The Collision Frequency of Fractal-like Aerosols in the Free Molecular Regime

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Aerosol technology is used routinely in large scale production of commodities like pigmentary titania, carbon black and fumed silica. Recent advances in combustion and aerosol sciences have led to aerosol synthesis of sophisticated materials from catalysts to gas sensors, biomaterials and even nutritional products (Strobel and Pratsinis, 2007).

The manufacturing of some of these simple oxide commodities have taught us that the dynamics of aerosol reactors and the product nanoparticle characteristics span 10-15 orders of magnitude in length and time. So systematic process design requires interconnected models for different length and time scales that can be distinguished into continuum, mesoscale, molecular dynamics and quantum mechanics, comprising the so-called multiscale process design (Buesser and Pratsinis, 2012). One important, if not the most important, design criterion is the *high temperature particle residence time*. It determines the nanoparticle growth by gas and surface reaction, coagulation and sintering. Typically gas phase chemistry is so rapid that coagulation and sintering control particle growth. So knowing particle dynamics is necessary to design processes for particle manufacture.

The coagulation rate of spherical particles is reasonably well understood. However nanoparticles form fractal-like aggregates (chemically- or sinter-bonded) and agglomerates (physically bonded) of primary particles (Eggersdorfer and Pratsinis, 2013). Typically the collision radius of such structures is approximated with the radius of gyration, r_g, of equivalent spheres in the classic coagulation rate. Langevin Dynamics simulations corroborated the notion that r_g scales the collision radius in the free molecular regime (Pierce et al., 2006) but Mulholland et al. (1988) found that the actual collision radius is ~21% larger than r_g.

Here, the formation of nanoparticles by coagulation and sintering is simulated in the free molecular regime by a discrete element method (DEM, mesoscale). The particles follow random ballistic trajectories with the mean thermal velocity according to kinetic theory at volume fraction, $\phi = 10^{-7}$. The formation of agglomerates is traced in time to extract the detailed collision frequency, also for non-spherical particles. The system is doubled in size once the number of agglomerates halved (Figure 1). Simulations were carried out continuously to determine the collision frequency and agglomerate mass and size distributions for coagulation-agglomeration. Modified collision kernels for the detailed and overall collision frequency are extracted.

Aggregate sintering is modeled by a multiparticle viscous flow sintering mechanism accounting for the PP
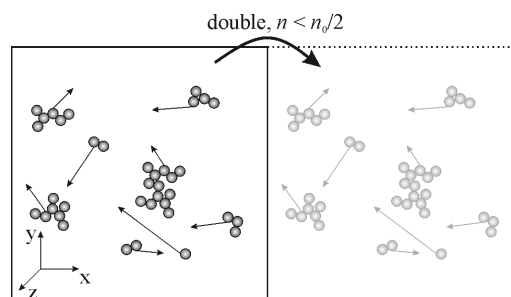

Figure 1. A sketch of the 3D simulations utilizing the detailed coordinates of each particle: The domain is doubled once the agglomerate number is halved from its initial value.

polydispersity and aggregate structure (Eggersdorfer et al., 2011). The ratio of characteristic sintering time, τ_s, to collision time, τ_c, solely defines the aggregate structure independent of T. Furthermore, the detailed aggregate size distributions can be determined quantitatively to get the detailed fractions of spherical particles, aggregates and agglomerates (Fig. 2).
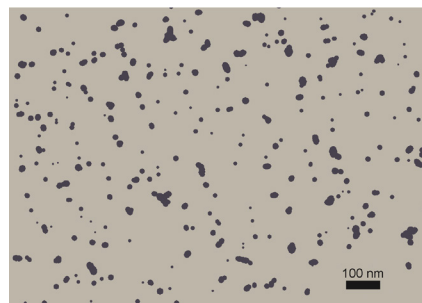

Figure 2: TEM-like image of SiO_2 nanoparticles grown by coagulation and sintering at 1900 K for *0.02* s simulated with up to $16 \cdot 10^6$ PPs. Mostly spherical particles are present at these conditions, though some of the larger have been aggregated already.

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