Multiscale design of aerosol synthesis of materials:
Effect of structure on TiO$_2$ & SiO$_2$ particle growth by coagulation and sintering

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Multiscale design of aerosol reactors for synthesis of nanomaterials includes continuum, mesoscale, molecular dynamics and quantum mechanics models spanning 10 - 15 orders of magnitude in length and time, respectively. Quantum mechanics account for the electronic structure of matter determining the interatomic potentials in molecular dynamic (MD) models for accurate estimation of sintering and crystallization rates. For example, Figure 1 shows how MD models reveal the dominance of surface diffusion in sintering of TiO$_2$ nanoaerosols by monitoring the lattice plane evolution (Buesser, 2011). Mesoscale models provide the transport properties and coagulation rate of multiparticle structures; Continuum models describe the effect of process variables on product particle size & morphology at various process temperatures and residence times (Buesser, 2012).

Here the effect of the rapidly evolving structure (fractal dimension, D$_f$) of TiO$_2$ & SiO$_2$ particles made by coagulation and sintering is explored on their primary particle and collision diameters. This is done over their process synthesis parameter space (Tsantilis, 2004; Gass, 2006) by interfacing MD, mesoscale (Eggersdorfer, 2012) & continuum models (Kruis, 1993). Structure is important as it affects particle transport, conductivity & scattering. Continuum models, however, typically assume a spherical or fractal-like shape at constant D$_f$ neglecting the effect of evolving structure on particle growth dynamics and final particle properties (Kruis, 1993). 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 full coalescence to that of non-coalescing agglomerates.

The time-evolution of primary and agglomerate particle diameter and morphology are investigated, accounting for simultaneous coagulation and sintering as well as for the D$_f$ evolution from mesoscale simulations (Eggersdorfer et al., 2012) with the characteristic sintering time of rutile titania (Fig. 1) from MD simulations (Buesser et al. 2011). The D$_f$ varies from 3 (full coalescence) to 1.8 (non-coalescing agglomerates by cluster-cluster agglomeration) and its effect on soft & hard agglomerate and primary particle diameters is monitored at various maximum temperatures, T$_{max}$ cooling rates, CR and precursor mole fraction, φ.

Accounting for the change in D$_f$ hardly affects the primary particle, d$_p$, and collision, d$_c$, diameters, even though it affects the transient evolution of d$_c$ (Fig. 2). In contrast, the evolution of D$_f$ seems to have a profound effect on the hard-agglomerate diameter, the agglomerate diameter, d$_{ag}$, at the end of particle sintering (Grass et al., 2006) especially at low maximum temperatures and high cooling rates.

Figure 1. Snapshots of cross sections of TiO$_2$ nanoparticles with Ti and O ions initially (t= 0 ns) green and red (bulk ions) or yellow and blue (surface ions), respectively, at a) t= 0, b) 0.03, c) 3, d) 30, e) 100, and f) 150 ns (Buesser et al., 2011).

Figure 2. Evolution of the agglomerate collision, d$_c$(,bold, black solid line), and primary particle diameters, d$_p$(,thin black solid line), with variable D$_f$(green line) at non-isothermal conditions (red line). The evolution of d$_c$ is compared to simulations with constant D$_f$ = 1.8 (dashed line) and 3 (dotted line).