

# The effect of structure by coagulation & sintering of fractal-like particles

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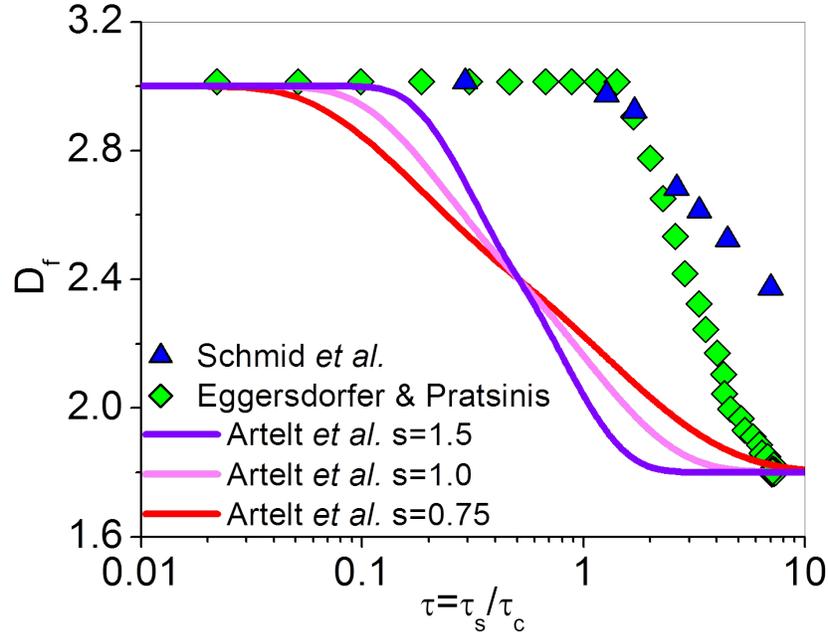
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Typically nanoparticle formation by coagulation results in fractal-like structures in atmospheric and industrial systems. Though the asymptotic form of such structures is described well with the so-called fractal dimension,  $D_f$ , by either diffusion-limited or ballistic cluster-cluster agglomeration, little is known for the evolution of  $D_f$ , from that of initially tiny spheres ( $D_f = 3$ ) to that of large fractal-like aerosol particles ( $D_f = 1.9-2.1$ ). In process design, typically, the evolution of  $D_f$  is neglected or simplified using a constant value. Notable exceptions are those of Xiong and Pratsinis (1993) and Artelt et al. (2003) who had interpolated  $D_f$  at an arbitrary rate or slope from that of fully coalesced particles to that of non-coalescing agglomerates.

Here, the effect of the rapidly evolving structure  $D_f$  of newly formed  $\text{TiO}_2$  particles is explored on their primary particle and collision diameters over their process synthesis parameter space by interfacing molecular dynamics, mesoscale and continuum models. A monodisperse continuum model is employed accounting for simultaneous coagulation and sintering of  $\text{TiO}_2$  particles under non-isothermal conditions over the process synthesis parameter space (Tsantilis and Pratsinis, 2004; Kruis et al., 1993). The evolution of the agglomerate collision diameter and morphology is explored assuming a varying  $D_f$  based on mesoscale simulations (Schmid et al. 2006; Eggersdorfer and Pratsinis, in preparation) as well as constant and arbitrarily varying  $D_f$  (Artelt et al. 2003) using the characteristic sintering time of rutile titania from molecular dynamics (Buesser et al., 2011).

