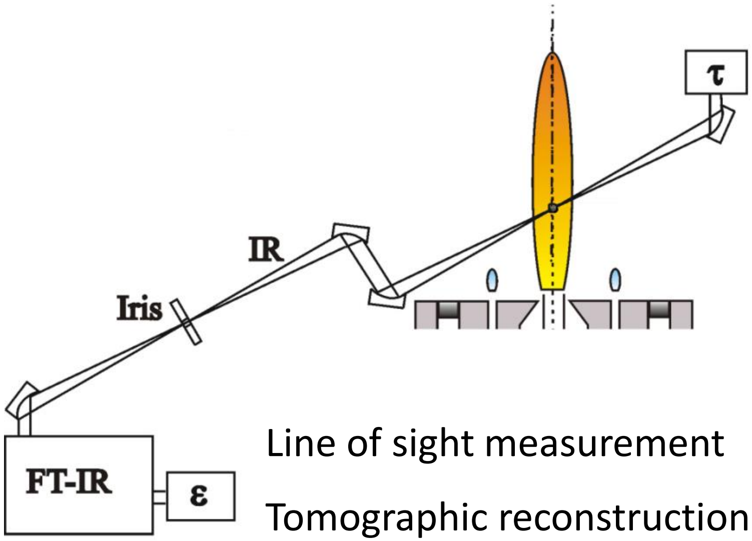
Geometric Standard Deviation – Radial Profiles



