The structure of agglomerates consisting of polydisperse nanoparticles

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Agglomerates of nanoparticles are encountered in many natural or industrial processes [1], typically at high temperatures, like fly ash from volcano eruption and coal combustion as well as aerosol manufacture of nanomaterials (carbon black, titania, fumed silica, alumina, Ni, Fe, Ag etc.). These nanoparticles collide by different mechanisms and stick together forming irregular or fractal-like agglomerates. Typically, the structure of these agglomerates is characterized with the mass fractal dimension, D_f, and pre-exponential factor, k_n, of simulated agglomerates of monodisperse primary particles (PP) for ballistic or diffusion-limited particle-cluster and cluster-cluster collision mechanisms [2]. The characteristic radius of the mass fractal dimension is the agglomerate radius of gyration, r_g (dashed red circle in Fig. 1). The mobility radius, r_m, of these structures is determined with their projected area equivalent radius (solid green circle in Fig. 1).

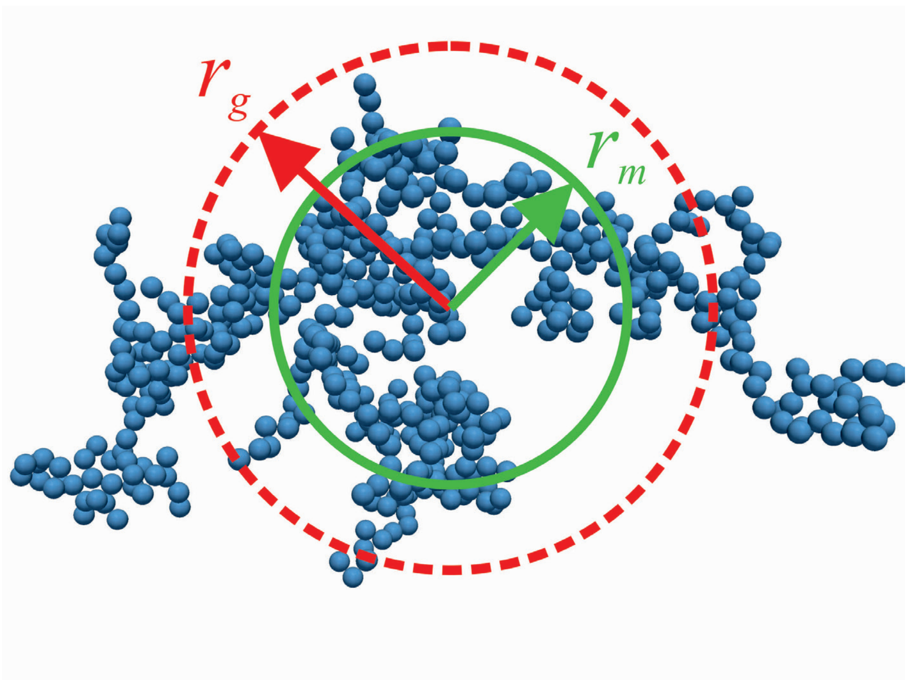

Figure 1: The radius of gyration, r_g (red), and mobility radius, r_m (green), of a diffusion-limited cluster-cluster agglomerate (DLCA) consisting of 512 monodisperse primary particles.

In practical systems, however, the primary particles have almost always a size distribution. For example, primary particles grown by Brownian coagulation and full coalescence upon collision obtain a self-preserving size distribution (SPSD) with a standard deviation of σ_g = 1.45 in the free molecular [3] and continuum regime [4]. The above D_f values have been developed mainly for agglomerates of monodisperse primary particles. Exceptions are Tence et al. [5] and Bushell & Amal [6] who examined the effect of primary particle polydispersity on the agglomerate structure and their scattering behavior. They generated ballistic and diffusion-limited cluster-cluster agglomerates of Gaussian-distributed [5] and of mono-, bi- and tridisperse primary particles [6] and found no effect on D_f for their investigated polydispersities.

Here, the effect of PP polydispersity on D_f and k_n is investigated with agglomerates consisting of 16 – 1024 PP with closely controlled size distribution (geometric standard deviation, σ_g = 1-3). These simulations are in excellent agreement with the classic structure (D_f and k_n) of agglomerates consisting of monodisperse PPs made by four different collision mechanisms as well as with agglomerates of bi-, tri-disperse and normally distributed PPs. Broadening the PP size distribution of agglomerates decreases monotonically their D_f and for sufficiently broad PP distributions (σ_g > 2.5) the D_f reaches about 1.5 and k_n about 1 regardless of collision mechanism [7]. Furthermore with increasing PP polydispersity, the corresponding projected area exponent, D_α, and pre-exponential factor, k_a, decrease monotonically from their standard values for agglomerates with monodisperse PPs. So D_f as well as D_α and k_a offer an indication for PP polydispersity in mass–mobility and light scattering measurements, if the dominant agglomeration mechanism is known, like cluster-cluster coagulation in aerosols.

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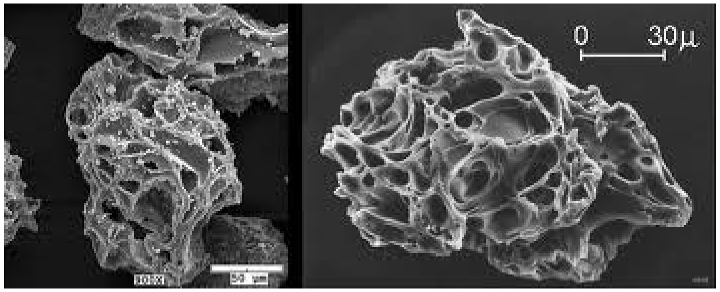
Volcanic Aerosols

