Published in final edited form as:

Chem Eng Technol. 2012 July ; 35(7): 1133–1143. doi:10.1002/ceat.201100723.

Multiscale Aspects of Modeling Gas-Phase Nanoparticle Synthesis

B. Buesser* and A.J. Gröhn

Particle Technology Laboratory, Institute of Process Engineering Department of Mechanical and Process Engineering ETH Zurich, 8092 Zürich, Switzerland

Abstract

Aerosol reactors are utilized to manufacture nanoparticles in industrially relevant quantities. The development, understanding and scale-up of aerosol reactors can be facilitated with models and computer simulations. This review aims to provide an overview of recent developments of models and simulations and discuss their interconnection in a multiscale approach. A short introduction of the various aerosol reactor types and gas-phase particle dynamics is presented as a background for the later discussion of the models and simulations. Models are presented with decreasing time and length scales in sections on continuum, mesoscale, molecular dynamics and quantum mechanics models.

1. Introduction

Aerosols are suspensions of small solid or liquid particles in gases and one encounters them every day as perfume sprays, cigarette smoke, smog, etc. [1]. Although aerosol processes play a key role in today's production of nanostructured materials and devices, they are not an invention of our time. Particles, maybe even nanoparticles, have been produced commercially by controlled flame aerosol processes probably since the ancient Chinese generated lamp (carbon) black by combustion of vegetable oils and used them as pigments in black inks [2].

Today carbon black has developed into *the* nanostructured material with the largest production volume of all aerosol-made materials and has found a number of essential applications [3]; for example, without these fluffy, aerosol made particles one would probably have to change the car tires every so often as the motor oil. Aerosol reactors are also used in other major business operations: Since the 1940's fumed silica is manufactured by flame hydrolysis with the AEROSIL process developed by Degussa (nowadays Evonik) [4]. Its development was initially driven by the need for a *white* carbon black as reinforcement agent and has found up today a large number of incredibly diverse applications. In 1951 DuPont de Nemour started producing pigmentary (white) TiO₂ particles with the chloride process [5]. More details of the history of these and other industrial aerosol processes for commodity materials [6] and the state-of-the-art of aerosol science and technology with its promising future applications [7] have been reviewed recently.

Nowadays, 80 – 90 % of all aerosol-made materials are synthesized in diffusion or spray flame reactors [8]. Figure 1 shows a typical laboratory pilot-scale flame spray pyrolysis reactor [9,10] for production rates up to e.g., 1.1 kg/h of SiO₂ nanoparticles, where solvent and precursor of the desired elements are sprayed and subsequently ignited by flamelets to

*Corresponding author: +41-44-632-7997; fax: -1595; buesser@ptl.mavt.ethz.ch.

drive the growth of the nanoparticles [11]. Approximately 10 % by volume and value of commercially available aerosol-made products are synthesized in hot-wall reactors [8] where the reactants flow through externally heated ceramic or metal tubes with well-defined temperature and velocity fields. The precursors can be either gases, as in the decomposition of SiH_4 for the synthesis of high purity bulk silicon [12], liquids, as in the spray pyrolysis of inorganic salt solutions [13], or solids, as for laser flash evaporation of powder mixtures to synthesize zinc-cobalt-oxide nanoparticles [14].

Plasmas are gases containing free electrons and ions in high energy environments usually generated between electrodes [15,16]. In such environments particles get charged which reduces their coagulation rate by Brownian motion and thereby narrows the particle size distribution considerably [17-19]. Plasma reactors have been developed for extremely high temperatures (thermal plasma) to decompose solid precursors [20] or fairly low temperatures (non-equilibrium plasma) to coat sensitive materials [21]. Microwave reactors create non-equilibrium plasmas with focused microwaves to evaporate solid precursors without solvents [22]. Laboratory scale reactors achieve quite high production rates of up to 10 g/h of silicon nanoparticles [23] and the extreme conditions inside the reactor allow synthesizing non-equilibrium crystal phases or solid solutions beyond the equilibrium solubility [22]. Laser reactors create plasmas with laser beams [24]. In the case of laser ablation the beam is aimed directly onto solid material surfaces to evaporate/sublimate it and create aerosol plumes to form nanoparticles [25].

Current research on aerosol reactors concentrates also on one-step modification of nanoparticles with thin coatings [26], functionalization with selected molecules [27] or preferential deposition of catalytically active materials in support material mixtures [28] while the nanoparticles are still suspended in gas-phase. Coating reactors have been developed based on hot wall [29] or flame [26] reactors with injection of coating precursor sequentially after the core particle growth has stopped. Aerosol reactors, established in material synthesis, receive increasing attention in manufacturing active and passive devices including particle films for gas sensors, membranes, fuel cells and electronic components [7,30,31].

The fundamentals of aerosol science and particle dynamics in gas-phase have been collected in text books written by Friedlander [1], Seinfeld and Pandis [32], Kudas and Hampden-Smith [33], or Hinds [34] to name only a few. Recent reviews have concentrated on the synthesis of flame-made nanoparticles [35], the fundamentals of particle formation in flames [36], flame spray pyrolysis [11,37,38], plasma reactors [15], developments from oxides to new salt and metal materials in gas-phase [39], industrial production of nanoparticles in pilot plants [9], or design of nanomaterial synthesis [40]. Reviews of applications of aerosol-made nanomaterials have been presented recently for catalysts [41], metals and biomaterials [39], gas sensors [42], magnetic nanocomposites [43], and nutritional materials [44].

This review presents an overview of the multiscale aspects of models and simulations for the design of aerosol reactors and the investigation of nanomaterials as mentioned in the reviews above. The focus is on the different length and time scales of the models and their efficient interconnection.

