Structure & dynamics of fractal-like particles made by agglomeration and sintering

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Submitted to:

AIChE Journal

June 23, 2020

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Abstract

The growth of silica nanoparticles by agglomeration and viscous flow sintering is studied from free molecular to transition regime by off-lattice even-driven (ED) simulations. Coagulation by simultaneous agglomeration and sintering takes place at high temperature environments, where sintering and collision rates are comparable. The effect of temperature on aggregate mobility and gyration radii, particle morphology and collisional enhancement is elucidated. The ratio between the characteristic sintering time and characteristic collision time controls the particle size and structure, quantified by the mass fractal dimension. The aggregate morphology depends solely on the ratio of characteristic times and is insensitive to the process temperature. When sintering is negligible, the overall collision frequency is 90% larger than that predicted by the classic Fuchs collision kernel for monodisperse agglomerates, in agreement with experiments. The ED-obtained quasi-self-preserving size distributions are consistent with mobility size distributions measured in hot-wall reactors and flame sprays.

Keywords: aerosols, coagulation, sintering, discrete element method

1. Introduction

Gas-phase reactors provide a versatile, scalable waste-free synthesis route capable of producing nanoparticles at tons per hour worldwide.¹ Most importantly, it allows for the manufacture of nanoparticles with fine-tuned size and

structural characteristics that can be used routinely for diverse applications, such as bone replacements,² dental fillers,³ photocatalysts^{4,5} and catalysts for environmental remediation,⁶ to name a few. As one example, flame-made luminescent CeO₂:Eu³⁺ nanoparticles have demonstrated highly sensitive biosensing activity for H₂O₂,⁷ whose presence is correlated with severe diseases.⁸ Aerosol synthesis processes, such as flame spray pyrolysis, hot wall reactors, and laser ablation, typically lead to the formation of fractal-like aggregates (chemically or sinter bonded spheres) or agglomerates (physically bonded spheres or aggregates). The degree of overlap among the constituent primary particles greatly affects the final product properties, such as their mechanical stability and electron transport. Tuning the primary particle size and the size of the sinter necks is key for the performance of catalysts and gas sensors.⁹ For instance, flame-made β -Bi₂O₃ catalysts with high degree of sintering exhibit stable fractal structure and increased current density which improved their performance in CO₂ electroreduction.¹⁰

One important design criterion for gas-phase (flame) reactors is the high temperature particle residence time, which determines nanoparticle growth by gas reactions, surface growth, sintering and coagulation. Typically, the chemistry is rapid so that nucleation can be neglected, and coagulation and sintering dominate the particle growth.¹¹ Hence, understanding the dynamics of aggregate formation during coagulation and sintering is necessary, especially in the transition regime. Knowing the collision frequency and sintering time can assist in modeling the particle growth mechanisms accurately,¹² which are reasonably well understood for spherical particles. However, *a priori* assumptions on the particle structure and sintering rate are often used to calculate the particle collision frequency function, which is used to describe the evolving particle number concentration in monodisperse population balance equation (PBE) models. The radius of gyration is commonly used as the collision radius in collision kernel equations,^{13,14,15} even though they might differ even up to 21%.¹⁶ Elaborate expressions of the collision radius have been developed by Monte Carlo (MC) simulations^{17,18} to improve the accuracy of the collision kernel. Discrete element method (DEM) simulations^{19,20,21} account for the velocity and detailed structural characteristics of individual aggregates or agglomerates and do not require *a priori* knowledge of a coagulation kernel. Recently, it was shown that agglomerates consisting of monodisperse primary particles in point contact attain their asymptotic fractal-like structure faster than those consisting of polydisperse primary particles,²⁰ as the later exhibit larger collisional area that increases the coagulation rate. Nonetheless, once the agglomerates attain their asymptotic fractal dimension, D_f , and their self-preserving size distribution (SPSD) they coagulate with identical

collision rates in the free molecular regime, regardless of primary particle polydispersity. This coagulation rate was 35% bigger than that of monodisperse agglomerates having $D_f = 1.9$.²⁰

Furthermore, during particle growth in the gas-phase, the aggregate structure evolves from $D_f = 3$, corresponding to spheres, down to ~ 1.8 , corresponding to fractal-like aggregates made by cluster-cluster agglomeration. Artelt et al.²² proposed an empirical evolution of D_f and showed the importance of accounting the evolving particle structure during early growth stages on the agglomerate collision frequency using PBE. The structural effect is significant in the free molecular regime where sintering and coagulation primarily take place at the high temperature region of aerosol reactors. Al Zaitone et al.²³ simulated the growth of nanoparticle structures by simultaneous coagulation, sintering and surface growth. Coagulation was modeled by a MC algorithm and sintering by the successive overlap of spheres along a backbone in an aggregate. An empirical relation between characteristic times and D_f was developed. Sander et al.²⁴ used a stochastic particle model to describe the formation of SiO₂, accounting for each contact between neighboring particles within an aggregate and the effect of polydispersity and fitted their results against experiments of Seto et al.²⁵ Goudeli et al.¹⁵ employed a DEM-derived¹⁹ D_f equation for unsintered agglomerates consisting of monodisperse primary particles in a simple monodisperse PBE model, showing that neglecting the evolving particle morphology can underpredict the agglomerate size by up to 30%. In the above models, however, the relation between structure, coagulation and sintering rates was not fully resolved. Furthermore, the effect of sintering on the collision frequency function of aggregates remains unknown.

