Dynamics of Fractal-like Aerosols during Sintering

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Gas-borne nanoparticles undergoing coagulation and sintering form irregular or fractal-like structures (agglomerates and aggregates) affecting their transport, light scattering, effective surface area and density [1]. The (real-time) characterization of these structures and their constituent primary particles is necessary for continuous monitoring of aerosol manufacturing and airborne pollutant particle concentrations. Significant advances have been made in characterization of agglomerates (physically –bonded particles) by employing fractal theory and relating agglomerate structure to its generation pattern through the fractal dimension, D_f. What might have been overlooked in characterization and simulations of fractal-like particles is that the above D_f values have been developed for agglomerates of *monodisperse* primary particles. For coagulating aerosols, however, this needs to be carefully examined as Brownian coagulation leads to polydisperse particles [2]. Furthermore, once coalescence or sintering starts between these primary particles, sinter necks are formed between them converting the agglomerates to aggregates [3]. Accounting for primary particle polydispersity is important as the characteristic sintering time depends strongly on primary particle size [4]. These properties may also affect their health impact [5], e.g. agglomerates may undergo restructuring & break-up [6] and release constituent primary particles.

Here, the formation of aggregates (chemically- or sinter-bonded particles) by viscous flow sintering of amorphous materials (silica, polymers) [3] and grain boundary diffusion sintering of crystalline ceramics (titania, alumina) or metals (Ni, Fe, Ag etc.) is investigated [7] by multiparticle sintering simulations. A scaling law is discovered between average aggregate projected area (or mobility diameter) and equivalent number of constituent primary

particles during sintering. The surface area mean primary particle diameter, d_{va}, is derived from this scaling law:

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

where v and d_m are the particle volume and mobility diameter, respectively, and k_a and D_α are the prefactor and exponent of the projected surface area scaling, respectively [7]. This is a relation essentially independent of time, material properties and sintering mechanisms. The surface area mean primary particle diameter is determined by (on-line) differential mobility analyzer (DMA) and aerosol particle mass (APM) analyzer measurements and this power law for aggregates (Fig. 1). This is in good agreement with the primary particle diameter obtained by nitrogen adsorption and particle counts from microscopic images.

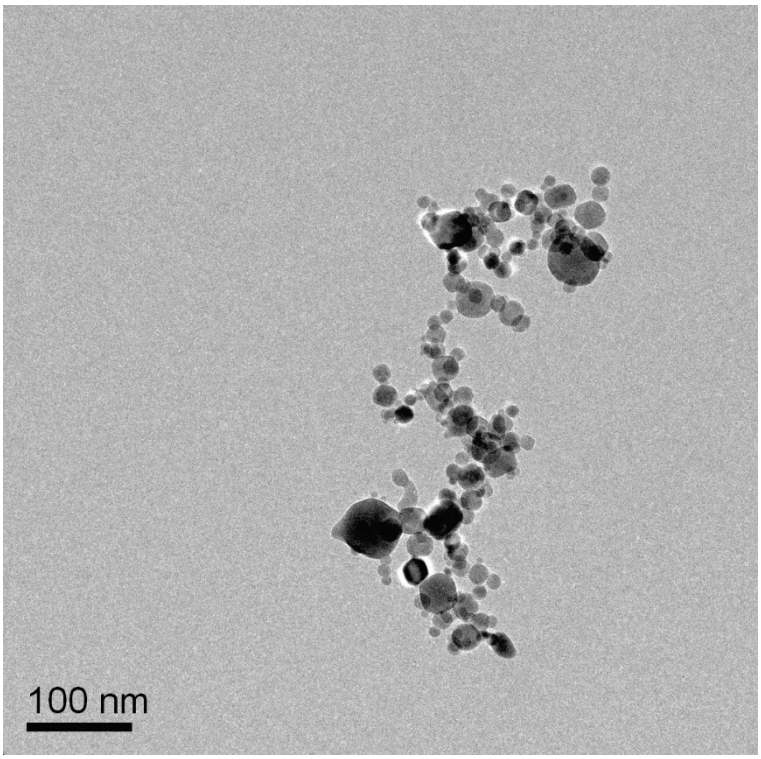

Figure 1: Size-selected zirconia agglomerate with d_m = 190 nm generated by scalable flame combustion. The primary particle diameter, d_{va}, determined by eq. 1 and mass-mobility measurements is in good agreement with counting microscopic images.

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Objective

Characterizing the morphology and average primary particle diameter, d_{va}, and number, n_{va}, of fractal-like agglomerates (physically-bonded) and aggregates (chemically- or sinter-bonded) is needed for monitoring material synthesis of gas-borne nanoparticles, emissions from combustion engines and atmospheric particles. 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.