2. Particle Growth in Gas-Phase

Figure 2 illustrates particle growth mechanisms and morphologies common in aerosol processes. In a first step the precursor molecules are transformed into gas phase (a), gaseous precursors are preferred but often liquid (c) or solid precursors (d) including evaporation/sublimation have to be utilized because of economic or availability reasons. In spray flames slow precursor evaporation can result in hollow particles which has been illustrated earlier

[35, Fig. 2]. In the gas phase the precursor molecules decompose to monomers (e), e.g., SiO₂ molecules which grow either as stable particles by molecular coagulation [45] or nucleation [46] to critical clusters (f). Surface reaction of precursor molecules increases the particle size proportionally to the particle surface area while evaporation/sublimation decreases the particle size forming monomers again. The nanoclusters grow in the high temperature region of the reactor by coagulation and instantaneous coalescence upon collision to bigger, mostly spherical particles (g). The final particle morphology (h-j) depends on the temperature profile (cooling rate) and primary particle size and can be distinguished into (h) single particles; (i) aggregates, where the primary particles are connected by strong sinter necks; or (j) agglomerates, where primary particles are held together by weak van der Waals forces. Single particles are formed when sintering is faster than coagulation. If sintering and coagulation rates are comparable aggregates are formed while negligible sintering leads to agglomerates (section 3.1.1). A distribution of temperature histories in the same reactor can lead to mixtures of these idealized morphologies. The dynamics of these steps (a-j) are fairly well understood and routinely applied.

Nevertheless, new aerosol reactors that increase the value and functionality of the particles by coating with nanothin shells to retain the bulk properties of the core materials while modifying its surface properties to those of the coating material (k-p) [26] or preferential deposition in nanoparticle mixtures (q-t) [47] are under development in laboratories and require new models for simulation and design.

Core particles (k) that have reached their final primary particle size are coated with different materials by mixing the core particle aerosol with the corresponding precursor vapor (l). The coating precursor forms either coating shells on the core particles by surface reaction or reacts in the gas phase forming coating monomers that either deposit on the core particles (m) or grow to free coating particles following the mechanisms discussed above (a-j). Coating shells are formed by coagulation between coating and core particles with increasing hermeticness (m-n). When coating particles become big enough, coagulation with core particles leads to the formation of rough or porous coating shells (o). Ideal processes synthesize coating shells that are homogeneously distributed on the core particles with a low fraction of uncoated core particle surface area and a minimal amount of un-deposited coating particles.

Mixtures of different precursors (q) lead to aerosols that form particles of two different materials (r). Usually the concentration of an expensive material like platinum acting as catalyst (green) is much smaller than that of the second material (orange) acting as support, resulting in smaller particles (green) deposited on top of the bigger particles (orange) (s). Mixing this particle aerosol with another particle aerosol (blue) leads to agglomerates composed of these three materials but with the smaller (e.g., catalytically active) particles (green) preferentially deposited on one of the two support materials (t). Such materials are for example developed for NSR catalysts where one of the “support” materials acts mainly as mechanical support and the other as storage materials of the NO_x reduction process.

3. Multiscale Design of Aerosol Reactors

As in other processes, the dynamics of aerosol reactors and the properties of nanoparticles depend on physical and chemical properties spanning 10 orders of magnitude in length (from Angstroms for the electronic structure up to meters for the reactor size) and 15 orders in time (from femtosecond for the oscillations of a hydrogen atom on the surface of a nanoparticle up to seconds for the reactor residence time). Models for various length and time scales can be distinguished into continuum, mesoscale, molecular dynamics (MD) and

quantum mechanics (QM) models (Fig. 3, [48]) and can be interconnected in a multiscale frame [49]. Continuum models like fluid mechanics provide important information on temperature, velocity and residence times of a reactor as a final result [50]. At the same time they are needed as input at the smaller time and length scales. Mesoscale models describe for example agglomerate particles with geometric bodies and elucidate the evolution of their morphology under coagulation and sintering [51]. The resulting fractal dimensions and coagulation rates serve as input for particle population balance simulations or primary particle coordination numbers define for example the setup of MD simulations. The MD simulations provide detailed insight into on sintering rates and mechanisms as function of particle size, composition and crystal phase and are used to drive the mesoscale models or describe the evolution of the surface area concentration in particle population balance models [52,53]. Quantum mechanics simulations are applied to develop simple force field for molecular dynamics models [54] or to determine thermochemical properties and reaction mechanisms [49] which are needed for the simulation of reacting flows using continuum fluid mechanics.

3.1 Continuum Models

Continuum models neglect the discrete nature of atoms, molecules or particles and rely on macroscopic material properties. That way it is possible to simulate length scales up to the size of reactors and provide information on temperature, velocity or particle concentration fields. Continuum models also describe detailed reaction kinetics of precursors to identify rate limiting reaction steps and develop more rigorous particle formation rates as input for particle population balance models or to identify the most abundant nanocluster sizes [55]. Even nanoparticles themselves can be described with continuum models by solving the Navier-Stokes equations for a viscous liquid representing the particle volume e.g. that of amorphous SiO₂ [56]. Such simulations show that the sintering rate is faster for compact agglomerate morphologies compared to open structured agglomerates and depends on the coordination number of the primary particles [56].

3.1.1 Characteristic Times of Processes—The comparison of the characteristic time of mechanisms like coagulation and sintering or the reactor residence time is an efficient engineering method to estimate the reactor conditions. For example the characteristic time of sintering, τ_s shown here for TiO₂ [57]:

$$\tau_s = 1.4 \times 10^{21} r^4 \exp\left(\frac{258'000}{RT}\right) \quad (1)$$

describes the time needed for coalescence of two nanoparticles of radius r at temperature T . The characteristic time of coagulation, τ_c , is [33]:

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

where β is the collision frequency and N the particle number concentration, defining the average time between two coagulation events. The comparison of τ_s and τ_c allows estimating the product particle morphology (Fig. 2h-j). If the τ_s is much shorter than τ_c ($\tau_c/\tau_s \gg 1$) the particles have enough time to fully coalesce until the next collision with another particle resulting in a compact (spherical-like) particles (Fig. 2h). If τ_s is longer than τ_c ($\tau_c/\tau_s \ll 1$) the particles have hardly any time to coalesce between the collisions and the particles form fractal-like agglomerates (Fig. 2j). Comparable τ ($\tau_c/\tau_s \sim 1$) result in aggregates (Fig. 2i). As an example: In the flame synthesis of zirconia nanoparticles [58] the particle number concentrations are 5.28×10^{17} and $8.59 \times 10^{16} \text{ m}^{-3}$ at height above the burner

$HAB = 100$ and 200 mm, respectively. With the collision frequencies of $\beta = 1.82 \times 10^{-15}$ and $2.19 \times 10^{-15} \text{ m}^3/\text{s}$ at these position the characteristic collision times become $\tau_C = 0.001$ and 0.0053 s whereas the characteristic sintering times for ZrO_2 are $\tau_S = 5.26 \times 10^{-8}$ and 1.14×10^{-2} s. The ratios $\tau_C/\tau_S = 1.90 \times 10^4$ ($HAB = 100$, spherical particles) and 0.465 ($HAB = 200$ mm, aggregates and agglomerates), respectively, are in agreement with the onset of soft-agglomerate formation at $HAB = 155$ mm [58, Fig. 11, vertical black line] and the TEM analysis of thermophoretic sampling [58, Fig. 8].