Here, the evolving ratio of the collision and sintering rates is fully resolved during aerosol growth from small spherical nuclei until the formation of fractal-like aggregates. The evolution of the particle morphology is determined on-the-fly and the dynamics of aggregate growth are quantified without making *a priori* assumptions on the coagulation rate. The formation of amorphous silica nanoparticles by coagulation and sintering in the free molecular and transition regimes is simulated by extending prior event-driven (ED) simulations of coagulation by pure agglomeration¹⁹ to account for concurrent multiparticle sintering dynamics. Aggregate sintering is modeled by a viscous flow sintering mechanism accounting intrinsically for primary particle polydispersity and aggregate structure. The collision frequency enhancement and particle size distributions are extracted from the simulations for particles coagulation by agglomeration and sintering at various temperatures ranging from 1000 to 2000 K. Silica, one of the largest aerosol commodities, is used as a model system for the present simulations. This approach provides detail at the single particle level and allows quantifying the effect of process temperature on the evolving

particle structure, size distribution and coagulation rate for large populations of small aggregates that are either difficult to determine experimentally or require tedious measurements, such as transmission electron microscopy (TEM) counting or differential mobility analyzer measurements coupled with mass spectrometry. These variables are required as input in larger length and time scale models, such as sectional models or particle dynamics coupled with fluid dynamics simulations, and their accuracy is critical for the design of aerosol reactors at industrial scale.

2. Theory

2.1 Agglomerate & aggregate size, structure and collision frequency

The agglomerate radius of gyration, r_g , and mobility radius, r_m , scale with the number of primary particles per agglomerate, n_p , by the following power laws:^{26,27}

$$n_p = k_n \left(\frac{r_g}{r_p} \right)^{D_f} = k_{fm} \left(\frac{r_m}{r_p} \right)^{D_{fm}} \quad (1)$$

where r_p is the primary particle radius, k_n and k_{fm} are proportionality constants and the particle structure descriptors D_f and D_{fm} are the mass fractal dimension and mass-mobility exponent, respectively. The r_g is calculated by the mean square displacement of the agglomerate mass from its center of mass and the r_m is calculated based on the rotationally averaged projected area of the agglomerate.²⁸ For sintered aggregates consisting of truncated primary particles, the surface area mean radius, $r_{va} = 3V/A$, where V and A are the aggregate volume and surface area, is used as an equivalent primary particle radius.

The dynamics of agglomerate formation are quantified by the overall collision frequency function. A widely used coagulation rate that is valid in the entire particle size spectrum region is the classic Fuchs interpolation formula, β_{Fuchs} .²⁹

$$\beta_{Fuchs} = \beta_{co} \cdot \left[\frac{d_i + d_j}{d_i + d_j + 2\delta_r} + \frac{8(D_i + D_j)}{\bar{c}_r(d_i + d_j)} \right]^{-1} \quad (2)$$

with

$$\delta_r = \sqrt{\delta_1^2 + \delta_2^2}, \text{ with} \quad (3a)$$

$$\delta_i = \frac{1}{3d_{p,i}\lambda_{a,i}} \left[(d_{p,i} + \lambda_{a,i})^3 - (d_{p,i}^2 + \lambda_{a,i}^2)^{3/2} \right] - d_{p,i} \quad (3b)$$

$$D_i = \frac{k_B T C_{S,i}}{3\pi\mu d_p} \quad (4)$$

and

$$\bar{c}_r = \sqrt{\bar{c}_1^2 + \bar{c}_2^2}, \text{ with} \quad (5a)$$

$$\bar{c}_i = \sqrt{\frac{48k_B T}{\pi^2 \rho_p d_{p,i}^3}} \quad (5b)$$

where β_{co} is the collision frequency function in the continuum regime, d_i and d_p are the diameter of the colliding species and primary particles, respectively, δ_i and δ_r are the mean and average mean distance, respectively, D is the diffusion coefficient, C_s is the Cunningham slip correction factor, μ is the viscosity of the surrounding fluid, λ_a is the agglomerate stopping distance ($\lambda_{a,i} = \frac{8D_i}{\pi\bar{c}_i}$), $\bar{c}_i$ and $\bar{c}_r$ are the mean and average mean particles velocity, and k_B , T and ρ_p are the Boltzmann constant, temperature and bulk particle density, respectively.

2.2 Numerical Implementation

Two thousand primary particles are randomly distributed in an initially cubic simulation domain with periodic boundary conditions as described by Goudeli et al.¹⁹ In the free molecular regime, each particle is assumed to be in thermal equilibrium with the surrounding gas, following a Maxwellian velocity distribution.³⁰ The particles follow ballistic trajectories with velocity that depends only on the particle mass.³¹ In the transition regime, where the gas mean free path is comparable to the agglomerate radius, the particle trajectories are a blend of ballistic and Brownian motion. During coagulation, particle sintering is accounted for, while other interparticle forces, such as van der Waals, electric and hydrodynamic interactions are neglected along with particle rotations. Particles stick inelastically upon collision with a sticking probability of unity. This is a reasonably good assumption for flame-made (amorphous), small silica nanoclusters (0.5 – 1 nm) exhibiting sticking probability of 1 for impact velocities at least up to 1000 m/s³², as well as for larger amorphous silica spheres with radii up to 15 nm³³, as evidenced by molecular dynamics simulations. Here, at least 92% of the 0.5 nm-initial primary particles travel with velocities lower than 1000 m/s.