Projected Aggregate Area Scaling[1]

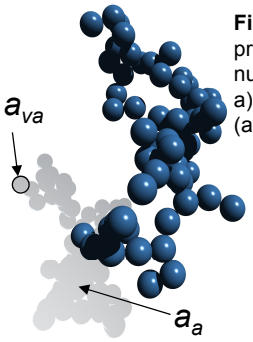
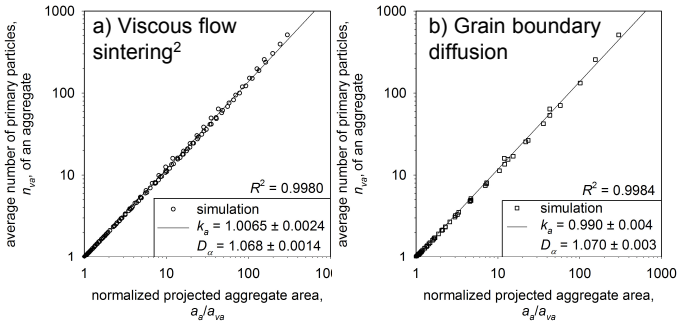


Figure 1: A power law holds between normalized projected aggregate area a_a/a_{va} and average number of primary particles n_{va} during sintering by a) viscous flow and b) grain boundary diffusion (average k_a = 0.998 & D_α = 1.069).

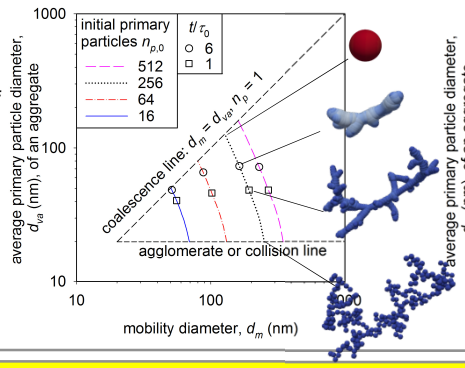
$$n_{va} = k_a \left(\frac{a_a}{a_{va}} \right)^{D_\alpha}$$

The d_{va} can be estimated from agglomerate Volume v , mobility size d_m and the relation[3]: $a_a = \pi\, d_m^2/4$.



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

Figure 2: The evolution of d_{va} as a function of aggregate mobility diameter, d_m, during sintering. For agglomerates of monodisperse spherical primary particles, $d_{va} = d_p$ independent of mobility size (horizontal agglomerate or collision line). The d_m decreases during sintering while d_{va} increases until a compact particle (D_f = 3) is reached (coalescence line).



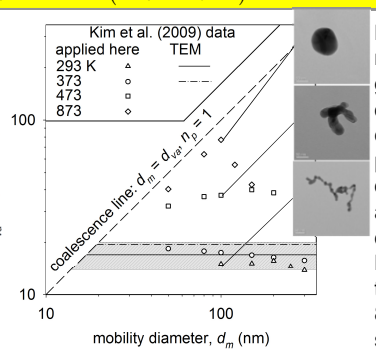
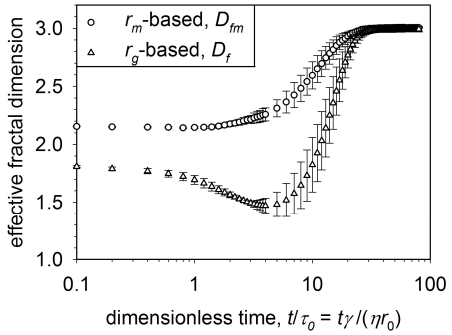
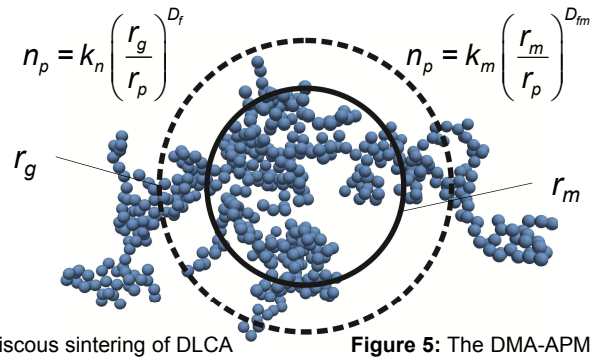


Figure 3: The d_{va} of Ag nanoparticle agglomerates generated by Kim et al.[4] is obtained by the proposed equation and compared to particle diameters d_p obtained by TEM[4] (grey area represents standard deviation of d_p at T = 293 K). Higher furnace temperatures (T = 473 – 873K) lead to faster sintering and larger d_{va}.

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





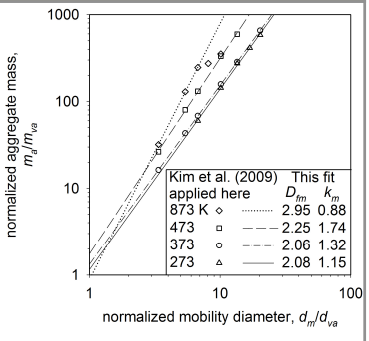


Figure 4: The evolution of D_f and D_{fm} during viscous sintering of DLCA agglomerates. The exponents (D_f, D_{fm}) are obtained by ensemble averaging over 50 agglomerates of each size. Only D_{fm} exhibits monotonic behavior and thus can be used to characterize the degree or extent of sintering of aggregates.

Figure 5: The DMA-APM data of silver nanoparticle aggregates sintered at different temperatures by Kim et al.[4] are post-processed here. The D_{fm} exhibits a monotonic increase consistent with our sintering simulations (Fig. 4).

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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. So D_{fm} can be used to characterize the degree of sintering.

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