Agglomeration of Polydisperse Primary Particles in the Free Molecular Regime

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Nanoparticles made in the gas phase typically form irregular, fractal-like aggregates (chemically- or sinter-bonded) and agglomerates (physically-bonded) of primary particles (PPs) by coagulation of environmental or industrial aerosols. Even though the characteristics of spherical particles, such as self-preserving size distribution, and coagulation rate, are reasonably well-understood (Friedlander, 2000), there is significant uncertainty for fractal-like agglomerates (Mulholland et al., 1988), especially for those consisting of polydisperse PPs, as coagulation determines largely their size, and structure (Eggersdorfer and Pratsinis, 2012). Such characteristics affect their optical, dispersion and transport properties (for example, the degree of particle anisotropy affects the refractive index of agglomerates).

Here coagulation of nanoparticles of varying polydispersity in the absence of coalescence, sintering or surface growth is investigated by a discrete element method in the free molecular regime (Goudeli et al., 2015). The purpose of this study is to quantify the effect of PP polydispersity on agglomerate size (radius of gyration, mobility radius and volume-equivalent radius), morphology (fractal dimension, mass mobility exponent and their prefactors) as well as on the attainment of the well-known asymptotic fractal-like structures and self-preserving size distributions.

Figure 1 shows the evolution by coagulation-agglomeration of fractal dimension, D_f, for agglomerates having PPs of log-normal size distribution (PPSD) with geometric standard deviation, $\sigma_{g,PP}$ = 1.0 (solid line), 1.5 (broken line), 2.0 (dot-broken line), 2.5 (double-dot-broken line) and 3.0 (dotted line) as a function of the mean number of PPs per agglomerate, n_p. Narrower PPSDs reach the asymptotic $D_f \approx 1.91 \pm 0.03$ (Ball and Jullien, 1984) with agglomerates of fewer PPs than broader PPSDs. With increasing width of the PPSD, the difference in size and mass of agglomerates having attained their asymptotic structure (e.g. D_f) increases. Small particles move very fast and collide with large ones that have larger collisional cross section. However, such a collision hardly affects the radius of gyration, r_g, or mass of the resulting particle. So the broader the distribution, the longer it takes until the large particles/agglomerates are affected by collisions with smaller ones to form fractal-like structures and thus delaying the transition of the asymptotic D_f.

Increasing the polydispersity of the constituent PPs from $\sigma_{g,PP}$ = 1 to 3 only delays the attainment of the asymptotic mass fractal dimension D_f, mass-mobility exponent D_{fm} and self-preserving size distribution (SPSD) of the resulting agglomerates. The crossover agglomerate size that marks the transition between D_f = 3 and 1.9 increases with PP polydispersity.

The polydispersity of the PP size distribution affects also the intermediate agglomerate size distributions and kinetics. Agglomerates of monodisperse PPs rapidly reach their SPSD, while for a PP size distribution with $\sigma_{g,PP}$ = 3.0, the r_g distribution becomes even broader than the initial PPSD. This is due to collisions between compact agglomerates or large spherical particles with small particles that hardly affect their mass.

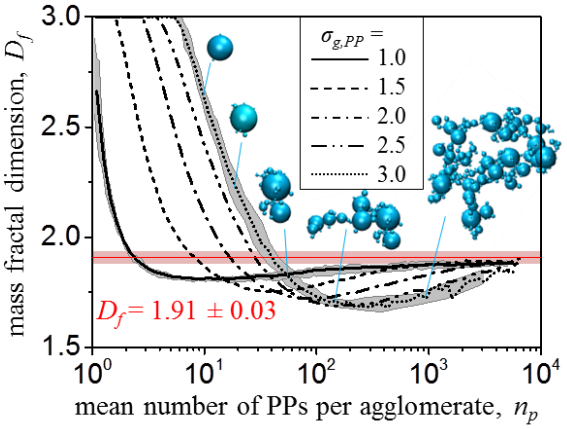

Figure 1: Evolution of D_f as function of mean number of PPs per agglomerate, n_p, during coagulation of polydisperse PP having a log-normal size distribution with $\sigma_{g,PP}$ = 1 – 3.

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