Brownian coagulation leads to time-invariant self-preserving size distributions (SPSD) independent of the initial particle size distribution [59]. Initially monodisperse or narrow particle size distributions broaden while broad distributions narrow until the PSD with a number-based geometric standard deviation of 1.44–1.46 is attained [60]. The characteristic time to attain a PSD, τ_{SPSD} , for monodisperse particles is around $10\text{--}12 \times \tau_C$ [61]. Higher particle concentrations lead to shorter τ_C and therefore faster attainment of the PSD. For residence times longer than τ_{SPSD} Brownian coagulation does not change the shape or polydispersity of the particle population anymore.

Holunga *et al.* [62] have used characteristic times to determine the conditions of their turbulent mixing aerosol coating reactor. Besides comparing τ_C and τ_S as discussed above τ_C was compared with the reactor space time, τ_R , to obtain non-agglomerated particles ($\tau_C > \tau_R$) or the characteristic time of turbulent mixing, τ_M [62,63]:

$$\tau_M = 3.3 \left(\frac{ML^2}{P} \right)^{\frac{1}{3}} \quad (3)$$

where M is the mass of fluid in the dissipation region, L is the integral dimension and P is the mechanical mixing power, to assure that particle concentration fluctuations are dissipated quickly by turbulence ($\tau_C \gg \tau_M$).

The characteristic time of the chemical reactions, τ_R , which in the case of first order reactions equals the reciprocal value of the reaction rate constant ($1/k$), is short if the temperature is high. The characteristic time of the turbulence, τ_T , is short for high turbulence intensity. Often the chemistry in aerosol reactors is referred to being fast and meaning that the chemical reactions are much faster than the turbulence ($\tau_R/\tau_T \ll 1$).

3.1.2 Particle Population Balance Models—Particle population balance models describe the evolution of the particle size and morphology distribution. A detailed review of particle dynamics models and simulations for gas-phase synthesis of nanomaterials has been presented by Kraft [64] and selected models are presented here. The continuous form of the general dynamic equation (GDE) that describes the change of number concentration, n , as function of particle size and time is [65]:

$$\begin{aligned} \frac{\partial n(v_p, t)}{\partial t} = & \int_{v_m}^{v_p} \beta(v_p - v, v) n(v_p - v, t) n(v, t) dv - \frac{1}{2} n(v_p, t) \int_{v_p}^{\infty} \beta(v_p, v) n(v, t) dv \\ & + S(v_p, t) \delta(v_p - v_m) + \frac{\partial}{\partial v_p} (I(v_p, t) n(v_p, t)) \end{aligned} \quad (4)$$

where the first two terms on the right hand side (RHS) account for coagulation, the third term for condensation and surface growth and the last one for nucleation. Unfortunately the GDE cannot be solved analytically for relevant cases and models have to be applied.

One-dimensional sectional models describe the evolution of the particle size distribution as function of number, surface area or volume concentration in bins with a fixed size width at

constant [66] or moving [67] particle size. Tracking number and area concentration [68] or number of primary particles [69] for each bin together allows describing the average morphology (spherical/fractal-like) of each bin. Two-dimensional sectional models describe the evolution of a second variable for each bin of a 1D-sectional model with a separate 1D-sectional model allowing a more detailed description of the particle morphology (Fig. 2h-j) distribution [70] or the primary particle polydispersity [71].

Methods of moments (MOM) describe the evolution of the moments M_k of order k of the particle size distribution:

$$M_k = \int_0^{\infty} d_p^k n(d_p) dd_p \quad (5)$$

However to close the system of equations for the evolution of such moments one needs additional assumptions like imposing a lognormal shape on the size distribution, which is close to the SPSPD but cannot represent bimodal distributions, as in the method of moments (MOM) [72], or with interpolative closure (MOMIC) [73], quadrature (QMOM) [74] and direct quadrature (DQMOM) [75]. However a considerable challenge in the later models is the reconstruction of the particle size distribution from the tracked moments.

Aerosol processes are typically operated at high temperatures and precursor loadings resulting in high particle concentrations where nucleation can be neglected and monomers treated as stable particles [45]. The rapid attainment of SPSPDs at these conditions (e.g., average size at 2 to 3 times the initial monodisperse particle size [76,77]) allows to drastically simplify the aerosol particle dynamics by replacing the elaborate polydisperse models above with a simple and effective monodisperse model [78]:

$$\begin{aligned} \frac{dN}{dt} &= -\frac{1}{2}\beta N^2 \\ \frac{dA}{dt} &= -\frac{A-A_{fc}}{\tau_s} \\ \frac{dV}{dt} &= 0 \end{aligned} \quad (2)$$

where the number concentration N changes by coagulation with the frequency β [32]. The influence of sintering on the surface area concentration, A , is described by the phenomenological sintering rate of Koch and Friedlander [79], where τ_s is the characteristic time for sintering (section 3.1.1) and A_{fc} is the total particle surface area concentration when all particles have coalesced to spheres (no agglomerate/aggregates structures). The τ_s is the time needed to reduced the excess of surface area $A-A_{fc}$ by 63% [70]. The volume concentration, V , is not affected by coagulation and sintering but can be decreased considerably by wall losses [40]. The number, surface area and volume concentration correspond to the zeroth, second and third moment, based on particle diameter of the size distribution. Terms for particle formation [78] or surface reaction [66] can be added. During particle formation the monodisperse model predicts a too low average particle size, because the continuous production of small monomers (Fig. 2e), but converges to the exact solution after particle formation has ceased and coagulation dominates the particle growth ($\tau_C \ll \tau_R$) [80]. During these early stages in aerosol reactors the bimodal model shows a better performance by accounting for the monomer generation by a separate equation [78,80,81].