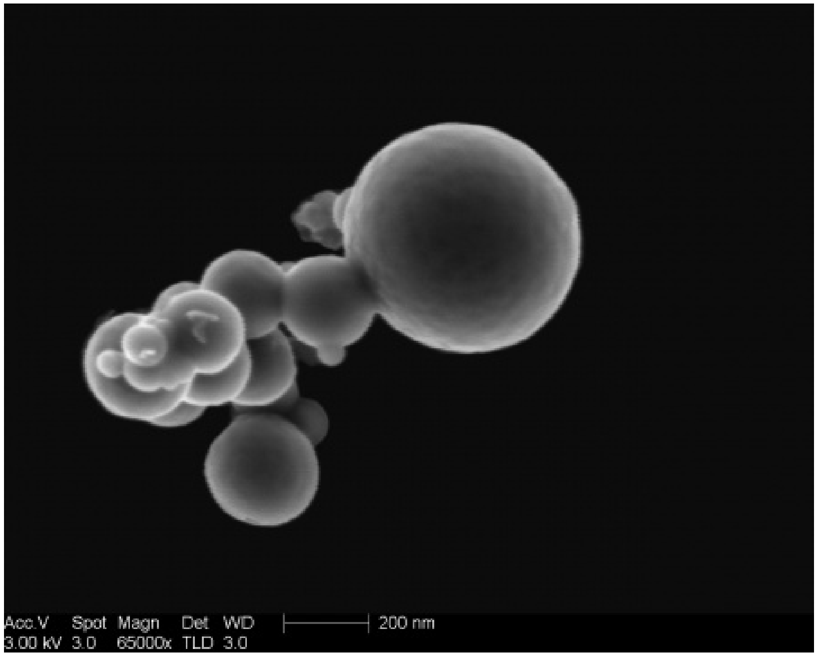


images by Pavel Izbekov and Jill Shipman, Alaska Volcano Observatory / University of Alaska Fairbanks, Geophysical Institute. U.S. Geological Survey.

Exhaust aerosols

Iceland, April, 2010

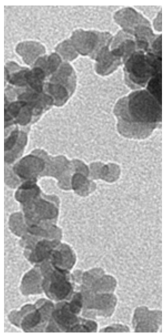
Power Plant Ply ash

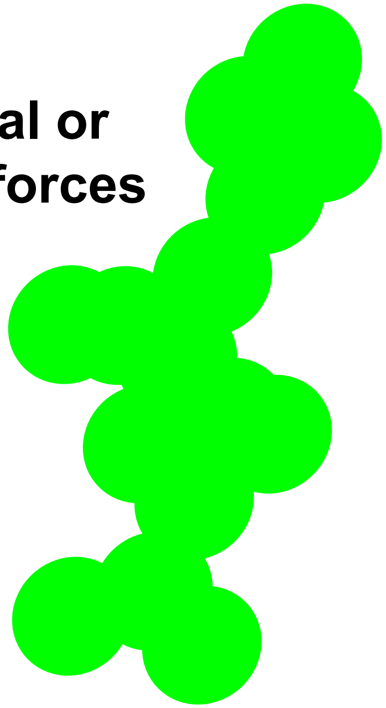


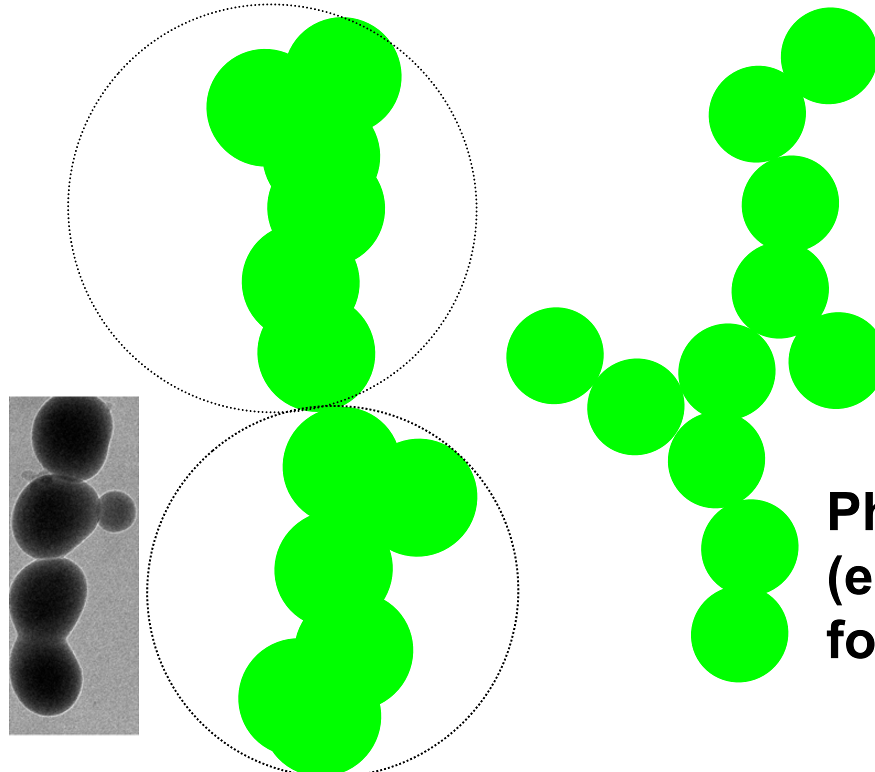
AluminoSilicate, by Esther Coz of CIEMAT/IDAEA-CSIC at RJ Lee Group, Inc.

