Multi-Particle Sintering Dynamics: From Fractal-like Aggregates to Compact Structures

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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]

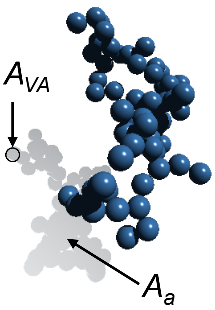
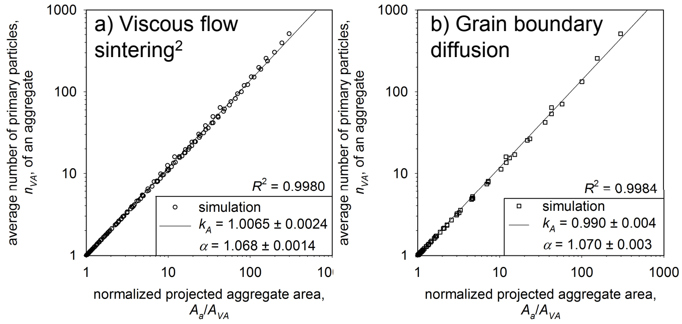


Figure 1: A power law holds between normalized projected aggregate area A_a/A_{VA} and average number of primary particles n_{VA} during sintering by a) viscous flow and b) grain boundary diffusion (average k_A = 0.998 & α = 1.069).

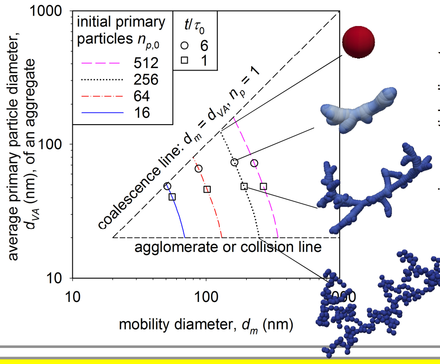
$$n_{VA} = k_A \left(\frac{A_a}{A_{VA}} \right)^{\alpha}$$

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}= $6V/A$ = $(\pi k_A d_m^{2\alpha}/(6V))^{1/(2\alpha-3)}$

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).



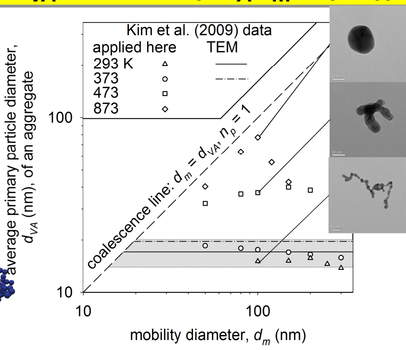
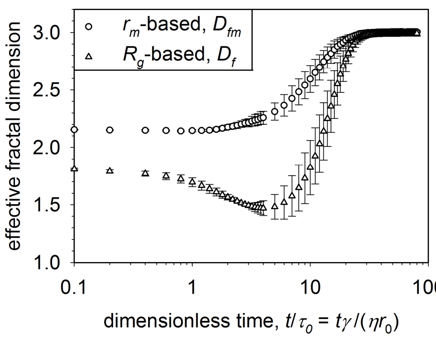
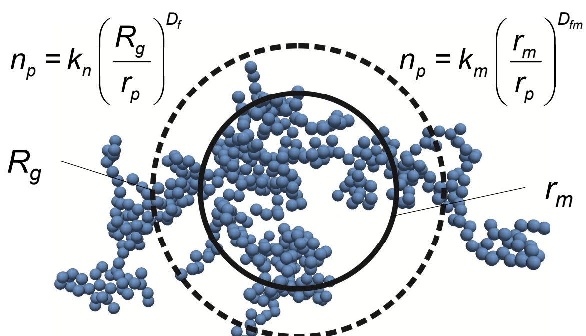


Figure 3: The d_{VA} of Ag nanoparticle agglomerates generated by Kim et al.[4] is obtained by the proposed equation and compared to particle diameters d_p obtained by TEM[4] (grey area represents standard deviation of d_p at T = 293 K). Higher furnace temperatures (T = 473 – 873K) lead to faster sintering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

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





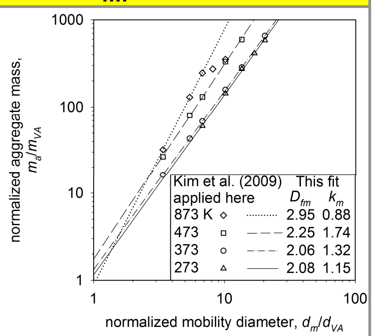


Figure 4: The evolution of D_f and D_{fm} during viscous sintering of DLCA agglomerates. The exponents (D_f, D_{fm}) are obtained by ensemble averaging over 50 agglomerates of each size. Only D_{fm} exhibits monotonic behavior and thus can be used to characterize the degree or extent of sintering of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

References

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Conclusions

1. The projected area scaling $n_{VA} = k_A \left(\frac{A_a}{A_{VA}} \right)^{\alpha}$ is valid during sintering.
2. The α and k_A are independent of sintering mechanism.
3. The d_{VA} obtained by this work is in reasonable agreement with counting 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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