Monte Carlo methods simulate particle size distributions by randomly selecting two particles and calculating the probability of a successful collision between two particles as function of the collision frequency between them [82,83]. These statistical models have the advantage that no prior assumption on the particle distributions is required to describe particle

coagulation and aggregation. Also nucleation coagulation and surface growth in dispersed systems and are very easy to implement.

Particle dynamics for charged particles have to account for the charge distributions and the effect of coulomb forces on the coagulation frequencies [19,84].

These particle population balance models are ready to be couple with computationally fluid dynamics models. However they required rates describing coagulation, sintering and particle formation which can be obtained from mesoscale, molecular dynamics or quantum mechanics simulations as shown later on.

3.1.3 Computational Fluid Dynamics—Aerosol reactor models based on computational fluid dynamics (CFD) simulate flow (laminar or turbulent), temperature and particle concentration fields by accounting for the reactor geometry, chemistry and particle dynamics. Turbulent flows require, with increasing accuracy and computational demand, either additional models like the Reynolds-averaged Navier-Stokes (RANS) models (standard and realizable k- ϵ and the Reynolds stress model), the large eddy simulations (LES) or resolution of all turbulence scales as in direct numerical simulations (DNS).

Laminar aerosol reactor models have been developed for diffusion flames [85] or hot wall reactors [86]. In the absence of turbulence particles remain mainly on the streamline where they had been formed but thermophoresis and diffusion can have a considerable influence on their radial distribution [85]. This can result in a large variety of temperature histories for the particles and therefore a broad particle morphology (Fig. 2h-j) distribution in the product. Turbulent diffusion flame reactor models have been developed for example for the synthesis of e.g. TiO_2 [87-89], Al_2O_3 [90] or SiO_2 [50,91] nanoparticles. Figure 4a shows axial temperature cross-sections of diffusion flames producing SiO_2 nanoparticles, for increasing the oxygen flow rate from (left to right) which results in shorter and more turbulent flames [50]. The simulated SiO_2 primary particle diameters (Fig. 4b, blue triangles) are in quite good agreement with the experimental data (Fig. 4b, red circles) [92]. Increasing the oxygen flow rate leads to smaller primary particles because of the shorter residence time at high temperature [50]. A model like this is very useful for scaling-up such reactors to higher production rates and adjusting the flow rates to obtain the desired particle size and morphology before the first experiment. The constant difference between experiment and simulations can be attributed to uncertainties in the sintering rate of SiO_2 nanoparticles. Often this has been fixed by modifying the sintering rate accordingly [87,90] resulting in *effective* sintering rates that are likely to be applicable only for the original reactor or maybe even conditions.

Aerosol coating reactors deposit hermetic coating shells on nanoparticles while they are still suspended in gas phase after formation. A coating reactor model [93,94] combining trimodal coating particle dynamics [95] and CFD was used to investigate SiO_2 coating of TiO_2 nanoparticles showing how increasing the mixing intensity between core particle aerosol and coating precursor vapor by increasing the mixing flow rate decreases the fraction of uncoated particles in agreement with experimental data [93,95]. Uncoated or partially coated particles are formed if the coating precursor jets are too weak to penetrate the core particle aerosol or mix with core particle passing in-between the jets [93] (Fig. 3a).

Recirculations in such enclosed reactors broaden the particle residence time distribution [96] and broaden that way the particle size distributions [97]. Nozzle configurations in aerosol reactors that are opposing or axi-symmetric [97] or single injections [98] lead to recirculations upstream while tangential and annular tangential nozzles reduce this back-mixing and result in narrower particle size distributions [97].

DNS is a powerful tool which has become more useful with the proliferation of high-performance computing. It is unique in predicting physico-chemical processes consistent with the basic equations describing the phenomena of interest by resolving all length and time-scales. However, industrially relevant problems often require too big ranges of scales to be resolved. Therefore an increasingly popular approach to reduce the computational costs is LES where large-scale features and interactions are resolved explicitly but the small-scale fluctuations and interactions are modeled to reduce the required resolution and compute-time. However modeling these small-scale fluctuations - especially in turbulent, reacting, multi-phase flows - is a significant challenge.

Figure 5 shows a fluid temperature iso-surface of a turbulent jet with the transition from laminar to turbulent regimes as obtained by a) DNS and b) LES. The DNS resolves all scales of turbulence (Fig. 5a) while the (high quality) LES only describes the large scale features (Fig. 5b). The two fields are similar in the mean but the small-scale mixing is clearly absent for the LES. The difference in detail is also reflected in the computational costs for a physical time of 20 ms of 192,000 CPU-hours for the DNS whereas the LES only requires 3,000 CPU-hours caused mainly by the different grid resolutions of $167'772'160$ ($640 \times 512 \times 512$) and $1'024'000$ ($160 \times 80 \times 80$) grid points required by the methods, respectively.

The high computational costs have often limited application of LES and DNS to local phenomena revealing for example the nanoparticle concentration gradients inside of turbulence eddies [99]. Large eddies downstream of planar co-flow jets broaden the overall size distribution beyond the SPSD by increasing the residence time of a fraction of the particles [100]. On average large eddies increase the particle polydispersity, but instantaneous, local values remain close to the SPSD value. The cores of jets have a more uniform particle size distribution than at the interface with their surrounding [101]. Better mixing of precursor with oxidants as observed in small eddies leads to faster precursor reaction and therefore larger particles [102].

Recently, LES has been applied for turbulent diffusion flame reactors for the synthesis of TiO_2 nanoparticles focusing on the description of the chemistry [103] and particle nucleation [104] using QMOM to describe the particle dynamics. Such models allow studying the influence of the large-scale turbulence on the nanoparticle evolution in detail.

3.2 Mesoscale Models

Mesoscale models represent particles as geometric bodies (e.g., spheres) and use rate models to describe their motion, size change and overlap during surface growth [105], sintering [51,106], coagulation [107] or fragmentation [108]. A typical mesoscale model of a fractal-like agglomerate consisting of 256 polydisperse primary particles ($\sigma_g = 1.45$) with a fractal dimension of $D_f = 1.79$ is shown in Figure 3b [109]. Such models provide important information about the evolution of the fractal dimension and the agglomerate sintering and coagulation rate which can be used as input for continuum population balance models.

