

Restructuring of Aggregates and their Primary Particle Size Distribution during Sintering

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Particle suspensions and films often exhibit unique properties that depend on particle size distribution, like the opacity of titania pigments, the color of quantum dot or plasmonic nanoparticle suspensions and the superparamagnetism of iron oxide nanoparticles to name a few. Typically a narrow size distribution facilitates harvesting these effects from paints to solar cells, bio sensors and light emitting devices.

Aerosol processes allow rapid and scalable production of nanoparticles over a wide range of sizes. In such processes, however, particles grow typically by Brownian coagulation that places a lower limit to the width of the size distribution, the so-called self-preserving size distribution with a geometric standard deviation of about 1.45. Such a constraint would limit aerosol-made particles in applications requiring narrow size distributions. Furthermore, when primary particles (PP) with different high temperature residence time histories (e.g. from different reactor streamlines or reaction rates) are mixed, fractal-like particles with quite polydisperse PP size distribution (PPSD) are obtained. This polydispersity, however, can be reduced by PP sintering (or coalescence) that proceeds inversely proportional to particle size, similar to condensation that is routinely used in generation of monodisperse aerosols.

During sintering (coalescence) of aggregates of polydisperse PP, restructuring takes place, the average PP size increases and the PPSD narrows affecting particle performance in a number of applications. Here, aggregate sintering by viscous flow, lattice and grain boundary diffusion is simulated by multiparticle discrete element methods focusing on PP growth dynamics and elucidating the detailed restructuring of aggregates during their coalescence.¹ The effect of initial PPSD and sintering mechanisms on the evolution of PP polydispersity (geometric standard deviation) and surface area mean diameter are presented. Each sintering mechanism results in a distinct evolution of PPSD but quite similar growth in average PP diameter. Grain boundary diffusion has the strongest impact among all sintering mechanisms and rapidly results in the narrowest PPSD as it has the strongest dependence on PP size. During sintering of aggregates with initially monodisperse PPs, the PPSD goes through a maximum width before narrowing again as PPs coalesce. A power law holds between projected aggregate surface area and number of PPs regardless of sintering mechanism and initial PP polydispersity. This law can be readily used in aerosol reactor design and for characterization of aggregates independent of material composition, initial PP polydispersity and sintering mechanism.²

Figure 1 shows the relation between d_m and d_{va} for aggregates consisting of 256 PPs with geometric mean diameter, $d_{p,g} = 20$ nm, and $d_{va} = 20, 28.2, 63.3$ nm for $\sigma_{g,0} = 1.0, 1.45$ and 2.0 during sintering. The sintering mechanism has no influence on the geometric relation between d_m and d_{va} . However the temporal evolution depends on process and material parameters as well as sintering mechanism.