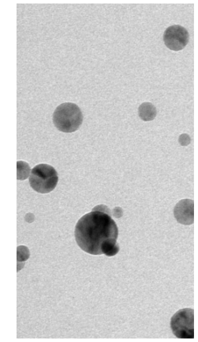
Aggregates and Agglomerates

Chemical or Sinter-forces









Physical (e.g.vdW) forces

Catalysts, lightguides, devices

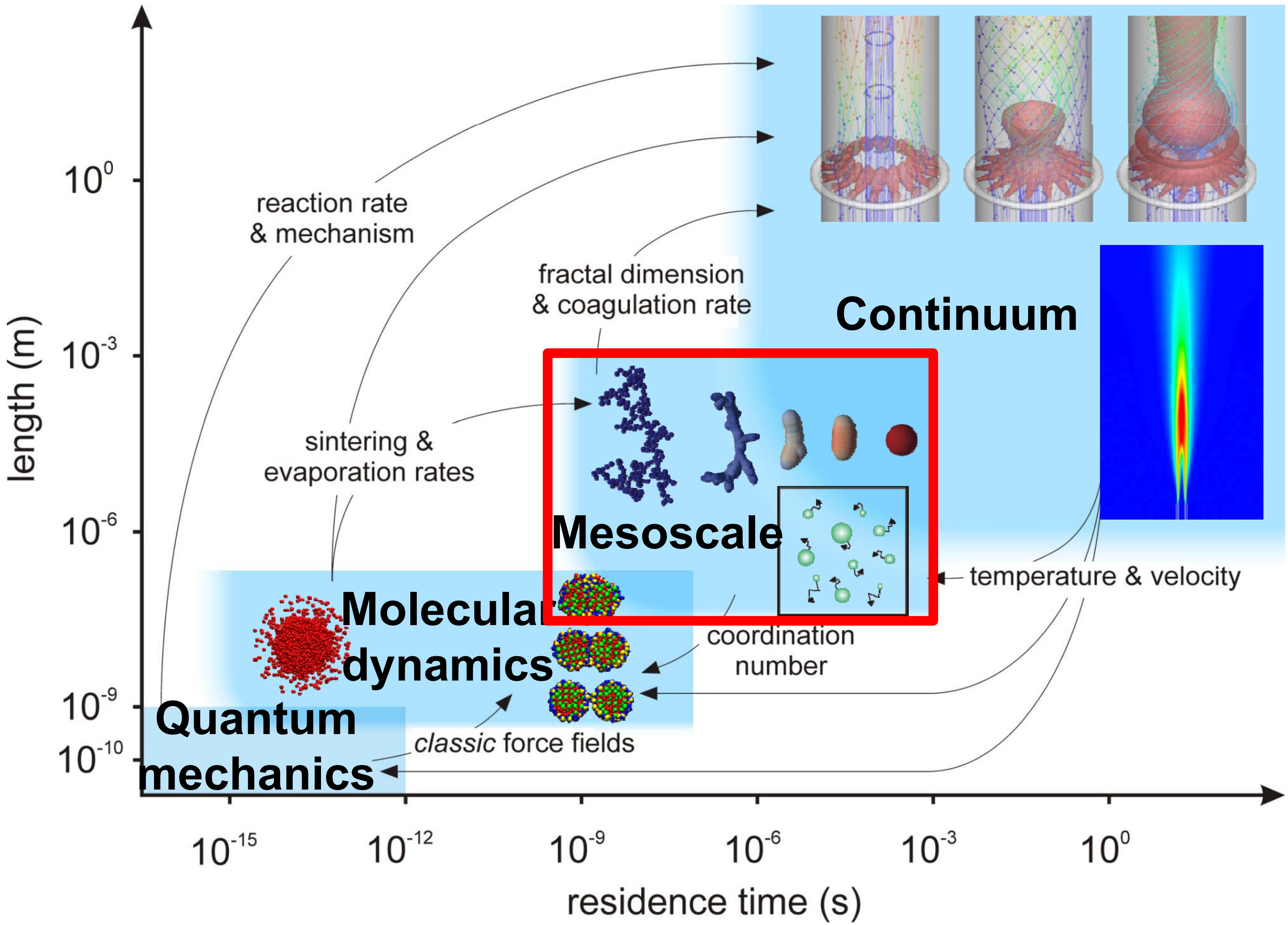
Less toxic?

Nanocomposites, paints

Potentially toxic?

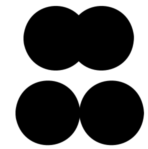
Aerosol instruments cannot distinguish them

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**.



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

Characteristic Agglomerate Radius



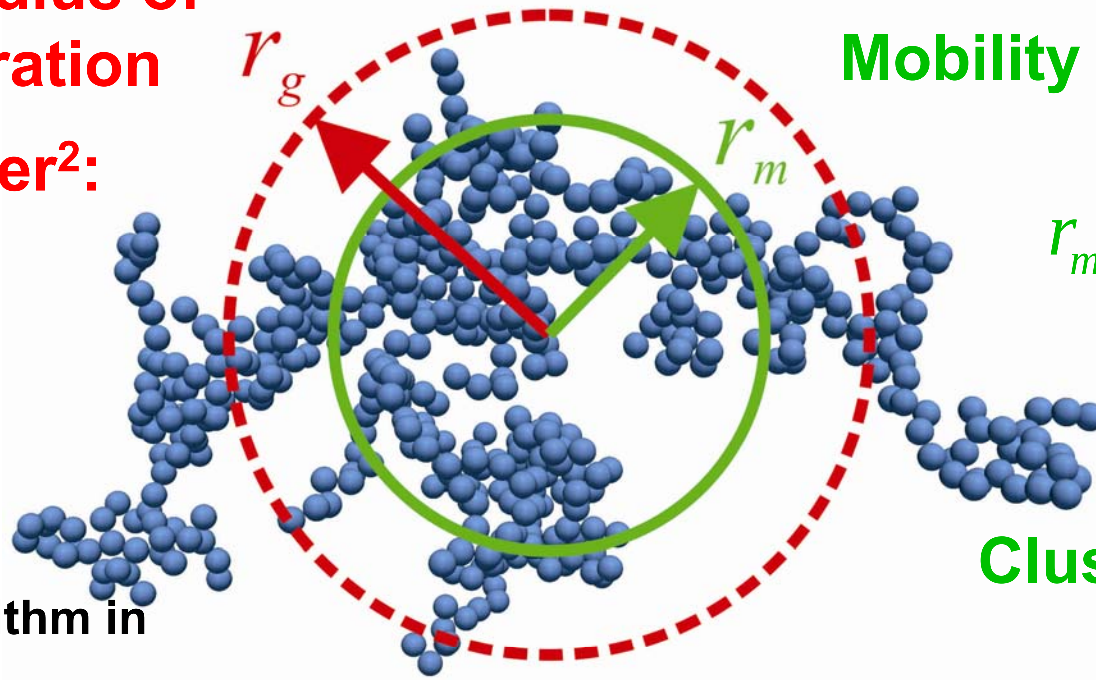
Mass fractal dimension[1], D_f

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

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]:

$$D_{fm} \approx 2.15$$

Agglomerates are generated with a hierarchical algorithm in 3 dimensions.