The above assumption of a sticking probability of 1, needs to be revisited depending on the particle size, material and the nature of inter-particle interactions. For example, rebound becomes significant when combustion generated carbonaceous nanoparticles are colliding, exhibiting collision efficiencies bellow 1, especially for primary particle radii smaller than 5 nm³⁴. Furthermore, for big nano-sized amorphous primary particles ($r_p > 15$ nm)^{33,35} or for micron-sized granules with viscous binding liquid coatings³⁶, rebound events are probable. Such rebound events

can be accounted for in the present off-lattice ED model for example by introducing different restitution coefficients for various particle sizes.

Once a particle collides with another particle or once it or has traveled its persistence length, it changes direction. The trajectories of the newly formed particles are calculated by the momentum balance. The particle drag is quantified by using the Stokes friction coefficient with the Cunningham correction factor. The particle bombardment from the surrounding fluid molecules is quantified by a stochastic, fluctuating force in the transition regime, as described in Heine and Pratsinis³⁷. Aggregates or agglomerates are formed by subsequent particle-particle, particle-cluster and cluster-cluster collisions. Cluster-cluster coagulation is dominant, especially at long residence times that single spherical particles have been consumed and mostly large aggregates are present.

The relaxation time for particles to adjust to a change in the flow velocity is:³⁸

$$\tau_p = \frac{2r_m \rho_p C_s}{18\mu} \quad (6)$$

and is much shorter³⁸ than the collision time, τ_c , which is defined as:³⁹

$$\tau_c = \frac{2}{\beta N} \quad (7)$$

at isothermal conditions. The β and N in eq. 7 correspond to the collision frequency function and the number concentration, respectively, at every time step. The time between particle collisions is calculated with an event-driven algorithm.⁴⁰ The primary particles are initially monodisperse with solid volume fraction of $\phi_s = 10^{-4}$ in all simulations. The effective volume fraction, ϕ_{eff} , increases as fractal-like aggregates of agglomerates are formed with void space in-between their branches. Here, particle growth is elucidated at dilute conditions, so ϕ_{eff} remains below 0.01 at all simulations to avoid high concentration effects on the collision frequency function and particle size distribution.^{31,37} High concentrations can result in coagulation that proceeds much faster than the Smoluchowski coagulation and particles reach gelation very quickly.^{37,41}

The degree of aggregation depends on the evolution of the ratio of the characteristic collision time, τ_c , and the characteristic sintering time τ_s . Various sintering rates have been proposed^{42,43,44} for amorphous silica nanoparticles based on viscous flow sintering mechanism due to low viscosity. For example, Kirchhof et al.⁴⁴ derived experimentally the sintering rate of silica particles in high-temperature sintering flow reactors for primary particle diameters of 8 – 80 nm at temperatures of 1300 – 1600 °C. Here, the sintering rate of Tsantilis et al.⁴³, which is derived from Frenkel's theoretical equation on the viscous flow mechanism⁴⁵, using the material properties of

silica⁴², is used:

$$\tau_s = 6.5 \cdot 10^{-13} d_p \exp \left(\frac{8.3 \cdot 10^4}{T} \left(1 - \frac{1 \cdot 10^{-9}}{d_p} \right) \right) \quad (8)$$

for the range of process temperature (1000 – 2000 K) and primary particle diameters ($d_p = 1 - 10$ nm) employed in ED simulations. Equation 8 accounts for an empirical correction for the effect of melting temperature on small particle sizes that sinter rapidly. The detailed derivation of eq. 8 is discussed in Tsantilis et al.⁴³

Figure 1 shows the schematic representation of the various growth mechanisms taking place depending on the ratio of sintering rate, τ_s , and the collision rate, τ_c . The time between two collision events sets the simulation time step, Δt_c . For $\tau_s \ll \tau_c$ (Fig. 1a), particles behave as liquid-like spheres and coalesce fully upon collision. In the next timestep, the two colliding particles are replaced by a larger sphere with the same mass as the sum of the masses of the coalescing species. The mechanism of full coalescence is significant at high temperature flame regions. Further downstream in flames, particles have grown upon consecutive collisions while temperature starts to drop. In those flame regions, the sintering and collision rates are comparable (Fig. 1b, $\tau_s \sim \tau_c$) and particles coalesce partially (sinter). During Δt_s , the colliding particles start forming necks between them that grow (based on eq. 8) until the sintered aggregate collides with another particle, forming a larger aggregate at $t + \Delta t_c$. The free accessible surface, volume and neck contract areas between the sintered particles (truncated spheres) are determined with Vorlume⁴⁶. In the limit of pure agglomeration $\tau_s \ll \tau_c$ (Fig. 1c), sintering is less significant and the particles form fractal-like agglomerates with their constituent primary particles in point contact. The particle growth at conditions where the limit of pure agglomeration is dominant (Fig. 1c), has been presented in Goudeli et al.^{19,20}

Figure 1

The overall collision frequency function is calculated by the present ED simulations by:³⁷

$$\beta = 2 \left(\frac{1}{N(t)} - \frac{1}{N(t - \Delta t)} \right) / \Delta t \quad (9)$$

where N is the number concentration at timesteps t and $t - \Delta t$, respectively. The detailed simulation parameters and material properties are shown in Table 1. More rigorous equations of the binary rate of colliding particles during granulation of microparticles have been proposed by Reinhold and Briesen⁴⁷, that apply to constant particle size distributions. Here, eq. 9 is used to derive the integral collision kernel as it can be applied to the evolving particle size distribution of the simulated aggregate populations.

