Aggregate Morphology Evolution by Sintering: Number and Diameter of Primary Particles

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The structure of fractal-like agglomerates (physically-bonded) and aggregates (chemically- or sinter-bonded) is important in aerosol synthesis of nanoparticles, and in monitoring combustion emissions and atmospheric particles. Agglomerate and aggregate morphology and primary particle size strongly affect aerosol behavior and properties. The aerosol mobility in the free molecular and transition regime depends on structure, number and diameter of constituent primary particles. Besides particle transport, also energy (heat) transfer is determined by primary particle size and agglomerate/aggregate morphology.[1] The light scattering and absorption of open-structured aerosol agglomerates ($D_f < 2$) is a function of structure and primary particle size.[2] Furthermore the mechanical stability of nanoparticle layers, electron transport and sensitivity of gas sensors and electrical conductivity are significantly influenced by constituent primary particle and aggregate size and degree of sintering.

Recently a new modeling technique for multiparticle sintering dynamics has been developed.[3] Here the evolution of particle coalescence by viscous flow sintering (e.g. SiO_2, polymers) and grain boundary diffusion (e.g. TiO_2, metals) of agglomerates consisting of 16 – 512 primary particles is monitored in detail: from fractal-like agglomerates to aggregates to eventually

compact spheres.[4] The focus is on projected aggregate surface area, mobility diameter, radius of gyration and aggregate morphology (D_f, D_{fm}) in the free molecular and transition regime where nanoparticle sintering typically takes place at high process temperatures. A scaling between number of primary particles and projected area is combined with the relation between projected area and mobility diameter to calculate the average number and diameter of primary particles in aggregates (Fig. 1). That way the evolution of D_f (radius of gyration-based) and D_{fm} (mobility diameter-based, Fig. 2) and prefactors are investigated during sintering as they are used to characterize fractal-like particles by light scattering[2] and mass-mobility[5] measurements. This method is applied to sintering of silver aggregates[5] to estimate their degree of sintering as they have been characterized by mass-mobility measurements.