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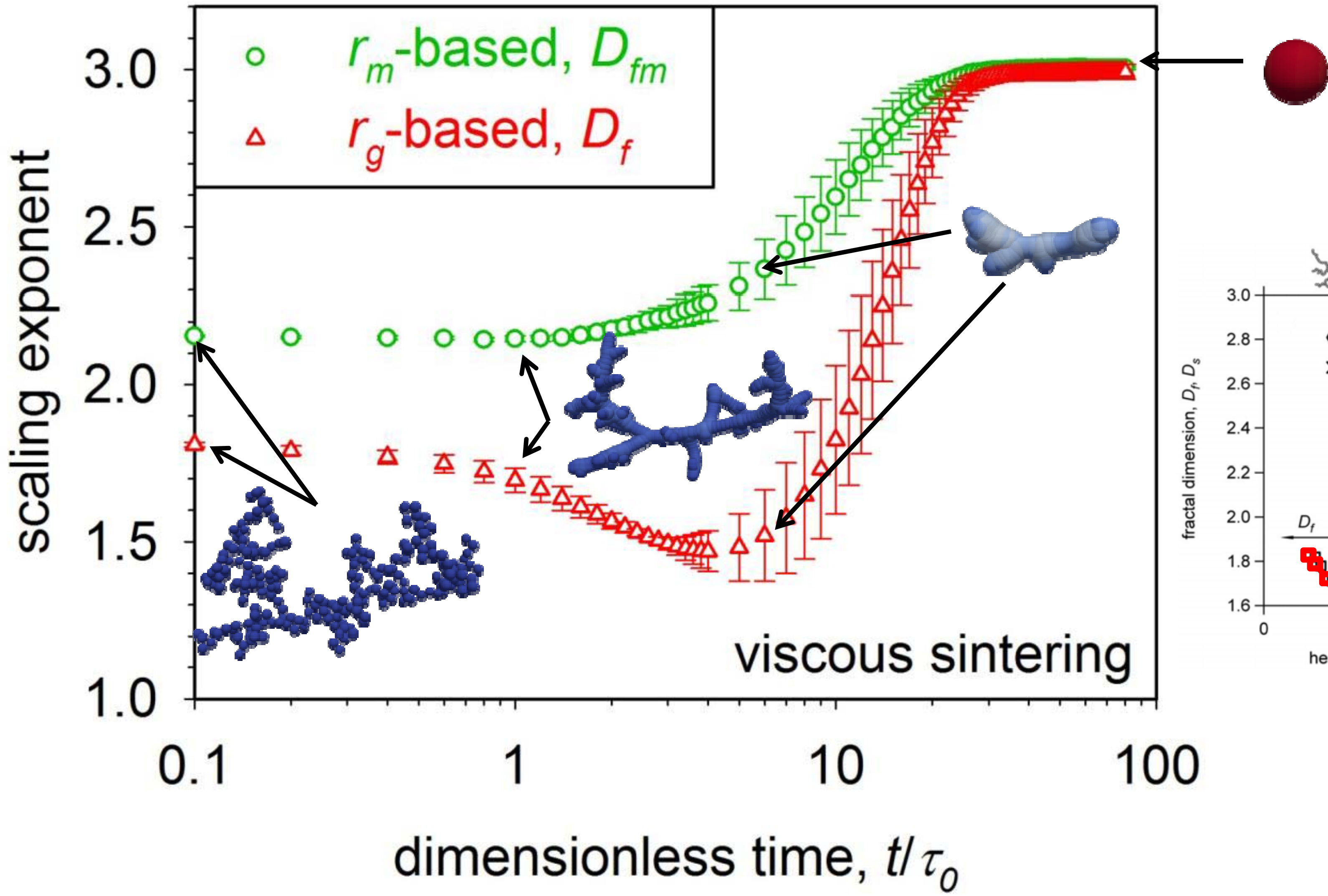
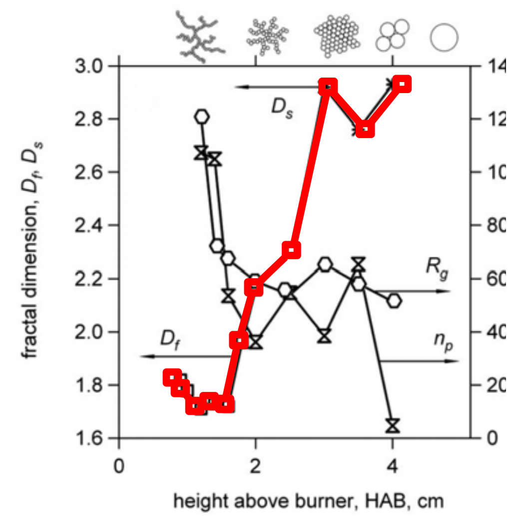
2. C.M. Sorensen, *Aerosol Sci. Technol.* 45 (2011) 755-769.
3. K. Park, F. Cao, D.B. Kittelson & P.H. McMurry, *Environ. Sci. Technol.* 37 (2003), 577-583.