Table 1

3. Results and Discussion

Full coalescence ($\tau_s \ll \tau_c$) and coagulation by pure agglomeration ($\tau_s \gg \tau_c$) are limiting cases of particle growth in aerosol particle synthesis. Coagulation by full coalescence is dominant at high temperatures environments or for small particles sizes and is typically encountered at the early stages of particle formation in flames, plasmas, hot-wall or laser reactors. For large particle sizes and low temperature regions, e.g. downstream in aerosol reactors with high cooling rates, coagulation by agglomeration prevails. Non-spherical fractal-like aggregates are formed at process conditions where both coagulation and sintering take place.

3.1 Validation with Full Coalescence

The present ED simulations are validated for coagulation of particles by full coalescence ($\tau_s \ll \tau_c$). For fully coalescing nanoparticles, perfect spheres are formed upon collision and a coagulation rate $\sim 18\%$ higher than theoretical collision kernel for spherical particles in the free molecular regime under dilute conditions is obtained.⁴⁸ In the transition regime, the ED-obtained collision rate follows closely the collision frequency of Fuchs²⁹ (Supplementary Information: Fig. S2a). These spherical particles rapidly reach their SPSPD (Supplementary Information: Fig. S2b) with number- and volume- based geometric standard deviations $\sigma_{g,n} = 1.46$ and $\sigma_{g,v} = 1.33$, respectively.⁴⁹ The viscous flow sintering simulations have been validated in Eggersdorfer et al.⁵⁰

3.2 Coagulation - Agglomeration

Figure 2 shows snapshots of exemplary aggregates growing by agglomeration and sintering at temperature, $T = 2000$ K, and initial primary particle radius, r_p , of 0.5, 1, 2 and 5 nm. The aggregates are shown at different stages of their growth, corresponding to increasing effective number of primary particles per aggregate, n_p . During coagulation spherical particles collide forming either bigger spherical nanoparticles or sintered aggregates increasing their radius of gyration, r_g , and mobility radius, r_m . The equivalent number of primary particles per aggregate with radius $r_{p,0}$ also increases. When the initial size of primary particles is small (i.e., $r_{p,0} = 0.5$ nm, left column) sintering prevails leading to large primary particles among which big sinter necks are formed. As the initial $r_{p,0}$ increases, sintering contributes less to the growth of primary particles and at sufficiently long times (or increased n_p) agglomeration

takes over completely leading to branched, fractal-like agglomerates. For a given n_p (e.g., 515), more compact structures are formed when $r_{p,0}$ is small, while more fractal-like aggregates are formed when the constituent primary particles are large. For example, these structural differences are evidenced by the differences in the r_g of aggregates with $r_{p,0} = 5$ nm ($r_g = 119$ nm) which is about 30 times larger than those consisting of primary particles with $r_{p,0} = 0.5$ nm ($r_g = 4.1$ nm). The aggregate r_m is 71.7 nm for $r_{p,0} = 5$ nm while for small $r_{p,0}$ ($= 0.5$ nm), the r_m is comparable to r_g , due to increased particle compactness.

Figure 2

Figure 3 shows the evolution of the geometric mean radius of gyration, r_g (broken lines), mobility radius, r_m (solid lines), and primary particles (PP) radius, r_p (dotted lines), as function of the effective number of PPs per aggregate/agglomerate, n_p , with initial PP radius, $r_{p,0} = 1$ nm, at (a) 1000, (b) 1500, (c) 1750 and (d) 2000 K. The highlighted areas represent the onset of aggregation, where the formed aggregates are perfect spheres ($r_m = r_p$) as sintering is more prevalent than agglomeration, i.e. the characteristic sintering time, τ_s , is smaller than the characteristic coagulation time, τ_c ($\tau_s < \tau_c$). However, these characteristic times change continuously during particle growth as the primary particles increase in size.

At $T = 1000$ K (Fig. 3a), sintering practically does not take place and agglomeration is the most dominant growth mechanism ($\tau_s \gg \tau_c$). Thus, the r_p remains constant as the agglomerates grow upon collisions increasing only their r_g and r_m . It should be noted here that, due to lack of sintering, all agglomerates consist of monodisperse primary particles (Fig. 3a: insets). As temperature increases, sintering becomes more dominant and the size of the constituent primary particles, r_p , increases with increasing n_p (or time). At high temperatures, nanoparticle sintering becomes more dominant, resulting in continuous increase of the average r_p , which has not reached the final particle diameter for the conditions investigated here. At the early stages of particle growth, aggregates grow by particle-particle and particle-cluster collisions and fully coalesce up to a critical n_p (Fig. 3b – d: diamonds) above which $r_m > r_p$. The critical n_p required to form non-spherical aggregates with $D_f < 3$ (as discussed in Fig. 7) corresponds to about 4 primary particles at $T = 1500$ K and increases to about 10 and 30 when temperature increases to 1750 and 2000 K, respectively.