Mitchell and Frenklach [105] developed a mesoscale model to investigate the morphology evolution of soot particles. The competition between simultaneous coagulation and surface growth revealed that if coagulation is faster than surface growth, conditions found early-on in aerosol reactors with high concentrations of small particles, fractal-like soot particles are formed. If surface growth becomes faster than coagulation, later-on in the reactor, the morphology transforms to spherical-like particles because the surface reaction lets the primary particles grow and overlap proportionally to their exposed surface area. Finally, the precursor reaction ceases and the morphology changes back to fractal-like dominated by coagulation [105].

Similar, the competition between sintering and coagulation influences the fractal dimension, D_f [106,110] which increases from 1.85 for diffusion limited coagulation ($\tau_C/\tau_S \rightarrow 0$) to a value of $D_f = 3$ (spherical) for fast sintering already at $\tau_C/\tau_S > 4$ (section 3.1.1). Adding simultaneous surface growth shifts the D_f to smaller τ_C/τ_S ratios corresponding to denser agglomerate structures. A master curve for D_f as function of an empirical characteristic time was developed to apply these D_f in multiscale models [111]. Figure 6 shows snapshot of the sintering evolution (left to right) of an agglomerate with an initial $D_f = 1.8$ undergoing sintering to full coalescence where the color from blue to red represents the increasing primary particle diameters [51].

Langevin dynamics describes the Brownian motion of particles as a stochastic process. The particles follow trajectories, which differentiates this method from the Monte Carlo methods used for particle population balance models, and allows simulating aerosols undergoing coagulation without knowing the coagulation frequency prior to the simulation [76]. Coagulation rates for low particle volume fractions can be described based on continuum assumptions [112]. However they break down at volume fractions around 1 vol%, a value which is easily approached by the *effective* volume fraction of fractal-like particles [113]. Langevin dynamics can simulate such coagulation rates and the corresponding particle size distributions at high concentrations in the continuum [76] and continuously from the free molecule through transition into the continuum [107] regime. Increasing the solid volume fraction up to 20 vol% accelerates the coagulation rate up to 30 times and broadens the particle size distribution beyond the SPSD. This enhancement of the coagulation rate has been quantified by empirical expressions as function of particle size and volume fraction as input for population balance models [107].

3.3 Molecular Dynamics

Molecular dynamics (MD) models account for the discrete nature of the atoms, which is neglected in continuum and mesoscale models, limiting MD to shorter length and time scales. MD simulations have been used for example to investigate sintering rates and mechanisms [52] (Fig 3c), evaporation [114] or mechanism of laser ablation [115].

In aerosol reactors the sintering rate defines the final primary particle diameter and crystallinity and with this the major part of the product particle performance in its application. Therefore its accurate knowledge is essential to design temperature residence histories of the particles to the target product. The evolution of crystal phase during sintering [53] and its characteristic time [52] can be extracted from MD simulations for various materials like silicon [116], gold [117] or titania [52]. An important issue in MD simulations is the temperature control as it directly influences the atom trajectories. A very realistic setup is to immerse the sintering nanoparticles in an inert-gas to completely avoid any temperature control algorithm on the particles [118]. The surface area of small, sintering nanoparticles evolves in three distinct stages [118]. First it decreases upon contact and adhesion of the two particles without involvement of atom diffusion. This is followed by an increase of the sinter neck size between them up to the primary particle diameter where the particles attain an oval shape while the surface area does not change much. Finally the particles coalesce into a single spherical one accompanied by the major part of surface area reduction and thermal energy release because of the surface energy reduction [118]. The sintering particles have the same temperature as the surrounding gas as the excess energy is transferred into the gas by gas-molecule collisions [118].

The MD sintering rate of TiO_2 nanoparticles converges to the experimentally validated theory for larger particles at primary particles sizes around 5 nm [52]. Figure 7 shows snapshots of cross-sections of two TiO_2 nanoparticles ($d_p = 3.5$ nm) where titanium and oxygen atoms are initially (Fig. 7a) colored yellow and blue at the surface and green and red

in the bulk, respectively [52]. The sintering neck increases suddenly upon adhesion and increases up to the primary particle size by surface diffusion (Fig. 7b). The atom colors show that the initial sintering neck is filled mainly by initial surface atoms (yellow/blue) whereas the initial bulk atoms (green/red) remain mainly together. This indicates that that surface diffusion of highly mobile surface atoms is the dominant sintering mechanism for rutile TiO_2 nanoparticles and to smaller extent grain boundary diffusion. Calculating the surface area of such simulations returns the characteristic sintering time after the excess surface area has decreased by 67 % [52,57,70] which is close to the 63 % of phenomenological models [79]. Like the depression of the melting temperature for small nanoparticles there is a depression of the characteristic sintering time which can decrease several orders of magnitude [52] and be quantified by MD.

3.4 Quantum Mechanics

Quantum mechanics models describe molecules and matter very accurately but are because of the high computational costs limited to very small systems of 1 to 100 atoms. Density functional theory (DFT) has become very popular among the various QM methods since the development of improved functionals, which cannot be derived analytically, for the exchange and correlation interactions to solve the electron-electron many body problem. It requires a relatively low computational effort compared with other methods. The derivation of the functionals by fitting is the main reason why DFT leads to good results in many cases and to wrong results in others. A further disadvantage is that it does not account for van der Waals forces properly.

However DFT elucidates reaction rates and mechanisms [119], crystal [120] or nanocluster structures [121] and their dynamic behavior [122] (Fig. 3d), or investigates thermodynamic properties of molecules required to develop gas-phase reaction systems [55]. Such reaction rates of precursors are important for aerosol reactor design as they can affect the particle morphology [105] and polydispersity [123] considerably.

Catlow *et al.* [121] have reviewed the recent developments in computer simulation of nanoclusters and nucleation focusing on the search for global energy minima of nanoclusters. The positions of all atoms of a nanocluster of a certain size are varied until theoretically all configurations have been visited. The total energy is calculated for each configuration by DFT and the one with lowest energy indicates the most stable and therefore abundant structure. Often increasing the cluster size results in monotonically higher energies like for $(\text{TiO}_2)_N$ nanoclusters with $N = 1 - 15$ where such minima have been found by evolutionary algorithms [124]. But this is not always the case. It can be that adding or removing an atom results in more unstable particles like for the optimized structures of $(\text{SiO}_2)_N$ clusters resulting in global energy minima where certain N are more stable than $N - 1$ and $N + 1$. Such cluster sizes with “magic” N represent more stable particles and might represent likely cluster growth paths which are awaiting experimental confirmation [125]. The understanding of the early stages of nanoparticle formation in gas-phase is very important for the design of the smallest nanoparticles with sizes around 1 nm that are for example promising candidates for high performance catalysts.