Evolution of D_f & D_{fm}

Ensemble average over 200 clusters with 16-512 PPs





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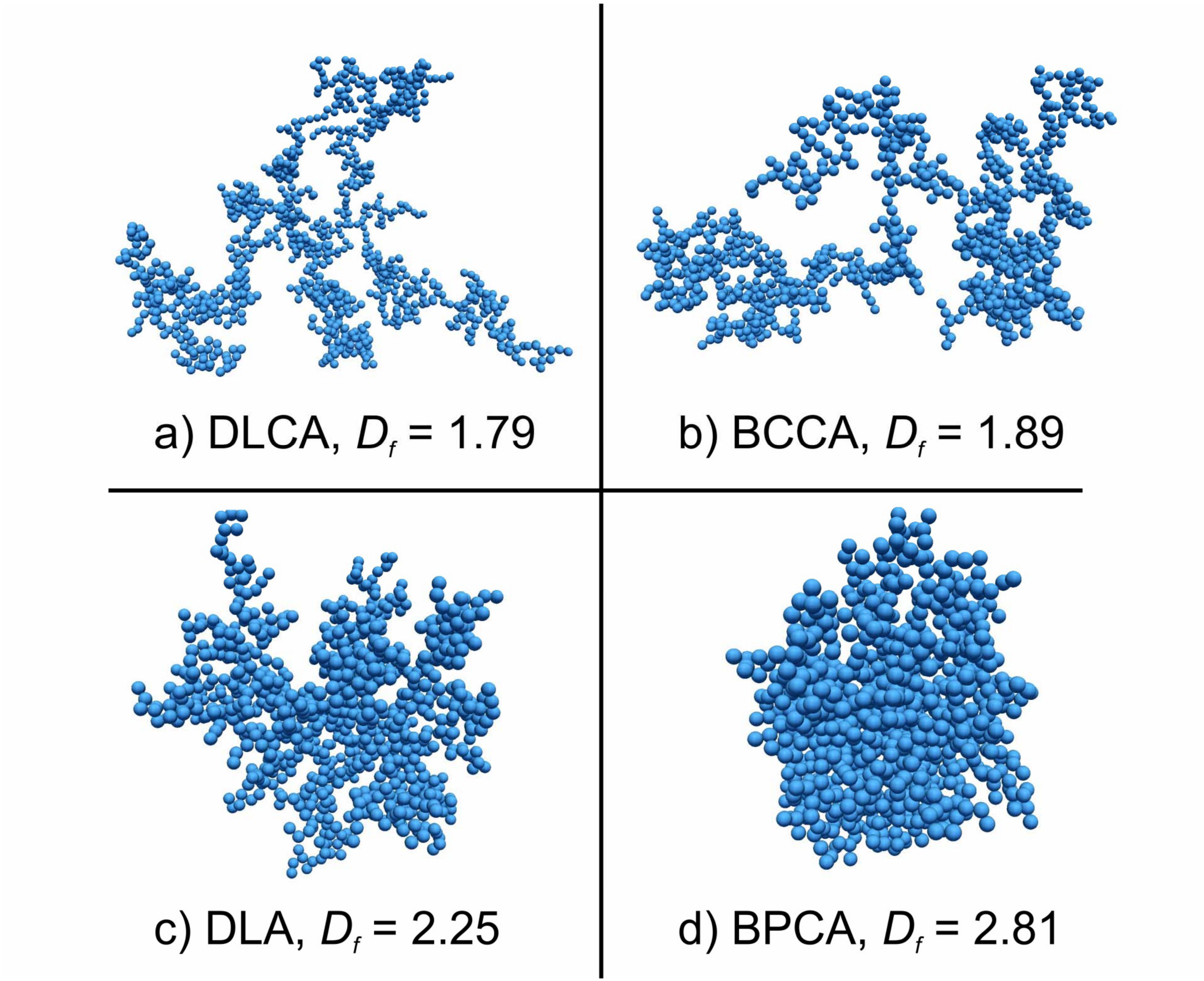