Figure 3

Figure 4 shows the evolution of the number-based geometric standard deviation of the radius of gyration, $\sigma_{g,g}$ (broken lines), mobility radius, $\sigma_{g,m}$ (solid lines), and volume-equivalent radius, $\sigma_{g,v}$ (dotted lines), as function of

the effective number of PPs per aggregate/agglomerate, n_p , with initial PP radius, $r_{p,0} = 1$ nm, at (a) 1000, (b) 1500, (c) 1750 and (d) 2000 K. The highlighted areas represent the region where $r_m = r_p$, similar to Fig. 3. At $T = 1000$ K, where particles grow solely by agglomeration, the geometric standard deviations are initially ($n_p = 1$) equal to 1, corresponding to a population of monodisperse primary particles. As n_p increases, the $\sigma_{g,g}$, $\sigma_{g,m}$ and $\sigma_{g,v}$ increase attaining their free molecular SPSP values of 2.27, 2.03 and 1.41 (horizontal lines), respectively, consistent with Goudeli et al.¹⁹ When large agglomerates with $n_p > 300$ are formed, σ_g decreases as particle growth takes place in the transition regime.

When sintering prevails (i.e., at higher reactor temperature), the attainment of the quasi-SPSP is delayed and narrower aggregate size distributions are observed. In fact, sintered aggregates exhibit geometric standard deviations that lie between the SPSP limits for pure agglomerates ($\sigma_{g,g} = 2.27$, $\sigma_{g,m} = 2.03$ and $\sigma_{g,v} = 1.41$) and perfect spheres ($\sigma_{g,n} = 1.46^{49}$ and $\sigma_{g,v} = 1.33^{49}$, Supplementary Information: Fig. S2b) in the free molecular regime. Before the onset of aggregation ($\tau_s < \tau_c$), $\sigma_{g,m}$ is comparable to $\sigma_{g,v}$, and they only start to differentiate when bigger aggregates are formed. Once the coagulation rate becomes bigger than the sintering rate, the $\sigma_{g,m}$ increases exhibiting values below 1.75, consistent with differential mobility analyzer experiments in flame sprays that revealed $\sigma_{g,m} = 1.45 - 1.58$, even for bigger aggregates.⁵¹ The quasi-SPSP σ_g derived from ED simulations are also in agreement with the evolution of TEM-obtained $\sigma_{g,g}$ and $\sigma_{g,v}$ for small flame-made zirconia nanoparticles⁵² with the same volume-equivalent radius ($r_{va} = 5$ nm) and radius of gyration (Supplementary Information: Fig. S3).

As the temperature increases and sintering is enhanced, both the r_g - and the r_m -based quasi-SPSP narrow down, in agreement with small-angle X-ray scattering (SAXS) measurements in laminar diffusion flames⁵³ and mobility measurements in flame spray pyrolysis reactors⁵¹ that showed narrower silica size distributions as the particles become more compact (the D_f and D_{fm} decreases). For example, at $T = 2000$ K (Fig. 4d), the quasi-self-preserving $\sigma_{g,m}$ drops by ~20% from the self-preserving $\sigma_{g,m}$ of 2.03 corresponding to pure agglomeration, as sintering suppresses particle growth. At all temperatures, however, $\sigma_{g,v}$, reaches its self-preserving value which is identical to the $\sigma_{g,v}$, of pure agglomeration in the absence of sintering. The average aggregate and primary particle size (Fig. 3) and their corresponding geometric standard deviations (Fig. 4) can be used to obtain the detailed particle size distributions from monodisperse models without solving population balances.

The ED simulations employed here can also capture the growth of larger flame-made particles. The r_g and r_m of silica aggregates consisting of primary particles with initial $r_{p,0} = 10$ nm, obtained by transmission electron

microscopy (TEM) and scanning mobility particle sizing (SMPS) measurements, respectively, exhibit the same evolution with zirconia aggregates having BET radius of ~ 10 nm, formed by flame spray pyrolysis with 5 mL/min precursor solution and 2 L/min dispersion oxygen⁵⁴ (Supplementary Information: Fig. S4a). In fact, the present ED can capture accurately the particle growth early on, where the temperature employed in the simulations is comparable to the flame temperature, but underestimate the aggregate size further downstream the flame, where temperature drops by more than 1000 K and coagulation prevails. Furthermore, the $\sigma_{g,g}$ of those flame-made zirconia aggregates is larger than their $\sigma_{g,m}$, consistent with the present results (Supplementary Information: Fig. S4b). The simulations are in better agreement with the experimental r_m and $\sigma_{g,m}$ rather than with r_g and $\sigma_{g,g}$, possibly due to the fact that the 3D nature of the fractal-like aggregates is not accurately quantified by 2D TEM image counting. Notably, the simulations are performed without any fitting to the experimental data but serve as a guidance for experiments.

Figure 4

Figure 5 shows the ED-derived mobility size distributions of silica aggregates with $r_{p,0} = 1$ nm growing by simultaneous agglomeration and sintering for $5.8 \cdot 10^{-8}$ (squares), $1.2 \cdot 10^{-7}$ (triangles), $4 \cdot 10^{-7}$ (circles), $6 \cdot 10^{-7}$ (diamonds) and $3 \cdot 10^{-6}$ s (down triangles) at (a) 1000, (b) 1500, (c) 1750 and (d) 2000 K. Representative aggregate structures are shown exemplarily at $6 \cdot 10^{-7}$ s for three different temperatures (insets). At $T = 1000$ K, agglomeration is the dominant growth mechanism. The agglomerates attain quickly the SPSD in the free molecular and quasi-SPSD in the transition regime, as shown by the evolution of the geometric standard deviations based on the radius of gyration, mobility radius and volume equivalent radius (Fig. 4a). As temperature increases, sintering prevails and suppresses the growth of fractal-like aggregates. Instead, more compact structures are formed, which exhibit narrower mobility size distributions that are shifted to smaller average mobility diameters.