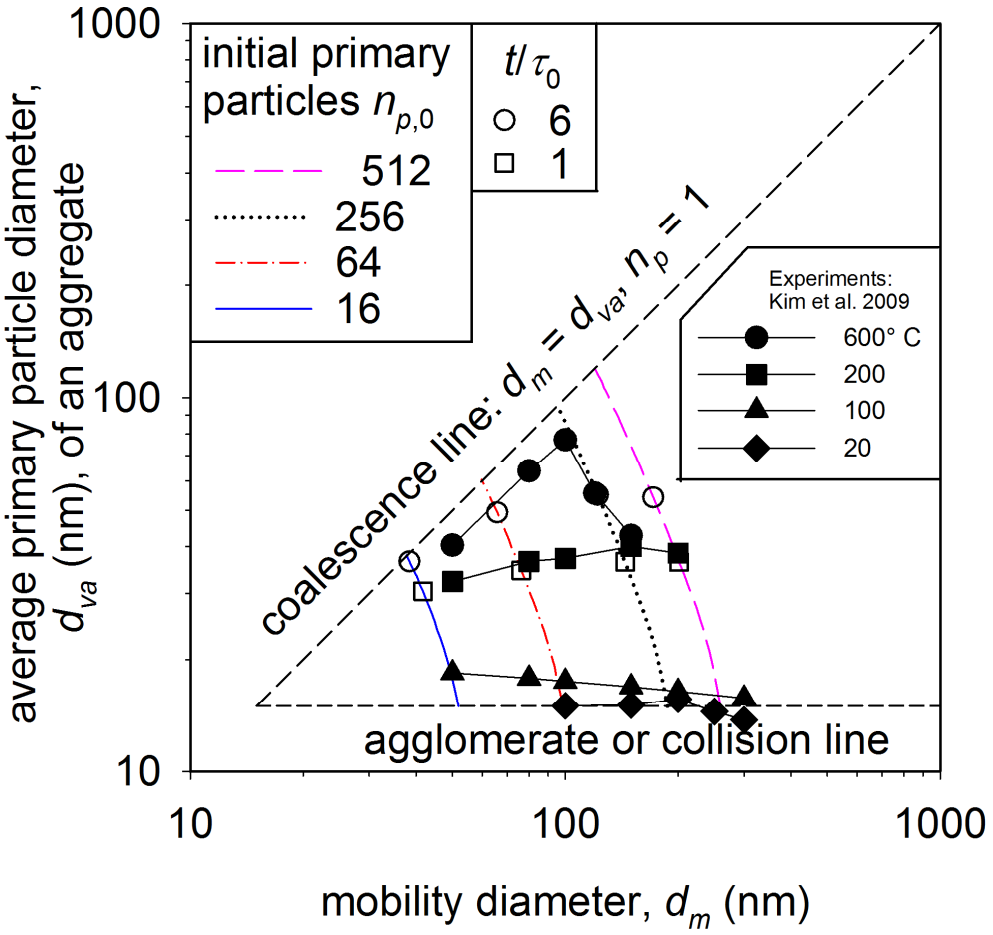

Figure 1: *Evolution of average diameter of primary particles in aggregates, d_{va}, as a function of mobility diameter, d_m, for the sintering of initial agglomerates of 16 – 512 primary*

particles compared to experimental results by Kim et al[5]. For agglomerates of monodisperse spherical primary particles, $d_{va} = d_p$ independent of mobility size (agglomerate or collision line). d_m decreases during sintering while d_{va} increases until $D_f = 3$ (coalescence line).