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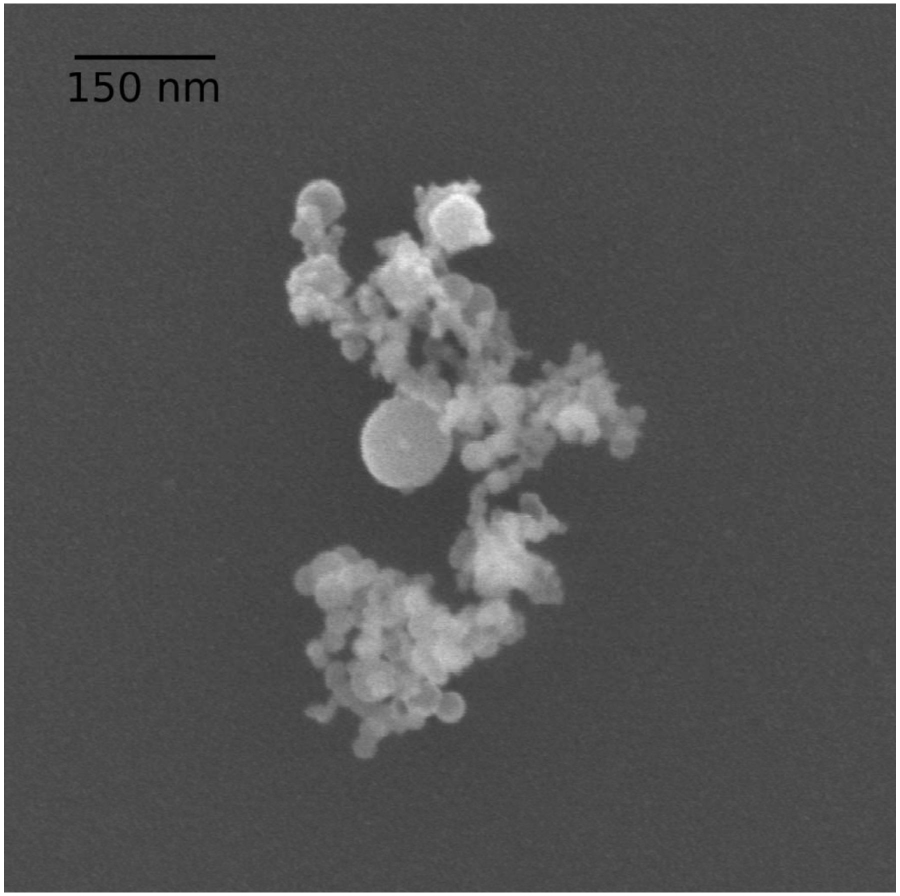
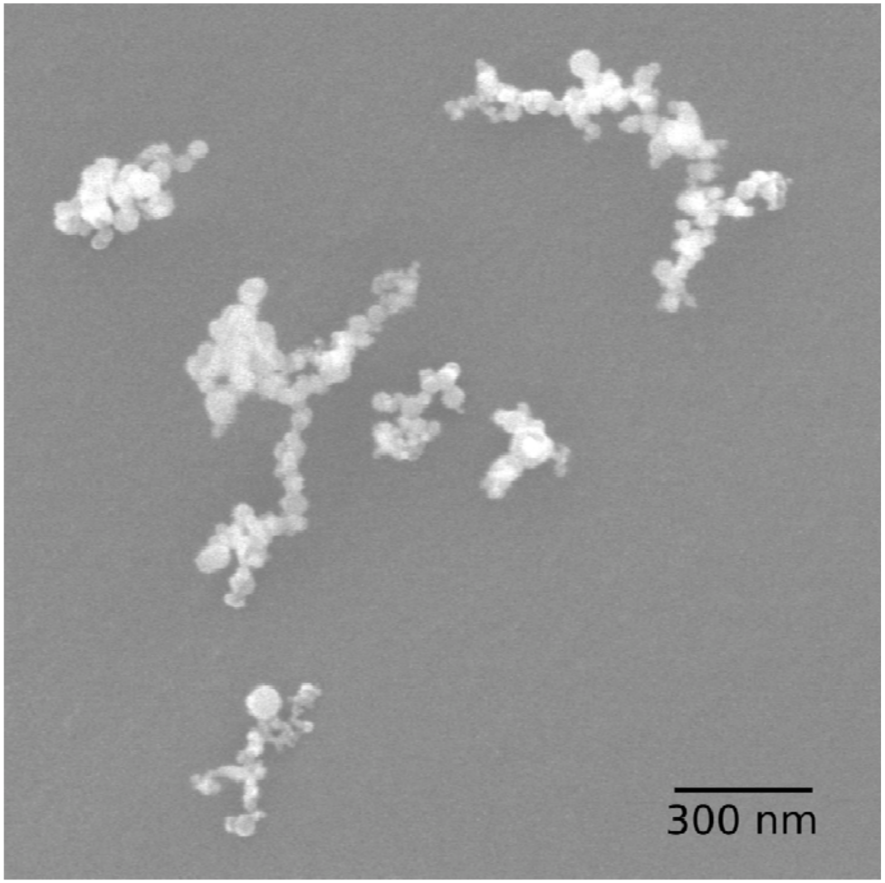
Flame-made SiO_2 agglomerates and aggregates