Doping nanoparticles with tracer concentrations of a different element allows adjusting their properties like melting temperature, characteristic sintering time and crystal phase [126]. DFT simulations of TiO_2 explain how nitrogen [127] or carbon [128] doping influences the photoactivity and the contrary effects in anatase and rutile crystals by the different structures and electron densities. Further it allows calculating the energy of formation as function of oxygen concentration and temperature and finding optimal synthesis conditions [128].

4. Conclusions

This review presents a short overview of recent developments of models and simulations at multiple length and time scales for the design of aerosol reactors synthesizing nanoparticles. Particle population models and their combination with computational fluid dynamics enable detailed reactor design and are routinely applied. Uncertainties persist however with required inputs on precursor reaction rates or coagulation and sintering rates of spherical and fractal-like particles that have to be investigated further with models at the appropriate smaller length and times scales.

Mesoscale models can be very useful for investigating the properties of fractal-like agglomerates and their evolution during coagulation, sintering and surface reaction. Molecular dynamics models bear a lot of potential if reliable force fields are available, especially for the detailed analysis of nanoparticle sintering. Quantum mechanics calculations are the most accurate simulations of matter and methods like DFT in combination with new high-performance computing tools extend its range of application to sizes relevant for aerosol and nanomaterials science. The challenge is to provide the results accessible to the models at other time and length scales. For example better MD force fields developed with DFT provide more rigorous sintering rates that can be used in mesoscale models to elucidate the agglomerate structure evolution or as input in continuum particle population balance models. Many future contributions to multiscale aerosol reactor design can be expected to begin at these smallest scales in time and length based on quantum mechanics.

Acknowledgments

The authors would like to thank Prof. Dr. Sotiris E. Pratsinis (ETH Zürich) for discussing and supporting this work. Financial support from European Research Council is gratefully acknowledged. The authors would like to thank Prof. Dr. Sean C. Garrick (University of Minnesota, USA) for contributing figures and text for the discussion of DNS and LES, Dr. Robert Büchel (ETH Zürich) for providing a picture of a flame spray pyrolysis reactor and discussing the manuscript, and Max Eggersdorfer (ETH Zürich) for providing figures of mesoscale simulations of a polydisperse agglomerate and a sintering aggregate.

6. References

1. Friedlander, SK. Smoke, dust and haze: Fundamentals of aerosol dynamics. 2nd ed. Oxford University Press; New York: 2000.
2. Ulrich GD. Chem. Eng. News. 1984; 62:22. [PubMed: 11541976]
3. Kühner, G.; Voll, M. Manufacture of Carbon Black. In: Donnet, J-B.; Bansal, RC.; Wang, MJ.; Dekker, M., editors. Carbon Black. 2nd. CRC Press; New York, NY: 1993. p. 1-66.
4. Klopfer, H. Verfahren zum Reinigen von hochdispersen Oxyden von Metallen bzw. Metalloiden. DE Patent. 762723. 1942. assigned to Degussa AG
5. Mezey, EJ. Pigments and Reinforcing Agents. In: Powell, CF.; Oxley, JH.; Blocher, JM., editors. Vapor Deposition. Wiley; New York: 1966. p. 423-451.
6. Pratsinis, SE. History of Manufacture of Fine Particles in High-Temperature Aerosol Reactors. In: Ensor, D., editor. Manufacture of Fine Particles. RTI Press; 2011.
7. Pratsinis SE. AIChE J. 2010; 56:3028.
8. Wegner K, Pratsinis SE. Chem. Eng. Sci. 2003; 58:4581.
9. Wegner K, Schimmoeller B, Thiebaut B, Fernandez C, Rao T. KONA. 2011; 29
10. Mueller R, Madler L, Pratsinis SE. Chem. Eng. Sci. 2003; 58:1969.
11. Madler L, Kammler HK, Mueller R, Pratsinis SE. J. Aerosol Sci. 2002; 33:369.
12. Alam MK, Flagan RC. Aerosol Sci. Technol. 1986; 5:237.
13. Messing GL, Zhang SC, Jayanthi GV. J. Am. Ceram. Soc. 1993; 76:2707.
14. Djenadic R, Akgül G, Attenkofer K, Winterer M. J. Phys. Chem. C. 2010; 114:9207.