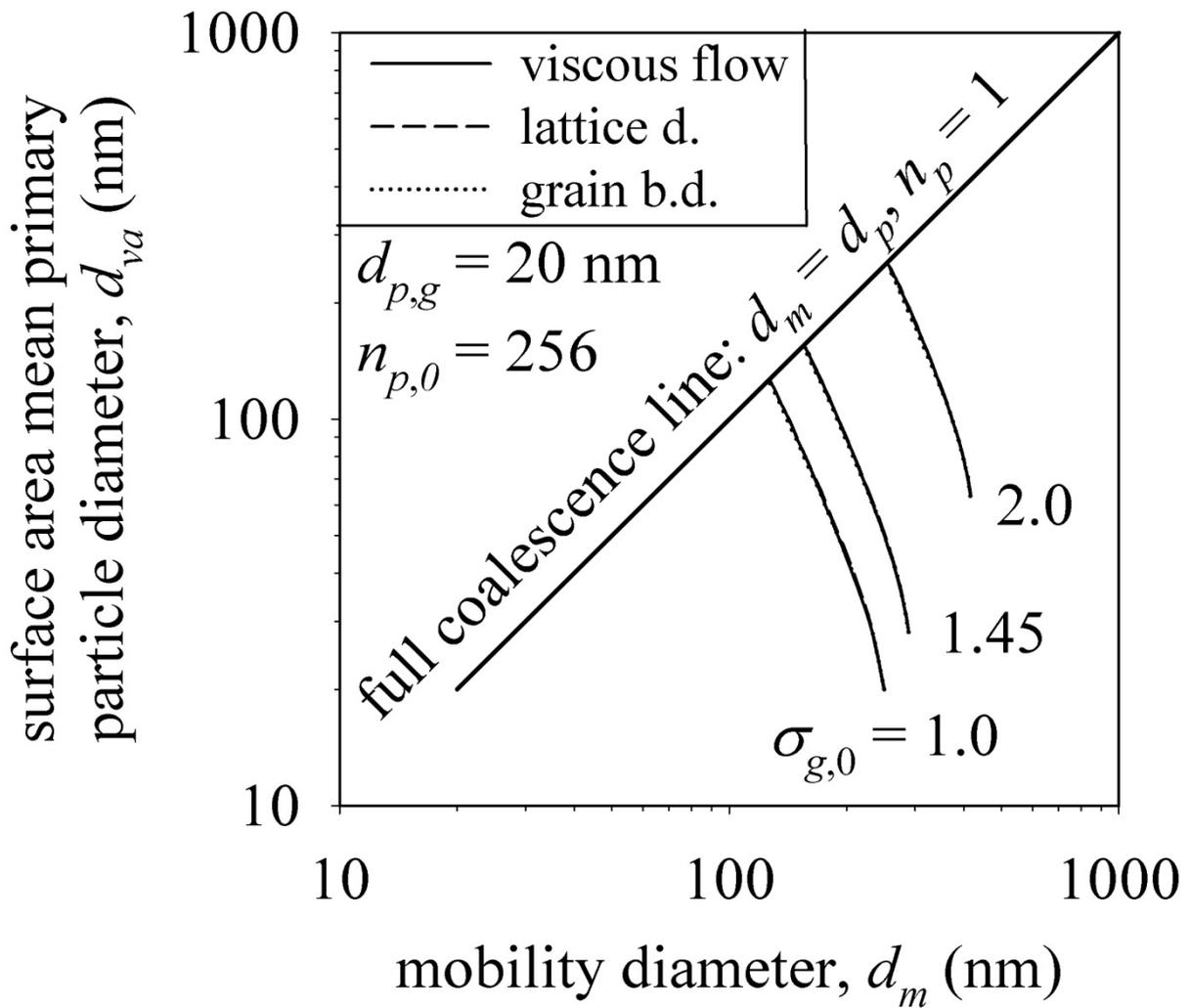


Figure 1: The average primary particle diameter, $d_{va} = 6v/a$, as a function of mobility diameter, d_m , for aggregates during viscous flow, lattice and grain boundary diffusion sintering having a log-normal primary particle size distribution with geometric standard deviation $\sigma_{g,0} = 1.0, 1.45$ and 2.0 with 20 nm geometric mean diameter. During sintering d_{va} grows while d_m decreases until a spherical particle is reached with $d_m = d_p = d_{va}$ (full coalescence line). The relation between d_m and d_{va} is independent of sintering mechanism.

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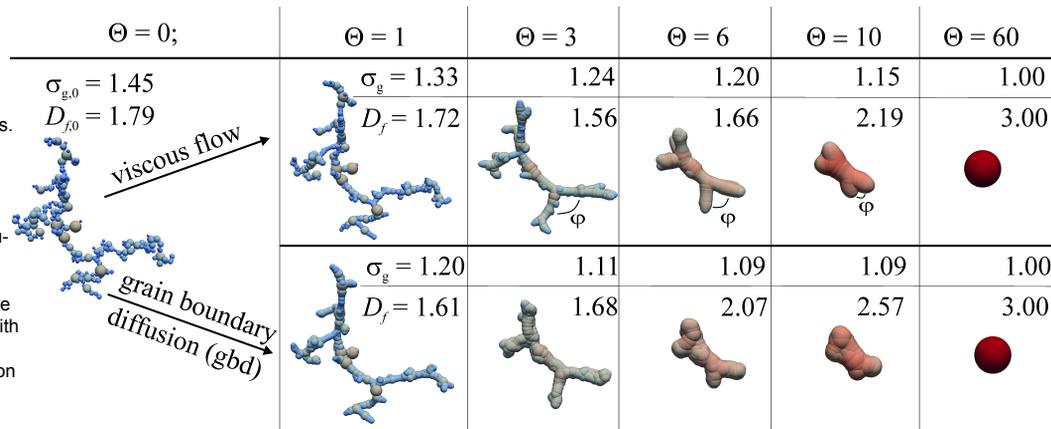
Restructuring & Morphology Evolution

During sintering or coalescence of aggregates of polydisperse primary particles (PP), the average PP size increases and the PP size distribution (PPSD) narrows affecting particle performance in a number of applications.

Aggregate sintering by various sintering mechanisms is simulated by multiparticle discrete element methods [1,2] focusing on PP growth dynamics and, in particular, the detailed restructuring of aggregates during their coalescence [3].

Fig. 1: Snapshots of one agglomerate consisting of 256 PPs and $D_{f,0} = 1.79$ with $\sigma_{g,0} = 1.45$ undergoing sintering by viscous flow and grain boundary diffusion (gbd) at different dimensionless times,

$$\Theta = (t/\tau_0)^{2/\gamma}$$



Quantitative Evolution of Primary Particle Size Distribution

Fig. 2: a) An agglomerate of 16 PPs having an initial size distribution of $\sigma_{g,0} = 1.45$ and its cross section with selected PP diameters highlighted by broken lines. b) At $\Theta = 0.8$ and sintering by grain boundary diffusion, the initial agglomerate has become an aggregate with a narrower size distribution of PPs ($\sigma_g \approx 1.25$).