Figure 5

Figure 6a shows the mobility size distributions of Fig. 5 normalized by the geometric mean mobility diameter, $\langle d_m \rangle$, for aggregates formed by initial primary particles having $r_{p,0} = 0.5$ (purple triangles), 1 (red circles) and 5 nm (blue diamonds) derived by ED simulations (symbols) at 1750 K. The ED simulations are in agreement with mobility size measurements obtained in hot wall reactors (gray solid line²⁵) and flame sprays (dot-broken orange line⁵¹). The volume-based geometric standard deviation, $\sigma_{g,v}$, is presented in Fig. 6b as function of the gas-based Knudsen number, $Kn = \lambda/r_m$, and the SPSD limits for the aggregates of Fig. 6a having $r_{p,0} = 0.5$ (dotted purple

line), 1 (dot-broken red line), 2 (broken green line) and 5 nm (solid blue line). The horizontal lines correspond to the $\sigma_{g,v}$ of the SPSD for fully coalescing nanoparticles and agglomerates in point-contact attaining a fractal dimension, D_f , of 1.9.

Initially, the particles coalesce fully upon collision at 1750 K, regardless of their initial primary particle size, as $\tau_s \ll \tau_c$. Aggregates with small initial primary particle size (i.e., 0.5 nm), reach the SPSD of full coalescence with $\sigma_{g,v} = 1.33$ down to $Kn \approx 200 - 400$. Then the distributions become broader approaching the SPSD limit for agglomeration ($\sigma_{g,v} = 1.41$) at $Kn \approx 150$. Larger particles do not have sufficient time to fully coalesce between collisions and form small aggregates, as shown in Fig. 2. As such, their $\sigma_{g,v}$ exceeds the SPSD limit of full coalescence approaching the self-preserving limit of 1.41 for pure agglomeration in the free molecular regime. At longer simulation times (smaller Kn), the $\sigma_{g,v}$ decreases as the aggregates approach the transition regime.

Figure 6

The aggregate structure affects various particle properties, such as their mechanical and optical properties as well as the overall collision frequency function. The D_f is commonly used to quantify the morphology of aggregates and agglomerates, taking values of 3 for spheres and 1.9 for agglomerates made by ballistic cluster-cluster agglomeration.⁵⁵ Here, the D_f is determined by fitting eq. 1 to an ensemble of 1000 – 2000 aggregates at each time step. Figure 7a shows the evolution of the mass fractal dimension, D_f , of silica aggregates made by agglomeration and sintering of initially monodisperse primary particles with radius of 0.5 (solid line), 1 (broken line), 2 (dot-broken line) and 5 nm (dotted line) at 2000 K as function of the effective n_p . Initially, the simulation box contains only spherical primary particles, which results to an average D_f of 3 for the entire simulated population. As these spheres with $D_f = 3$ grow even more, they require longer times to coalesce, leading to compact but non-spherical aggregates with $D_f < 3$, upon concurrent agglomeration with other nanoparticles. The particles with $r_{p,0} = 5$ nm are the first to form aggregates, as discussed in Fig. 2. The critical n_p that indicates the onset of aggregation in Fig. 3 corresponds to the n_p where D_f first becomes smaller than 3, i.e. the first non-spherical particles are formed. At a given temperature, this critical number increases as the initial primary particle size increases, indicating that the formed aggregates maintain their spherical shape longer. The critical n_p indicating the onset of aggregation is only 2 for $r_{p,0} = 5$ nm but increases to 300 for constituent number of primary particles with $r_{p,0} = 0.5$ nm.

Figure 7b shows the evolution of the exponents D_f (thick lines) and D_{fm} (thin lines) as function of the dimensionless characteristic time, τ_s/τ_c , of silica aggregates with $r_{p,0} = 1$ nm at $T = 1500$ (solid gray lines), 1750

(broken green lines) and 2000 K (dot-broken red lines). The τ_s/τ_c indicates the regions that sintering and agglomeration are more significant. The τ_c is determined by eq. 7 using the ED-derived β (eq. 9) and N , while τ_s is obtained by the sintering rate of Tsantilis et al.⁴³ (eq. 8) using the geometric mean primary particle radius at each time step. The simulated populations of aggregates maintain an average D_f of 3 for $\tau_s/\tau_c < 1$ and follow the same evolutions with the dimensionless characteristic time independent of temperature. Therefore, only the ratio τ_s/τ_c determines the particle structure, consistent with the literature.^{56,57} Specifically, the D_f decreases from 3 at $\tau_s/\tau_c \approx 0.6$ -0.8 down to $D_f = 1.8$ within a narrow τ_s/τ_c range (at $\tau_s/\tau_c = 0.6 - 3$). So, when τ_s is about 3 times larger than τ_c , the collision mechanism determines the particle structure, although sintering still takes place. The D_{fm} starts dropping already from $\tau_s/\tau_c \approx 0.01$ and continues to decrease within a broader range of τ_s/τ_c ratios than D_f . The ED-obtained D_f is compared to the equilibrium D_f of aggregates generated by MC assuming constant τ_s/τ_c ratio (circles⁵⁸). Even though both the ED- and the MC-derived D_f start dropping at $\tau_s/\tau_c \approx 0.6 - 0.9$, the ED-obtained D_f decreases within a narrower range of τ_s/τ_c ratios, indicating that aggregates quickly attain their asymptotic D_f of ~ 1.8 once sintering is suppressed. In fact, the D_f obtained⁵⁸ at constant τ_s/τ_c follows more closely the evolution of the ED-derived D_{fm} at $\tau_s/\tau_c > 2$. The time evolutions of D_f and D_{fm} is shown for aggregates with $r_{p0} = 1$ nm in Fig. S5 of the Supplementary Information.