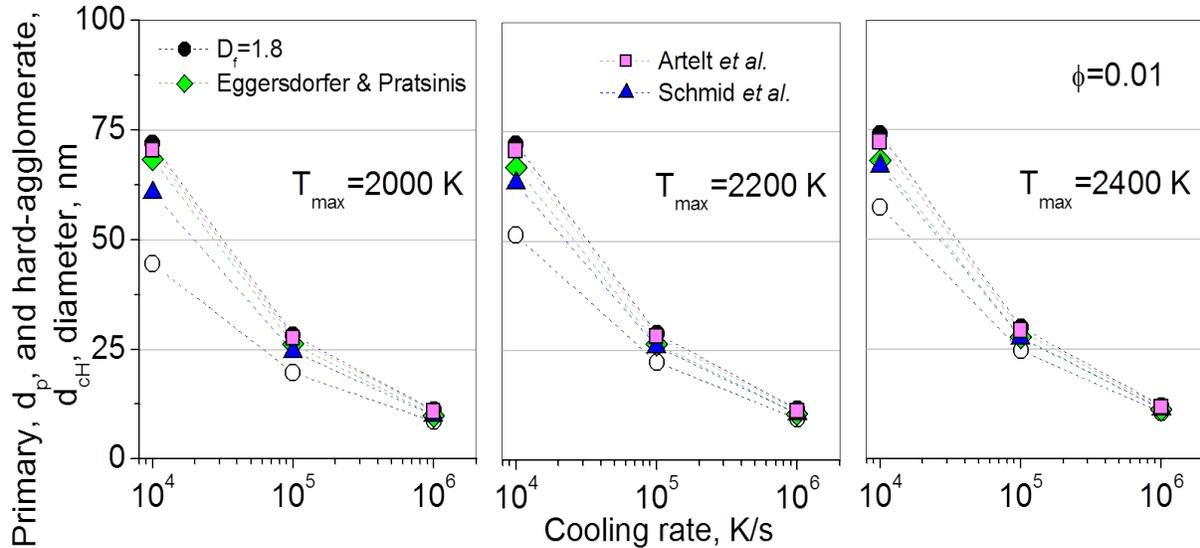
Figure 1 shows the evolution of the mass fractal dimension  $D_f$  as a function of the dimensionless characteristic time  $\tau$  defined as the ratio of the characteristic sintering time to the characteristic collision time,  $\tau = \tau_s/\tau_c$ . The models of Artelt et al. (2003) for  $s=0.75$  (red line), 1.0 (pink line) and 1.5 (blue line), Eggersdorfer and Pratsinis (in preparation; green diamonds) and Schmid et al. (2006; blue squares) are compared. The model of Artelt et al. (2003) bridges the constant values of  $D_f = 1.8$  and 3 for the limiting cases of  $\tau_s \gg \tau_c$  and  $\tau_s \ll \tau_c$ , respectively and was empirically derived for the transition regime. The duration of the transition region depends on the employed  $D_f$  model, with the power law of Eggersdorfer and Pratsinis (in preparation) predicting a narrow, abrupt  $D_f$  change, Schmid et al. (2006) a slower transition to the constant asymptotic value and Artelt et al. (2003) model a smooth transition of variable, arbitrarily defined rate (depending on parameter  $s$ ) from fully fused spheres to fractal-like aggregates.

The effect of process conditions, such as the maximum operation temperature, cooling rate and initial number concentration on the primary particle, hard- and soft-agglomerate diameters are investigated. Accounting for the evolution of  $D_f$  hardly affects the primary particle and agglomerate diameters even though it alters the transient evolution of the agglomerate collision diameter up to 25% during the hard-aggregate to soft-agglomerate transformation.



**Figure 1.** Evolution of mass fractal dimension as a function of the dimensionless characteristic time, defined as the ratio of characteristic sintering to characteristic collision time. The models of Artelt *et al.* (2003) for  $s=0.75$  (red line), 1.0 (pink line) and 1.5 (blue line), Eggersdorfer & Pratsinis (in preparation; green diamonds) and Schmid *et al.* (2006; blue triangles) are shown. Artelt *et al.* (2003) assumed an empirical evolution of the fractal dimension, Schmid *et al.* (2006) determined the equilibrium fractal dimension at different constant characteristic times and Eggersdorfer & Pratsinis (in preparation) described the evolution of fractal dimension during particle growth of amorphous silica by coagulation and sintering accounting for the change in the characteristic time.

Figure 2 shows the primary (open circles) and hard-agglomerate (filled symbols) particle diameter of titania for three maximum flame temperatures ( $T_{max} = 2000, 2200$  and  $2400\text{K}$ ) as a function of the cooling rate ( $CR = 10^4, 10^5$  and  $10^6$  K/s) at precursor molar fraction  $\phi = 0.01$  for the models of Eggersdorfer and Pratsinis (in preparation; green diamonds), Artelt *et al.* (2003) for  $s = 1$  (pink squares) and Schmid *et al.* (2006; blue triangles) which are compared against the corresponding diameters using constant  $D_f = 1.8$  (black circles). The evolution of  $D_f$  has a minor effect on the primary particle diameter, as also depicted in Figure 3, and hence only the  $d_{pH}$  for  $D_f=1.8$  is shown here. Even though with increasing maximum operating temperature the hard-primary particle diameter increases and the hard-agglomerate diameter is not significantly affected, the increasing cooling rates cause both  $d_{pH}$  and  $d_{cH}$  to decrease. More specific, at high cooling rates low agglomerated (indiscernible difference between  $d_{cH}$  and  $d_{pH}$ ) particles tend to form, a phenomenon that is more pronounced at higher maximum temperatures. Furthermore, the  $D_f$  models of Artelt *et al.* (2003) for  $s = 1, s = 0.75$  and 1.5 (not shown here) and Eggersdorfer and Pratsinis (in preparation) predict hard-agglomerate diameters close to that of constant  $D_f=1.8$  in contrast to Schmid *et al.* (2006) model that predicts a  $d_{cH}$  variation up to 25% for high precursor molar fractions, low maximum flame temperatures and low cooling rates. On the other hand, the hard-primary particle diameter is hardly affected by the evolution of fractal dimension (difference less than 4%), consistent with literature, regardless of the  $D_f$  model.