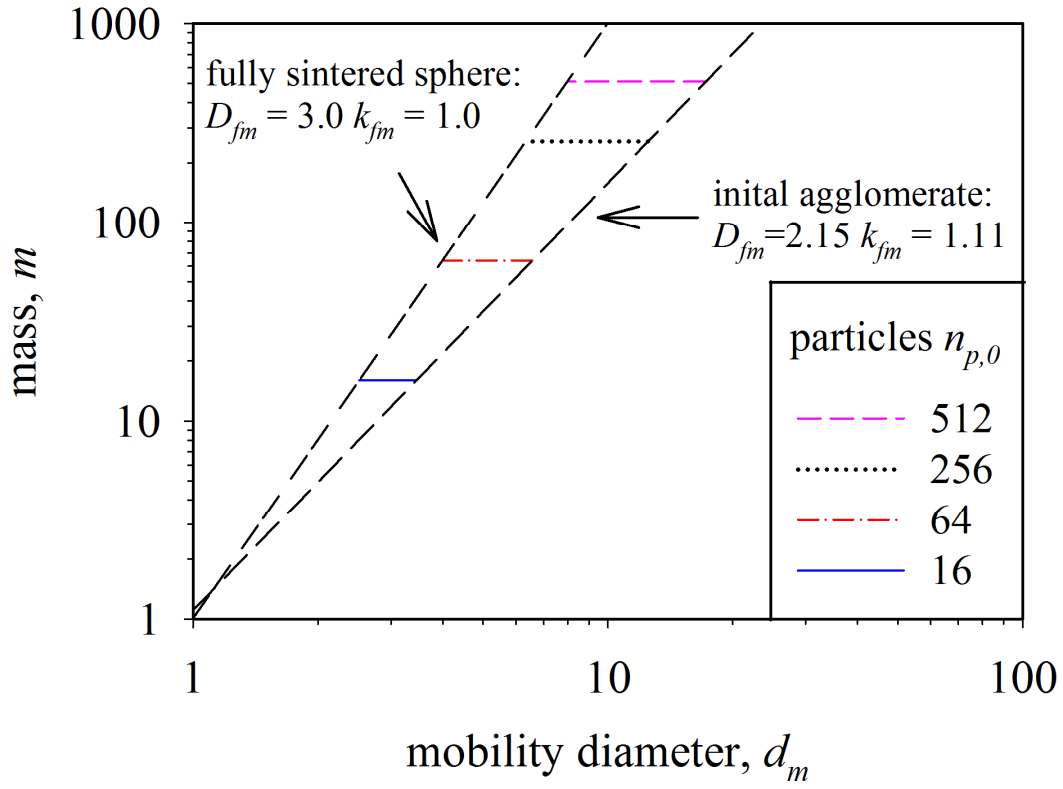

Figure 2: *At the beginning of sintering the initial agglomerates of 16 – 512 primary particles have a mass-mobility exponent $D_{fm} = 2.15$ and prefactor $k_{fm} = 1.11$. During the evolution of sintering their mass m is conserved but their mobility diameter d_m decreases resulting in a change in scaling until a fully sintered or coalesced sphere with $D_{fm} = 3$ and $k_{fm} = 1$ is reached.*

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3. Eggersdorfer, ML, Kadau, D, Herrmann, HJ, Pratsinis, SE (2011) Langmuir 27(10): 6358–6367.

4. Eggersdorfer, ML, Kadau, D, Herrmann, HJ, Pratsinis, SE (2012) J. Aerosol Sci. 46: 7-19.

5. Kim, SC, Wang, J, Emery, MS, Shin, WG, Mulholland, GW, Pui, DYH (2009) Aerosol Sci. Technol. 43: 344-355.

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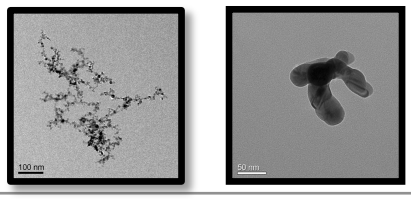
Motivation/Objective

The structure of fractal-like agglomerates (physically-bonded) and aggregates (chemically- or sinter-bonded) is important in aerosol synthesis of nanoparticles, and in monitoring combustion emissions and atmospheric particles. Agglomerate and aggregate morphology and primary particle size strongly affect aerosol behavior and properties. Here the evolution of particle coalescence by viscous flow sintering (e.g. SiO_2, polymers) and grain boundary diffusion (e.g. TiO_2, metals) of several agglomerates consisting of 16 – 512 primary particles made by diffusion limited cluster-cluster agglomeration (DLCA) is monitored in detail.

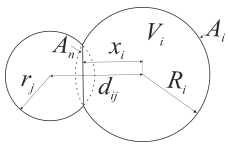
Model for Multi-particle Sintering

Experiments: Nanoparticle aggregates are partially sintered. The degree of sintering depends on residence time at high temperature (sinter time).

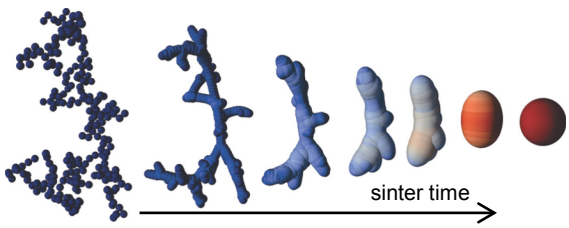


Geometric Model considers:

- Energy balance, e.g. for viscous sintering the decrease in surface energy equals viscous dissipation
- mass/volume balance



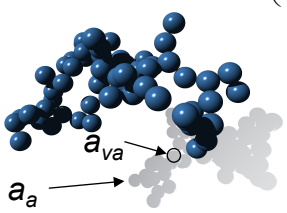
The sintering of agglomerates, including restructuring, can be simulated up to full coalescence.