15. Vollath D. J. Nanopart. Res. 2008; 10:39.
16. Phillips J, Luhrs CC, Richard M. IEEE T. Plasma Sci. 2009; 37:726.
17. Sankaran RM, Holunga D, Flagan RC, Giapis KP. Nano Lett. 2005; 5:537. [PubMed: 15755110]
18. Mangolini L, Thimsen E, Kortshagen U. Nano Lett. 2005; 5:655. [PubMed: 15826104]
19. Xiong Y, Pratsinis SE, Mastrangelo SVR. J. Colloid Interf. Sci. 1992; 153:106.
20. Ryu T, Choi YJ, Hwang S, Sohn HY, Kim I. J. Am. Ceram. Soc. 2010; 93:3130.
21. Roth C, Künsch Z, Sonnenfeld A, Rudolf von Rohr P. Surf. Coat. Technol. 2011; 205(Supplement 2):S597.
22. Vollath D, Sickafus KE. Nanostruct. Mater. 1992; 1:427.
23. Gupta A, Swihart MT, Wiggers H. Adv. Funct. Mater. 2009; 19:696.
24. van Erven J, Munao D, Fu Z, Trzeciak TM, Janssen R, Kelder E, Marijnissen JCM. KONA. 2009; 27:157.
25. Semaltianos NG. Cr. Rev. Sol. State. 2010; 35:105.
26. Teleki A, Heine MC, Krumeich F, Akhtar MK, Pratsinis SE. Langmuir. 2008; 24:12553. [PubMed: 18850688]
27. Teleki A, Bjelobrk N, Pratsinis SE. Langmuir. 2010; 26:5815. [PubMed: 20192157]
28. Büchel R, Strobel R, Krumeich F, Baiker A, Pratsinis SE. J. Catal. 2009; 261:201.
29. Powell QH, Kodas TT, Anderson BM. Chem. Vapor. Depos. 1996; 2:179.
30. Wegner K, Barborini E, Piseri P, Milani P. KONA. 2006; 24:54.
31. Tricoli A, Pratsinis SE. Nat. Nano. 2010; 5:54.
32. Seinfeld, JH.; Pandis, SN. Atmospheric chemistry and physics: From air pollution to climate change. 2nd ed. John Wiley & Sons; Hoboken, New Jersey: 2006.
33. Kodas, TT.; Hampden-Smith, MJ. Aerosol Processing of Materials. 2nd ed. Wiley and Sons Ltd; 1999.
34. Hinds, WC. Aerosol technology: Properties, behavior, and measurement of airborne particles. Wiley; New York: 1999.
35. Strobel R, Pratsinis SE. J. Mater. Chem. 2007; 17:4743.
36. Roth P. Proc. Combust. Inst. 2007; 31:1773.
37. Teoh WY, Amal R, Madler L. Nanoscale. 2010; 2:1324. [PubMed: 20820719]
38. Bickmore CR, Waldner KF, Treadwell DR, Laine RM. J. Am. Ceram. Soc. 1996; 79:1419.
39. Athanassiou EK, Grass RN, Stark WJ. Aerosol Sci. Technol. 2010; 44:161.
40. Buesser B, Pratsinis SE. Annu. Rev. Chem. Biomol. Eng. 2012; 3
41. Schimmoeller B, Pratsinis SE, Baiker A. ChemCatChem. 2011; 3:1234.
42. Tricoli A, Righettoni M, Teleki A. Angew. Chem. Int. Ed. 2010; 49:7632.
43. Wiggers H. KONA. 2009; 27:186.
44. Zimmermann MB, Hilty FM. Nanoscale. 2011; 3:2390. [PubMed: 21483965]
45. Ulrich GD. Combust. Sci. Technol. 1971; 4:47.
46. Girshick S, Chiu C. J. Chem. Phys. 1990; 93:1273.
47. Strobel R, Madler L, Piacentini M, Maciejewski M, Baiker A, Pratsinis SE. Chem. Mater. 2006; 18:2532.
48. Schaefer DW, Hurd AJ. Aerosol Sci. Technol. 1990; 12:876.
49. West RH, Celnik MS, Inderwildi OR, Kraft M, Beran GJO, Green WH. Ind. Eng. Chem. Res. 2007; 46:6147.
50. Gröhn AJ, Buesser B, Jokiniemi JK, Pratsinis SE. Ind. Eng. Chem. Res. 2011; 50:3159.
51. Eggersdorfer ML, Kadau D, Herrmann HJ, Pratsinis SE. Langmuir. 2011; 27:6358. [PubMed: 21488641]
52. Buesser B, Gröhn AJ, Pratsinis SE. J. Phys. Chem. C. 2011; 115:11030.
53. Koparde VN, Cummings PT. ACS Nano. 2008; 2:1620. [PubMed: 19206364]
54. Matsui M, Akaogi M. Mol. Simulat. 1991; 6:239.
55. Swihart MT, Girshick SL. J. Phys. Chem. B. 1999; 103:64.

56. Kirchhof MJ, Schmid HJ, Peukert W. *Phys. Rev. E*. 2009; 80:026319.
57. Kobata A, Kusakabe K, Morooka S. *AIChE J.* 1991; 37:347.
58. Gröhn AJ, Pratsinis SE, Wegner K. *Chem. Eng. J.* 2012 in press.
59. Friedlander SK, Wang CS. *J. Colloid Interface Sci.* 1966; 22:126.
60. Vemury S, Kusters KA, Pratsinis SE. *J. Colloid Interface Sci.* 1994; 165:53.
61. Landgrebe JD, Pratsinis SE. *J. Colloid Interf. Sci.* 1990; 139:63.
62. Holunga DM, Flagan RC, Atwater HA. *Ind. Eng. Chem. Res.* 2005; 44:6332.
63. Corrsin S. *AIChE J.* 1957; 3:329.
64. Kraft M. *KONA*. 2005; 23:18.
65. Gelbard F, Seinfeld JH. *J. Colloid Interf. Sci.* 1979; 68:363.
66. Tsantilis S, Kammler HK, Pratsinis SE. *Chem. Eng. Sci.* 2002; 57:2139.
67. Spicer PT, Chaoul O, Tsantilis S, Pratsinis SE. *J. Aerosol Sci.* 2002; 33:17.
68. Tsantilis S, Pratsinis SE. *AIChE J.* 2000; 46:407–415.
69. Park SH, Rogak SN. *J. Aerosol Sci.* 2004; 35:1385.
70. Xiong Y, Pratsinis SE. *J. Aerosol Sci.* 1993; 24:283.
71. Heine MC, Pratsinis SE. *J. Aerosol Sci.* 2007; 38:17.
72. Lee KW. *J. Colloid Interf. Sci.* 1983; 92:315.
73. Frenklach M, Harris SJ. *J. Colloid Interf. Sci.* 1987; 118:252.
74. McGraw R. *Aerosol Sci. Technol.* 1997; 27:255.
75. Marchisio DL, Fox RO. *J. Aerosol Sci.* 2005; 36:43.
76. Heine MC, Pratsinis SE. *Langmuir*. 2007; 23:9882. [PubMed: 17685639]
77. Landgrebe JD, Pratsinis SE. *Ind. Eng. Chem. Res.* 1989; 28:1474.
78. Kruis FE, Kusters KA, Pratsinis SE, Scarlett B. *Aerosol Sci. Technol.* 1993; 19:514.
79. Koch W, Friedlander SK. *J. Colloid Interface Sci.* 1990; 140:419.
80. Muhlenweg H, Gutsch A, Schild A, Pratsinis SE. *Chem. Eng. Sci.* 2002; 57:2305.
81. Jeong JI, Choi M. *J. Aerosol Sci.* 2003; 34:965.
82. Kruis FE, Maisels A, Fissan H. *AIChE J.* 2000; 46:1735.
83. Tandon P, Rosner DE. *J. Colloid Interf. Sci.* 1999; 213:273.
84. Bogaerts A, Eckert M, Mao M, Neyts E. *J. Phys. D: Appl. Phys.* 2011; 44:174030.
85. Yu S, Yoon Y, Müller-Roosen M, Kennedy IM. *Aerosol Sci. Technol.* 1998; 28:185.
86. Schild A, Gutsch A, Mühlenweg H, Pratsinis SE. *J. Nanopart. Res.* 1999; 1:305.
87. Johannessen T, Pratsinis SE, Livbjerg H. *Powder Technol.* 2001; 118:242.
88. Yu M, Lin J, Chan T. *Chem. Eng. Sci.* 2008; 63:2317.
89. Yu M, Lin J, Chan T. *Powder Technol.* 2008; 181:9.
90. Johannessen T, Pratsinis SE, Livbjerg H. *Chem. Eng. Sci.* 2000; 55:177.
91. Ji Y, Sohn HY, Jang HD, Wan B, Ring TA. *J. Am. Ceram. Soc.* 2007; 90:3838.
92. Scheckman JH, McMurphy PH, Pratsinis SE. *Langmuir*. 2009; 25:8248. [PubMed: 19594189]
93. Buesser B, Pratsinis SE. *AIChE J.* 2011; 57:3132.
94. Buesser B, Pratsinis SE. *Ind. Eng. Chem. Res.* 2011; 50:13831. [PubMed: 23658471]
95. Buesser B, Pratsinis SE. *Chem. Eng. Sci.* 2010; 65:5471.
96. Wegner K, Walker B, Tsantilis S, Pratsinis SE. *Chem. Eng. Sci.* 2002; 57:1753.
97. Manenti G, Masi M. *Chem. Eng. Sci.* 2009; 64:3525.
98. Akroyd J, Smith AJ, Shirley R, McGlashan LR, Kraft M. *Chem. Eng. Sci.* 2011; 66:3792.
99. Settumba N, Garrick SC. *J. Aerosol Sci.* 2003; 34:149.
100. Miller SE, Garrick SC. *Aerosol Sci. Technol.* 2004; 38:79.
101. Das S, Garrick SC. *Phys. Fluids*. 2010; 22:103303.
102. Garrick S, Wang G. *J. Nanopart. Res.* 2010; 13:973.
103. Mehta M, Sung Y, Raman V, Fox RO. *Ind. Eng. Chem. Res.* 2010; 49:10663.
104. Sung Y, Raman V, Fox RO. *Chem. Eng. Sci.* 2011; 66:4370.