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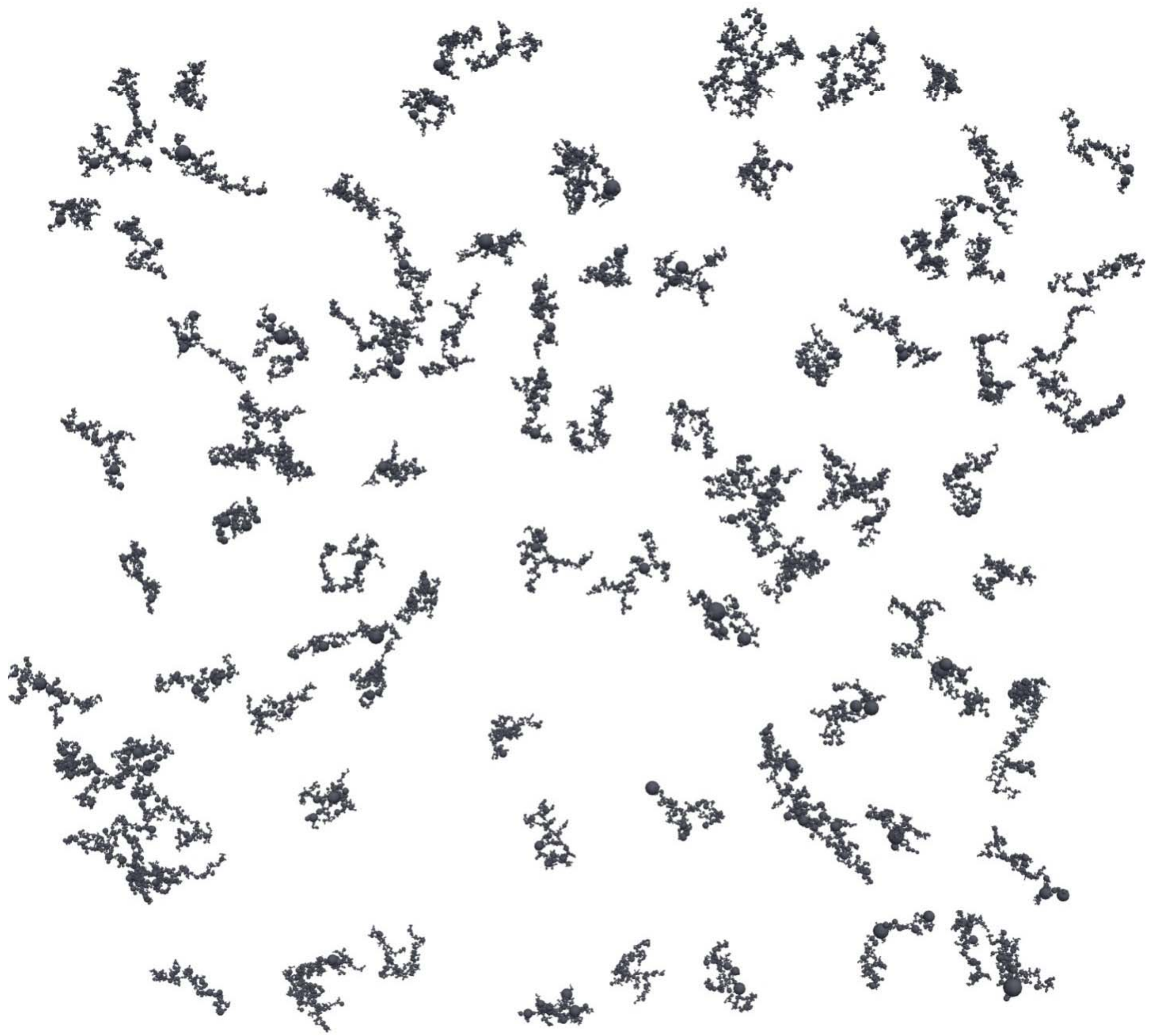
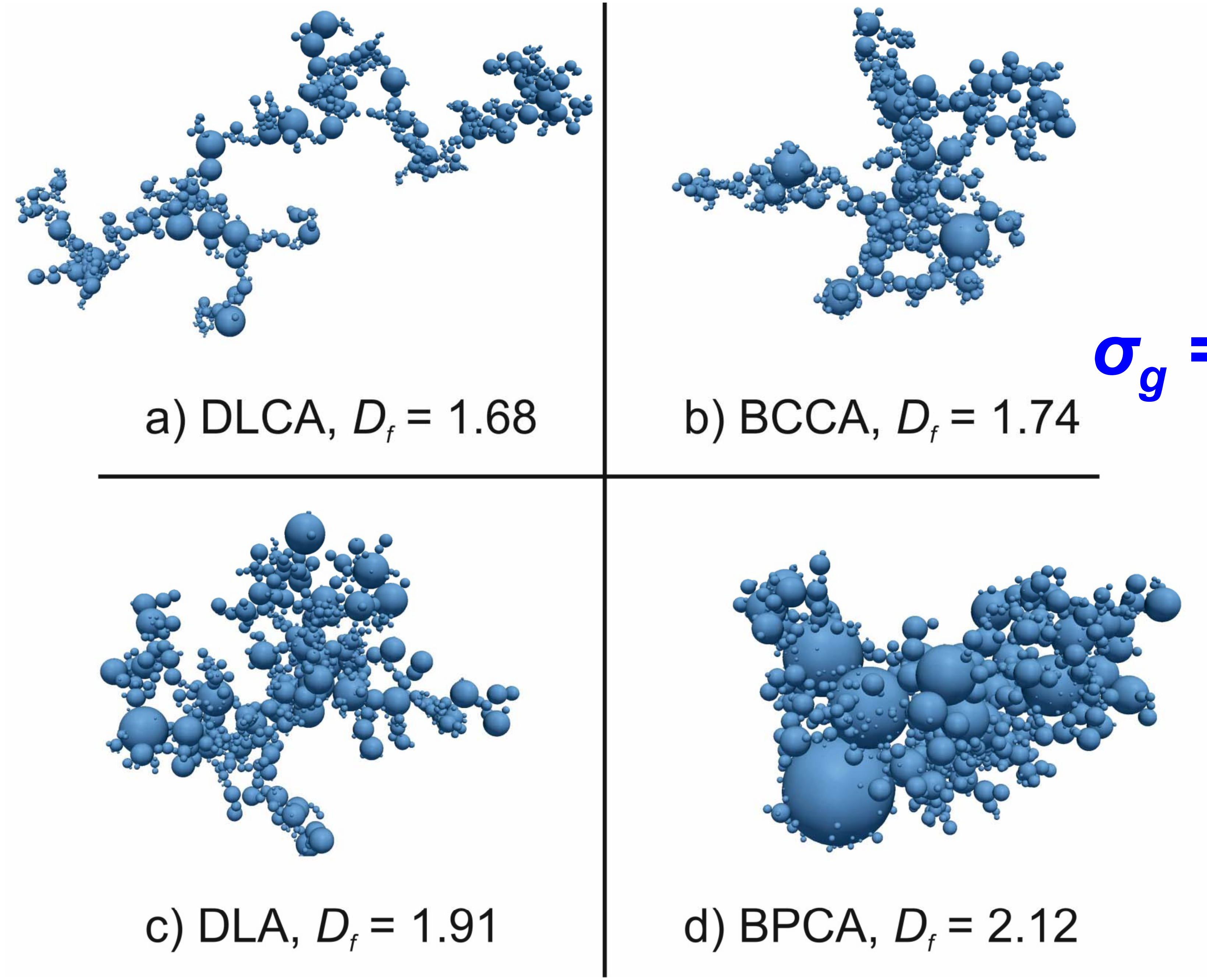