Figure 7

Figure 8 shows the fractal dimension, D_f , in the process parameter space of the reactor temperature, T , and the effective number of primary particles per aggregate/agglomerate, n_p (corresponding e.g., to increasing height above the burner in flame spray pyrolysis reactors), for $r_{p,0} = 1$ nm. The white top-right corner of the color map corresponds to non-simulated conditions, as ED simulations become computationally expensive for large sintered aggregates. The isotherms of $D_f = 2$ (broken line) and 2.5 (solid line) are also shown. Initially when aggregates are small consisting of $n_p < 2$, they are perfect spheres at all temperatures. As nanoparticles grow by simultaneous sintering and agglomeration, they form compact aggregates that, upon further collisions, lead to fractal-like agglomerates consisting of aggregates. The aggregates attain their asymptotic structure of ~ 1.8 for $n_p > 100$ at all temperatures investigated here, consistent with Jullien et al.⁵⁹ These results are consistent with wide-angle light scattering measurements in hot wall reactors⁶⁰ showing that the fractal-like morphology of silica aggregates is hardly affected at sintering temperatures below 1500 K, exhibiting $D_f \approx 1.6 - 1.7$, while compact spherical-like particles with $D_f = 2.5 - 2.8$ are formed at higher temperatures. The ED-derived D_f are also compared to those obtained by

SAXS measurements in flames (color-coded symbols based on the D_p) at 1665 (circle⁶¹), 1950 (square⁶²) and 2000 K (triangle⁶³), corresponding to 1.66, 2.28 and 2.5, respectively, in qualitative agreement with the present simulations. It should be noted, however, that the actual number of primary particles per aggregate/agglomerate that is typically counted by transmission electron microscopy is expected to be smaller than the effective one shown here, especially at high temperatures, which is based on the initial size of the primary particles.

Figure 8

The overall collision frequency function is commonly used in PBE models for the process design of aerosol reactors. At the early stages of particle growth, all particles are monodisperse and the time between collisions is sufficiently long to fully coalesce. Thus, bigger spheres are formed that collide with coagulation rate that increases with increasing particle size. However, bigger primary particles lead to increased sintering time and formation of aggregates, if the collision and sintering times are of the same order of magnitude. This enhances the collision frequency significantly as they collide more frequently with other particles in the free molecular regime. Figure 9 shows the enhancement of the ED-obtained collision frequency function, β , over the collision kernel of Fuchs, $\beta_{Fuchs,agglo}$ for monodisperse unsintered agglomerates, as function of the normalized aggregate/agglomerate mobility radius for aggregates made by primary particles (a) with $r_{p,0} = 5$ nm at 1000 (black line), 1500 (blue line), 1750 (green line) and 2000 K (red line) and (b) with $r_{p,0} = 0.5$ (purple line), 1 (red line), 2 (green line) and 5 nm (blue line) at 2000 K. Initially, the enhancement of the collision frequency over $\beta_{Fuchs,agglo}$ is close to 1. For big initial primary particles ($r_{p,0} = 5$ nm, Fig. 9a), the average collision frequency enhancement increases rapidly with increasing aggregate size reaching a plateau at $\sim 90\%$ (horizontal broken line) once the aggregate r_m doubles with respect to the initial primary particle size (i.e., at $r_m/r_{p,0} \approx 2$), regardless of the process temperature (Fig. 9a), so that:

$$\beta_{p,aggr} = 1.90 \cdot \beta_{Fuchs,agglo} \quad (10)$$

This enhancement of $\sim 90\%$ is observed in the near free molecular-transition regime, since the r_m -based gas Kn number of aggregates with $r_{p,0} = 5$ nm (Fig. 9a) is in the range of 2 – 85 at all temperatures shown here. At the conditions discussed in Fig. 9a, sintering is very limited and practically aggregates consisting of primary particles with small sinter necks are formed. The collisional enhancement of 90% is attributed to the sintering-induced polydispersity of the constituent primary particles of the silica aggregated that is not accounted for in the Fuchs kernel of monodisperse agglomerates. The ED-predicted enhancement of the collision kernel is in excellent agreement with the enhancement of uncharged titania nanoparticles obtained by experiments in premixed flames.⁶⁴ Equation 10 can be readily used in particle-fluid models for the simulation of industrial synthesis of fractal-like

aggregates with primary particles of $r_{p,0} \geq 5$ nm grown by coagulation and sintering for a wide range of process temperatures (1000 – 2000 K).