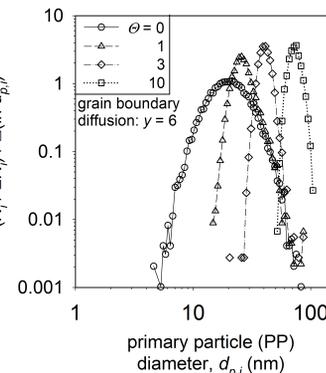
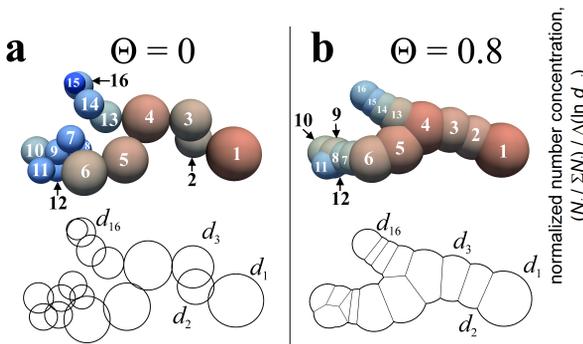


Fig. 3: The evolution of PPSSD during sintering by grain boundary diffusion having initially a geometric mean diameter, $d_{p,g} = 20$ nm, $n_{p,0} = 256$ and $\sigma_{g,0} = 1.45$. Initially, the smallest particles in the aggregate vanish first as they grow while the larger hardly change in size. Only when PPs have reached a similar size and hence a narrow size distribution aggregates start to discernibly become more compact.

Primary Particle & Projected Area Scaling

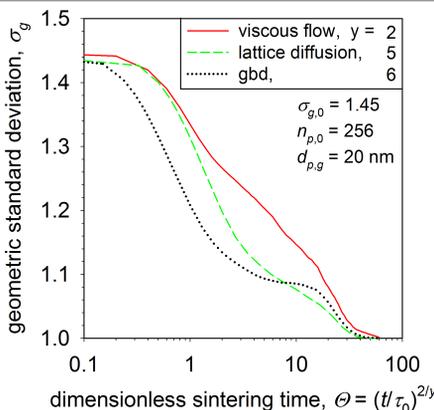


Fig. 4: Grain boundary diffusion (gbd, dotted line) reduces σ_g most rapidly (with Θ) as it has the strongest size dependence.

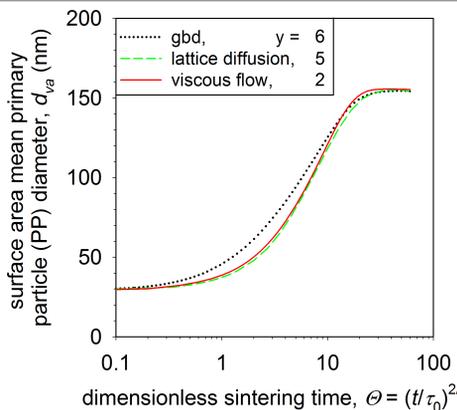


Fig. 5: Evolutions of aggregate structure are quite similar regardless of sintering mechanism. So these three mechanisms lead a fully coalesced sphere nearly at the same dimensionless time ($\Theta \approx 30$).

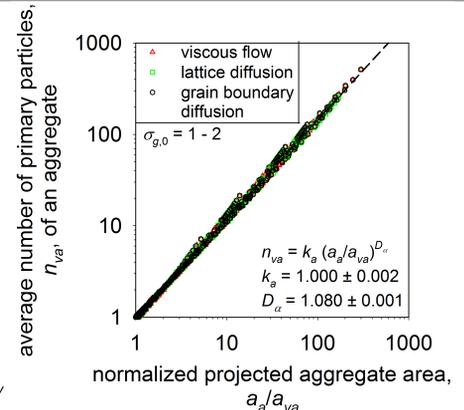


Fig. 6: A power law between projected aggregate area, a_a , and average number of primary particles, n_{va} , resulting in $k_a = 1.000$ and $D_a = 1.08$ for $\sigma_{g,0} = 1-2$ in agreement with experiments [4].

References

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Conclusions

1. Each sintering mechanism results in a distinct evolution of primary particle (PP) size distribution but quite similar growth in average PP diameter.
2. The Θ of monodisperse two-particle sintering also scales the evolution of d_{va} for aggregates consisting of polydisperse particles.
3. A power law holds between projected aggregate surface area and number of PPs independent of sintering mechanism and initial PP polydispersity.

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