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).
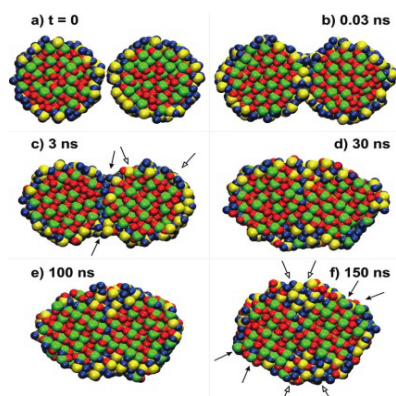

Figure 1. Snapshots of cross sections of TiO_2 nanoparticles with Ti and O ions initially (t= 0 ns) green and red (bulk ions) or yellow and blue (surface ions), respectively, at a) t= 0, b) 0.03, c) 3, d) 30, e) 100, and f) 150 ns (Buesser *et al.*, 2011).

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 intefacing MD, mesocale (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_{cH}, at the end of particle sintering (Grass et al., 2006) especially at low maximum temperatures and high cooling rates.
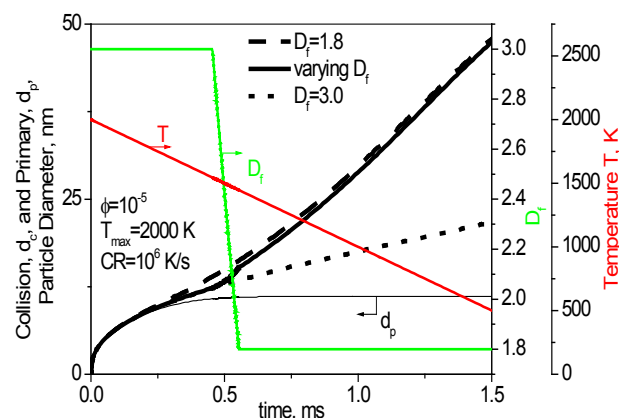

Figure 2. Evolution of the agglomerate collision, d_c (bold, black solid line), and primary particle diameters, d_p (thin black solid line), with variable D_f (green line) at non-isothermal conditions (red line). The evolution of d_c is compared to simulations with constant $D_f = 1.8$ (dashed line)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

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