**Figure 2.** Primary particle diameter (open symbols) and hard agglomerate collision diameter (filled symbols) of titania particles as a function of the cooling rate for three maximum operating temperatures (2000, 2200 and 2400K) for initial precursor molar fraction  $\phi=0.01$ . The models of Eggersdorfer & Pratsinis (in preparation; green diamonds), Artelt et al. (2003) for  $s=1$  (pink squares) and Schmid et al. (2006; blue triangles) are compared against the constant fractal dimension (black filled circles). The evolution of  $D_f$  has a minor effect on the primary particle diameter and hence only the  $d_{pH}$  of  $D_f=1.8$  is shown here.

A similar analysis is performed for amorphous  $\text{SiO}_2$  and the effect of two sintering rate descriptions on particle growth has been examined for the entire process parameter space. Generally, varying  $D_f$  practically does not affect the primary particle and hard-agglomerate diameter even though it affects the transient evolution of collision diameter for  $\text{SiO}_2$ , as also predicted for  $\text{TiO}_2$ . However, the sintering rate significantly affects both the transient and final primary particle and hard-agglomerate diameters that determine the final particle properties.

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## Motivation

- Investigation of the effect of time-evolving fractal dimension,  $D_f$  on primary and hard-agglomerate diameters of  $\text{TiO}_2$  and  $\text{SiO}_2$  flame-made particles by interfacing continuum, mesoscale and molecular dynamics models.
- Identification of process conditions that affect agglomeration of  $\text{TiO}_2$  and  $\text{SiO}_2$ .

## Aerosol Dynamics

Number Concentration,  $N$ :  $\frac{dN}{dt} = -\frac{1}{2} \beta N^2 \rho_g$

Agglomerate Area Concentration,  $A$ :  $\frac{dA}{dt} = -\frac{1}{\tau_s} (A - Na_s)$

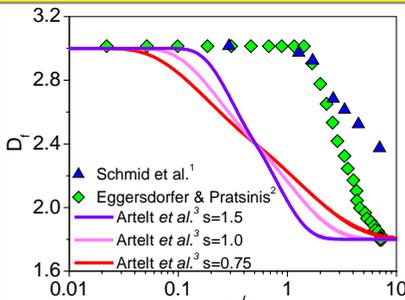
Agglomerate Volume Concentration,  $V$ :  $\frac{dV}{dt} = 0$

Primary Particle Diameter  $d_p$  and Collision Diameter  $d_c$

$$d_p = \frac{6V}{A}$$

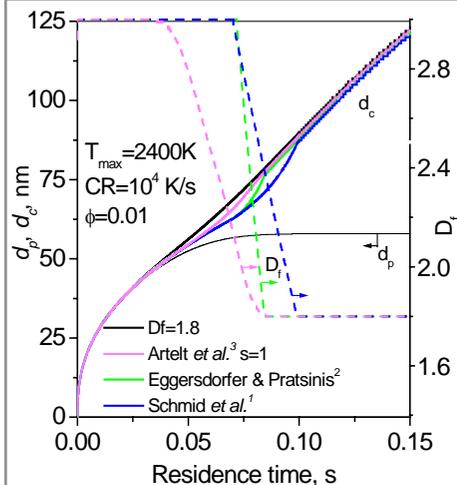
$$d_c = d_p \left( \frac{A^3}{36\pi N V^2} \right)^{1/D_f}$$

## Structure Evolution

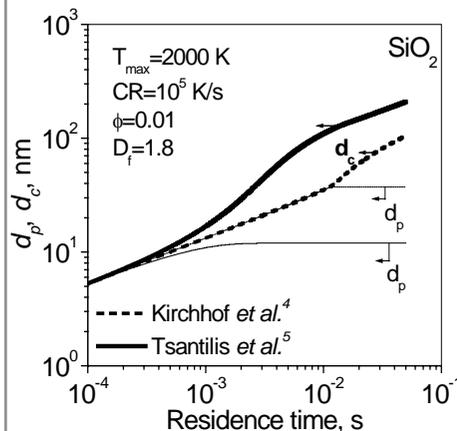


Evolution of  $D_f$  with the dimensionless characteristic time as predicted by mesoscale [1,2] and empirical [3] models.