At high temperature (Fig. 9b), the average enhancement is much lower during the particle growth investigated here for all $r_{p,0}$ smaller than 5 nm. This is attributed to the greater degree of sintering that leads to more compact aggregates, which tend to behave more like fully coalescing spheres than coagulating agglomerates. In fact, for very small $r_{p,0}$ (e.g., 0.5 nm) the enhancement becomes smaller than unity as particles grow practically by full coalescence, following more closely the collision rate of spherical particles (Fig. S4b). The collisional enhancement of the ED-obtained silica aggregates over the Fuchs kernel of monodisperse spherical nanoparticles, $\beta_{Fuchs,sph}$, is shown in the Supplementary Information (Fig. S4) for the conditions of Figure 9. The enhancement of the coagulation rate of fractal-like aggregates over $\beta_{Fuchs,sph}$ is between 2 – 3.7 (Supplementary Information: Fig. S4a), consistent with the experimentally-obtained collisional enhancement of flame-made titania nanoparticles calculated by particle size distribution measurements⁶⁵ and the enhancement derived by molecular dynamics simulations accounting for dipole-dipole interactions⁶⁶. In addition, the collisional enhancement over $\beta_{Fuchs,sph}$ increases with increasing process temperature for $r_{p,0} = 5$ nm (Fig. S4a), where the collision rate is bigger than the sintering rate, consistent with experiments⁶⁵ and simulations^{66,67}. At high temperatures and small initial sizes (e.g., Fig. S4b: e.g., for $r_{p,0} = 0.5$ nm), particles behave as fully-coalescing spheres early on ($r_m/r_{p,0} = 1 - 3$), exhibiting an enhancement of ~18% in the free molecular regime over the $\beta_{Fuchs,sph}$ of monodisperse spheres, consistent with the literature⁶⁸. As they grow further ($r_m/r_{p,0} > 3$), the sintering rate decreases and non-spherical aggregates are formed that coagulate faster than spheres with equivalent size, leading in larger collisional enhancement. However, since these non-spherical aggregates are still compact (Fig. 7a: $D_f > 1.8$ for $r_{p,0} = 0.5$ nm), they exhibit a collision frequency function which is in-between the limits of perfect monodisperse spheres (Fig. S4b, $\beta/\beta_{Fuchs,sph} > 1.18$ for $r_{p,0} = 0.5$ nm) and unsintered agglomerates (Fig. 9b, $\beta/\beta_{Fuchs,aggl} < 1$ for $r_{p,0} = 0.5$ nm).

Figure 9

4. Conclusions

Coagulation of silica nanoparticles by concurrent agglomeration and viscous flow sintering is investigated by off-lattice event-driven (ED) simulations at high temperatures from the free molecular to the transition regime, under dilute conditions. At low temperatures, coagulation by agglomeration is the dominant particle growth mechanism

resulting in the formation of agglomerates consisting of primary particles in point contact. At this limit of pure agglomeration, particles reach a self-preserving size distribution with gyration-, mobility- and volume-based geometric standard deviations of 2.27, 2.03 and 1.41, respectively, consistent with literature. At high temperatures (i.e., $T > 1500$ K), corresponding to the early stages of particle growth in flame reactors, sintering dominates, especially for small primary particles. In this particle growth region, the simultaneous agglomeration and sintering lead to narrower size distributions and delays the growth of fractal-like particles compared to growth by agglomeration in the absence of sintering. At all conditions investigated here, the volume-based geometric standard deviation attains a self-preserving value of 1.41 in the free molecular regime, regardless of the degree of aggregation. Ballistic cluster-cluster agglomeration with concurrent sintering leads to fractal-like particles with asymptotic fractal dimension, $D_f \approx 1.8$, consistent with experiments. However, when sintering prevails (i.e., at higher temperature), the attainment of the asymptotic D_f is delayed. This delay indicates aggregate densification and reduction in the particle surface area which, in turn, affects catalytic or sensing properties of the end-product. The mass-mobility exponent, D_{fm} , is typically evolving more slowly than the D_f and does not attain its asymptotic value when the sintering mechanism is significant. Nonetheless, the ratio of the characteristic sintering time to the characteristic collision time suffices to define the aggregate structure (D_f), regardless of process temperature or initial primary particle size. Therefore, the dimensionless time can be used as a design parameter to produce particles with desired structure (D_f), which is related to the nanomaterial optical properties.

The collision frequency function of aggregates coagulating by agglomeration and viscous flow sintering is also obtained by ED simulations and its enhancement over the theoretical coagulation rate of Fuchs for monodisperse agglomerates is determined. For compact aggregates that grow mainly by sintering the enhancement of their collision frequency function over the collision kernel of Fuchs is less than 30%, as they behave as fully coalescing spheres. However, for aggregates that grow primarily by agglomeration and little or no sintering, collision frequency enhancement is about 90%, consistent with experiments. The proposed simple-to-use collision kernel is obtained without making *a priori* assumptions about particle structure and accounts for the sintering-induced primary particle polydispersity as well as aggregate polydispersity. This collision kernel equation along with the simple relationship that quantifies the evolution of particle morphology with the dimensionless characteristic time can be readily employed in particle dynamics simulations (e.g., population balance models) coupled with computational fluid dynamics models to improve the design of aerosol processes at industrial scales.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgements

Financial support from The Melbourne School of Engineering of The University of Melbourne, Australia is gratefully acknowledged.

Supporting Information

Validation of the simulations based on the collision frequency function and geometric standard deviation of fully coalescing spheres, comparison of the simulated agglomerate size and geometric standard deviation with experiments, and time evolutions of particle structure descriptors are shown in the Supplementary Information.

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Title:

Structure and dynamics of fractal-like particles made by agglomeration and sintering

Date:

2020-12

Citation:

Eggersdorfer, M. L. & Goudeli, E. (2020). Structure and dynamics of fractal-like particles made by agglomeration and sintering. *AIChE Journal*, 66 (12), <https://doi.org/10.1002/aic.17099>.

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