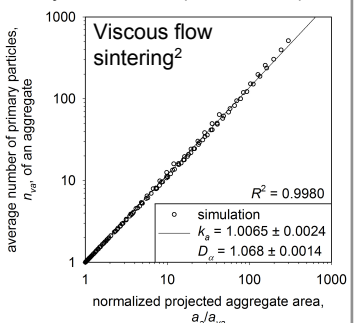


Projected Aggregate Area Scaling[1]

A power law holds between normalized projected aggregate area a_a/a_{va} and average number of primary particles n_{va} during sintering by viscous flow and grain boundary diffusion (not shown), average $k_a = 0.998$ & $D_\alpha = 1.069$:

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

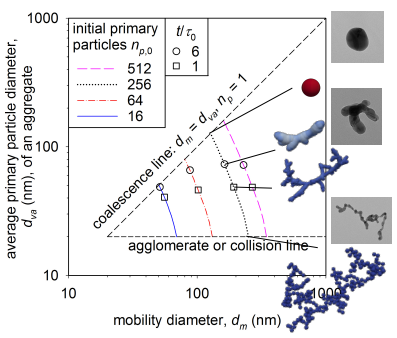




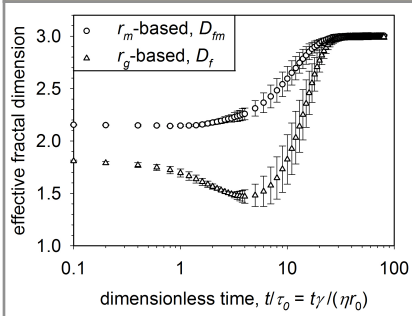
Average Primary Particle Diameter d_{va}

$$d_{va} = 6v/a = \left(\pi k_a d_m^{2D_\alpha} / 6v \right)^{1/(2D_\alpha - 3)}$$ (agglomerate Volume v, mobility size d_m, $a_a = \pi\, d_m^2/4$

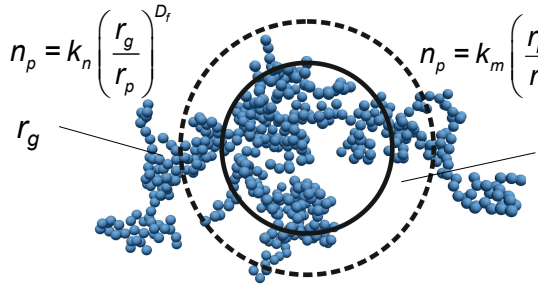
Evolution of d_{va} as a function of mobility diameter, d_m. For agglomerates of monodisperse spherical primary particles, $d_{va} = d_p$ independent of mobility size (agglomerate or collision line). d_m decreases during sintering while d_{va} increases until $D_f = 3$ (coalescence line).

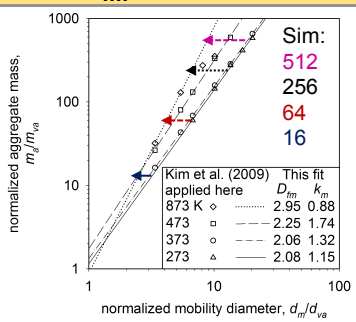


Effective fractal dimension D_f vs. mass mobility exponent D_{fm}



$$n_p = k_n \left(\frac{r_g}{r_p} \right)^{D_f} \qquad n_p = k_m \left(\frac{r_m}{r_p} \right)^{D_{fm}}$$





Evolution of D_f and D_{fm} during viscous sintering of DLCA agglomerates. The exponents (D_f, D_{fm}) are obtained by ensemble averaging over 50 agglomerates of each size. Only D_{fm} exhibits monotonic behavior and thus can be used to characterize the degree or extent of sintering of aggregates.

DMA-APM data of silver nanoparticle aggregates sintered at different temperatures (faster sintering for same sinter time) by Kim et al.[4] are post-processed here. The D_{fm} exhibits a monotonic increase consistent with our sintering simulations-

References

[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.
[4] 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.

Conclusions

1. The scaling $n_{va} = k_a \left(\frac{a_a}{a_{va}} \right)^{D_\alpha}$ holds during sintering.
2. The D_α and k_a are independent of sintering mechanism.
3. The d_{va} is in agreement with TEM images.
4. The mass-mobility exponent D_{fm} increases monotonically, while the fractal dimension D_f reaches a minimum. Thus, D_{fm} can be used to characterize the degree of sintering.