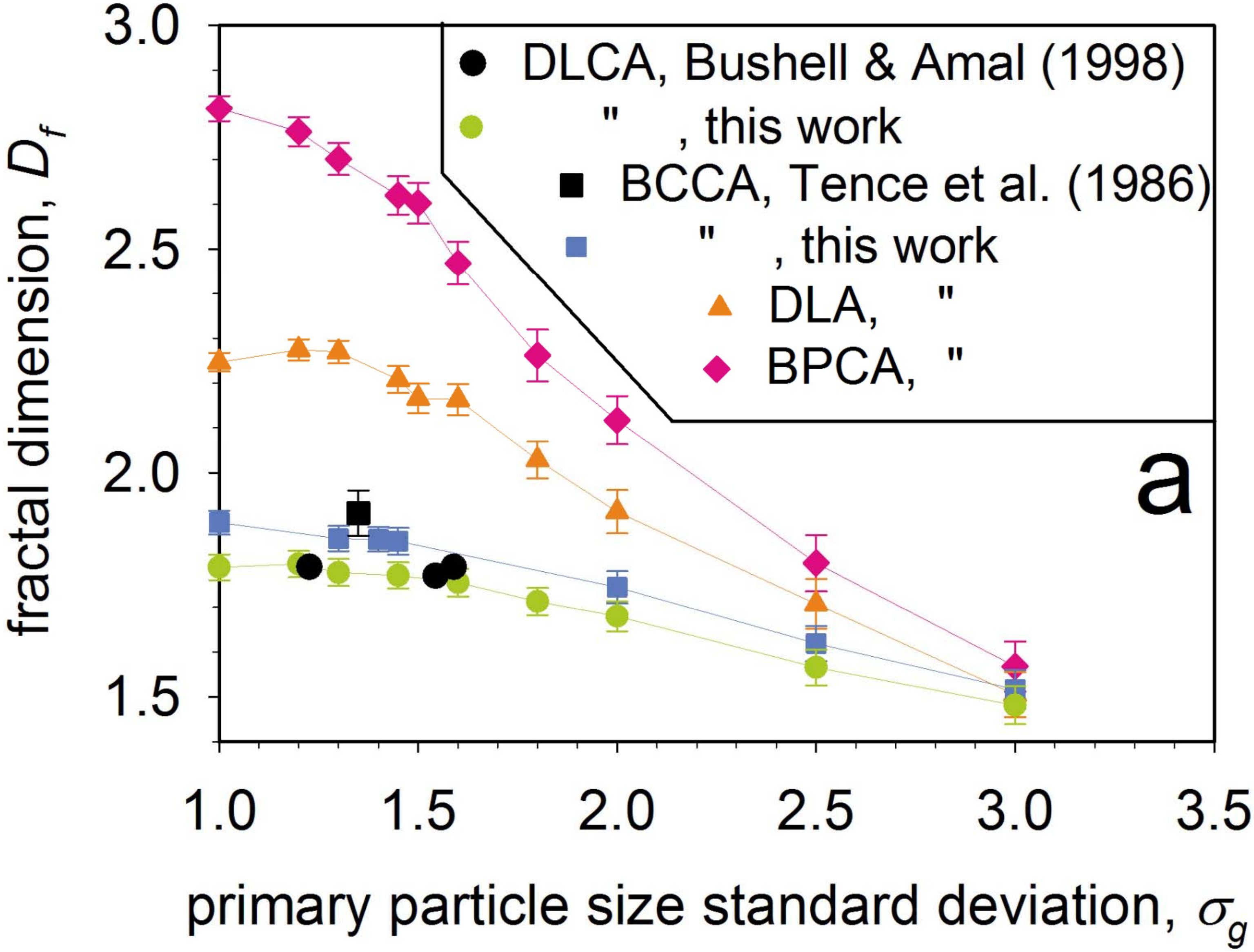
$\sigma_g = 2$

The Structure of Agglomerates consisting of Polydisperse Particles having
Geometric standard deviation $\sigma_g = 2$



$\sigma_g = 2$

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



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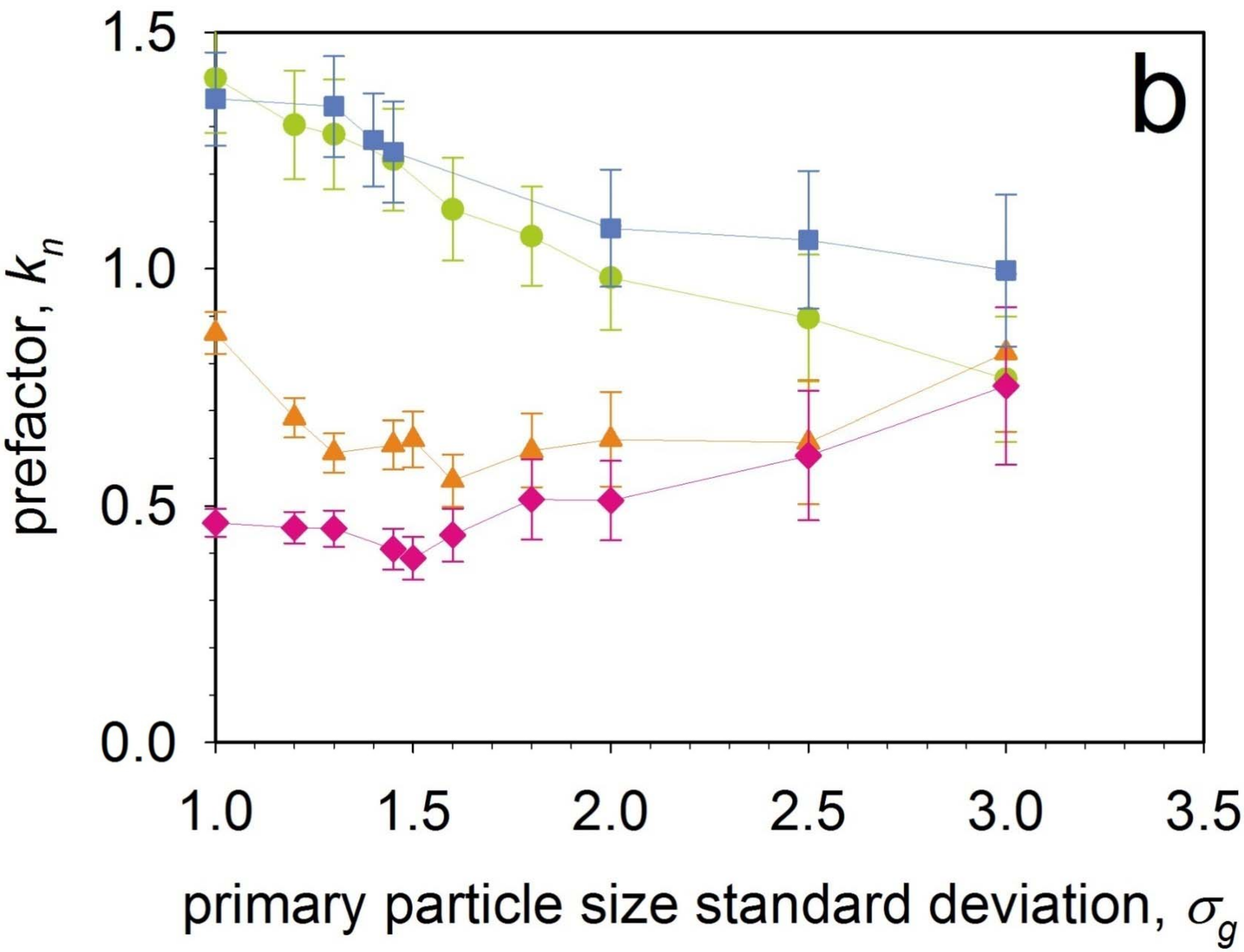

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Aerosol Sci. Technol., **46**, 347–353 (2012)

Conclusions

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

- Broad size distributions (σ_g>2) of primary particles determine the structure of their agglomerates rather than their collision mechanism.

  - **Posters** Extraction of soot's primary particle diameter from mass-mobility measurements

Thank you for your attention

Creux du Van, Neuchatel, August 22, 2011