## Particle Growth



Evolution of  $\text{TiO}_2$   $d_p$  and  $d_c$  with varying and constant  $D_f$ .



The evolution of  $\text{SiO}_2$   $d_p$  and  $d_c$  is sensitive to the characteristic sintering time.

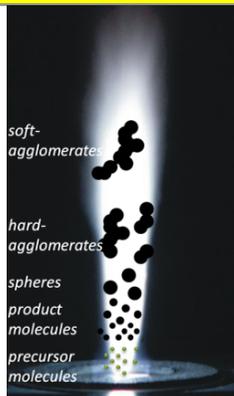
## Conclusions

- Varying  $D_f$  hardly affects  $d_p$  and  $d_{ch}$  even though it affects the transient evolution of  $d_c$  for both  $\text{TiO}_2$  and  $\text{SiO}_2$ .
- Particle growth depends on the characteristic sintering time. Over the process conditions no hard-aggregates of  $\text{SiO}_2$  are formed accounting for Kirchhof et al. [4] sintering rate.
- The trend of the results is consistent with experimental data with  $d_p$  [6].

## References

- [1] Schmid et al. (2006) *Chem. Eng. Sci.* **61**, 293.
- [2] Eggersdorfer & Pratsinis (in preparation).
- [3] Artelt et al. (2003) *J. Aerosol Sci.* **34**, 511.
- [4] Kirchhof et al. (2012) *J. Aerosol Sci.* **45**, 26.
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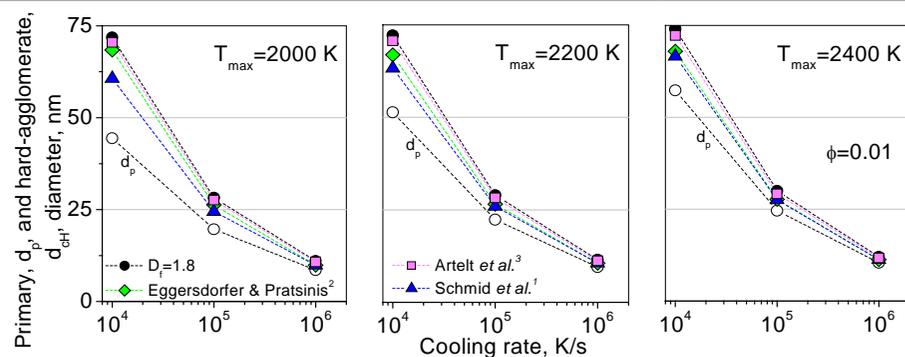
## Flame Spray Pyrolysis



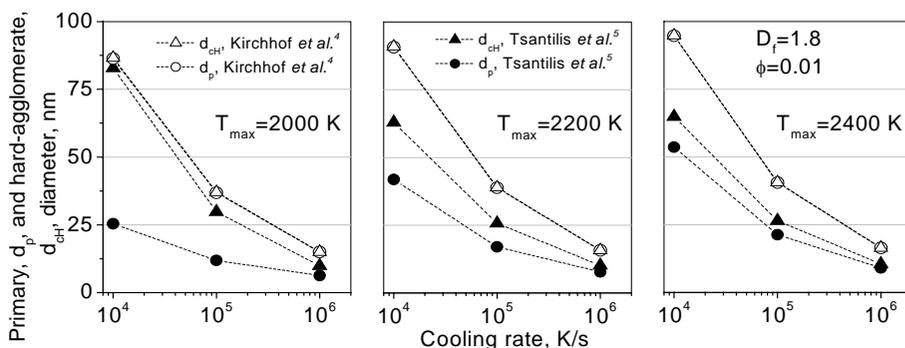
Spray flame producing nanoparticles: The precursor molecules react almost instantaneously, and particles are formed by condensation, sintering or coalescence and coagulation.

Hard-agglomerates are formed by sintering between particles. Soft-agglomerates are held together by physical forces and can be broken to their constituent parts more easily than hard-agglomerates.

## Effect of Process Parameters on $d_p$ and $d_{ch}$



Product diameters for various  $T_{max}$  and various  $D_f$  descriptions of  $\text{TiO}_2$ .



Product diameters for various  $T_{max}$  and two sintering rates of  $\text{SiO}_2$ .