Agglomerate Mass-Mobility Scaling



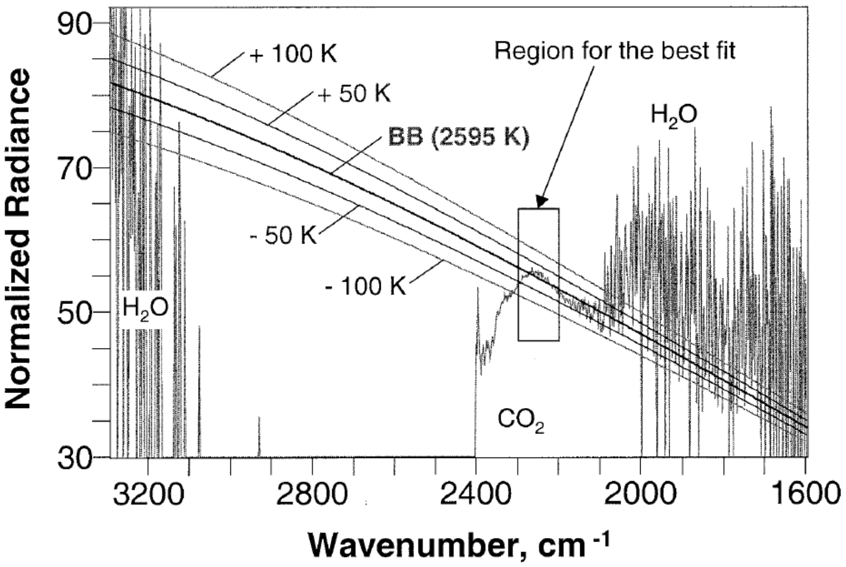
FTIR Flame Temperature



Line of sight measurement

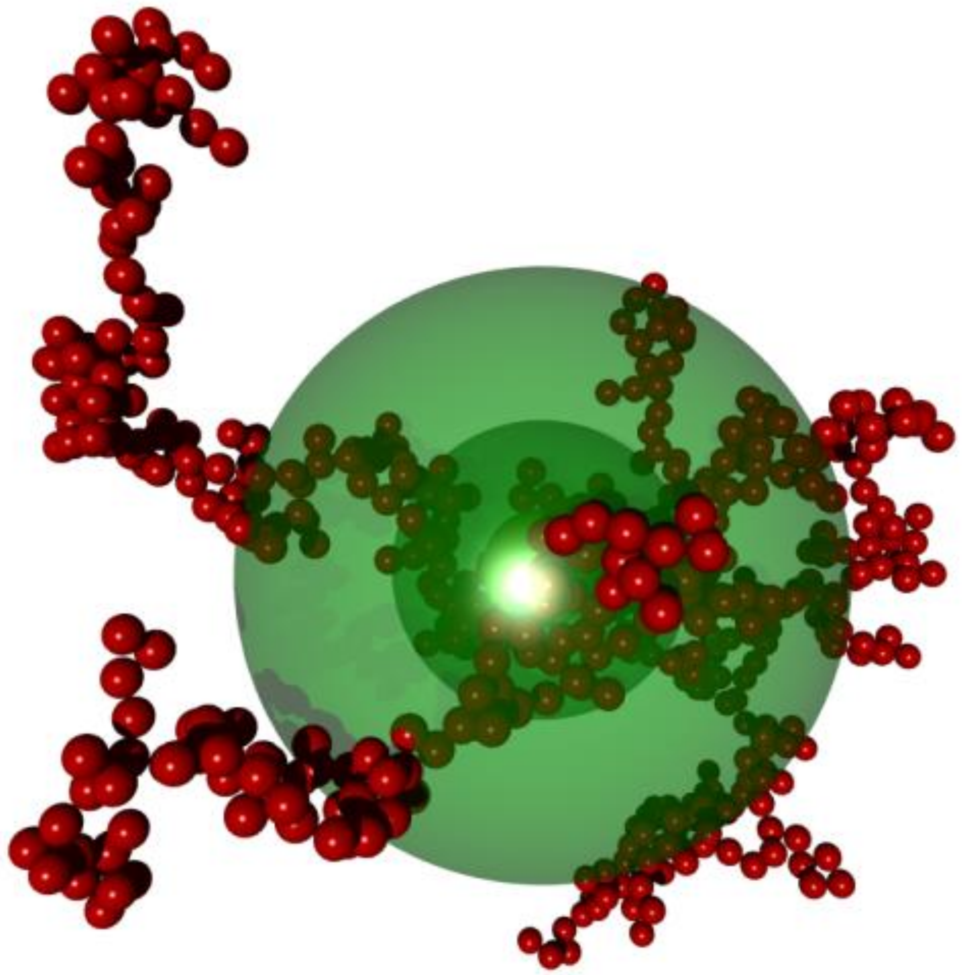
Tomographic reconstruction

- **Measures**
  Temperature
  Species concentration
- **Advantages**
  Non-intrusive
  No upper temperature limit



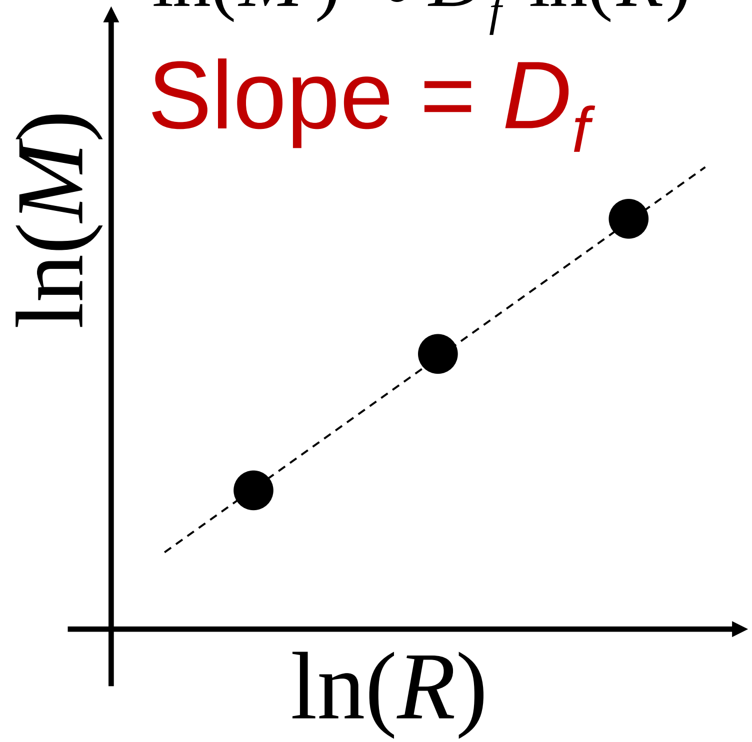
Kammler H. K., Pratsinis S. E., Morrison P.W.Jr, Hemmerling B, *Combust. Flame*, 2002, **128**, 369-381

Fractal Dimension of Agglomerates



$$M \propto R^{D_f}$$

$$\ln(M) \propto D_f \ln(R)$$



Method:

Algorithm of Forrest and Witten

S.R. Forrest & T.A. Witten, *J. Phys A.* **12** (1979) L109-L117.

Agglomerate Structure Characterization

Mass fractal dimension[1], D_f

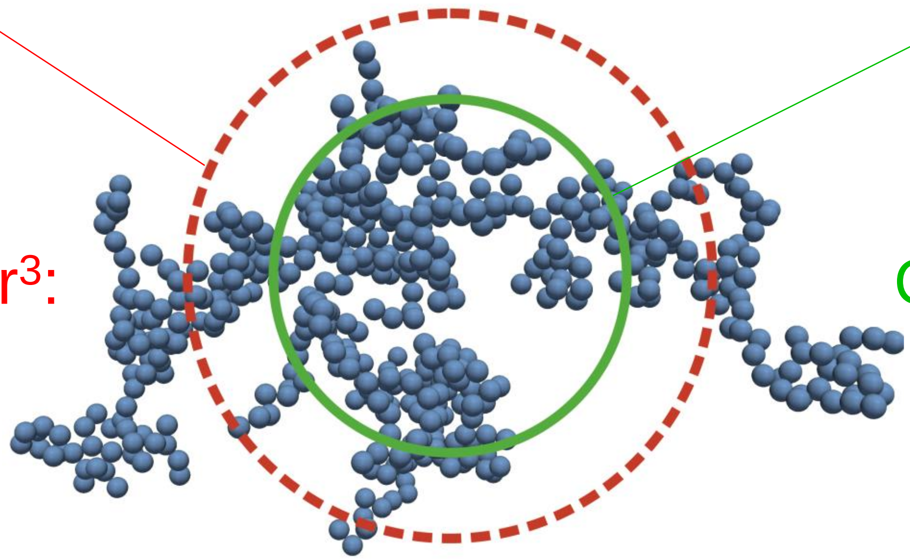
$$\frac{m}{m_p} = k_n \left(\frac{r_g}{r_p} \right)^{D_f}$$

Radius of gyration, r_g

$$r_g^2 = \frac{\int \rho(r) r^2 dr}{\int \rho(r) dr}$$

Cluster-cluster[3]:

$D_f \approx 1.8$



Mass-mobility exponent[2], D_{fm}

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

Mobility radius, r_m

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

Cluster-cluster[3]:

$D_{fm} \approx 2.15$

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

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

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

k_a = 1.0 & D_α = 1.07 for aggregates

k_a = 1.1 & D_α = 1.08 for agglomerates

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.