105. Mitchell P, Frenklach M. *Phys. Rev. E*. 2003; 67:061407.
106. Schmid H-J, Teiwani S, Artelt C, Peukert W. *J. Nanopart. Res.* 2004; 6:613.
107. Buesser B, Heine MC, Pratsinis SE. *J. Aerosol Sci.* 2009; 40:89.
108. Eggersdorfer ML, Kadau D, Herrmann HJ, Pratsinis SE. *J. Colloid Interf. Sci.* 2010; 342:261.
109. Eggersdorfer ML, Pratsinis SE. *Aerosol Sci. Technol.* 2011; 46:347.
110. Schmid H-J, Al-Zaitone B, Artelt C, Peukert W. *Chem. Eng. Sci.* 2006; 61:293.
111. Al Zaitone B, Schmid H-J, Peukert W. *J. Aerosol Sci.* 2009; 40:950.
112. Smoluchowski MV. *Z. phys. Chem.* 1916; 17:557, 585.
113. Heine MC, Pratsinis SE. *Part. Part. Syst. Char.* 2007; 24:56.
114. Thompson SM, Gubbins KE, Walton JPRB, Chantry RAR, Rowlinson JS. *J. Chem. Phys.* 1984; 81:530.
115. Zhigilei LV, Kodali PBS, Garrison BJ. *J. Phys. Chem. B.* 1997; 101:2028.
116. Zachariah MR, Carrier MJ. *J. Aerosol Sci.* 1999; 30:1139.
117. Arcidiacono S, Bieri NR, Poulikakos D, Grigoropoulos CP. *Int. J. Multiphas. Flow.* 2004; 30:979.
118. Lümmer N, Kraska T. *Phys. Rev. B.* 2005; 71:205403.
119. Shirley R, Akroyd J, Miller LA, Inderwildi OR, Riedel U, Kraft M. *Combust. Flame.* 2011; 158:1868.
120. Woodley SM, Catlow R. *Nat. Mater.* 2008; 7:937. [PubMed: 19029928]
121. Catlow CRA, Bromley ST, Hamad S, Mora-Fonz M, Sokol AA, Woodley SM. *Phys. Chem. Chem. Phys.* 2010; 12:786. [PubMed: 20066364]
122. Vargas A, Santarossa G, Iannuzzi M, Baiker A. *Phys. Rev. B.* 2009; 80:195421.
123. Tsantilis S, Pratsinis SE. *J. Aerosol Sci.* 2004; 35:405.
124. Hamad S, Catlow CRA, Woodley SM, Lago S, Mejías JA. *J. Phys. Chem. B.* 2005; 109:15741. [PubMed: 16852997]
125. Bromley ST, Illas F. *Phys. Chem. Chem. Phys.* 2007; 9:1078. [PubMed: 17311150]
126. Righettoni M, Tricoli A, Pratsinis SE. *Chem. Mater.* 2010; 22:3152.
127. Di Valentin C, Pacchioni G, Selloni A. *Phys. Rev. B.* 2004; 70:085116.
128. Di Valentin C, Pacchioni G, Selloni A. *Chem. Mater.* 2005; 17:6656.

Figure 1. Pilot-scale flame spray pyrolysis reactor for high production rates. The flamelets are hardly visible as light blue clouds at the nozzle tip. Courtesy of Robert Büchel (ETH Zürich).

Figure 2. Overview of particle morphologies and growth paths in aerosol synthesis of materials (a-j), coated particles (k-p) and nanomixtures with preferential deposition (q-t).

Figure 3.

Overview of a multiscale model for aerosol synthesis of materials following the schematic of Schaefer and Hurd [48] showing a) a continuum model for reactor flow field design of coating flame-made TiO_2 , Ag, or Fe_2O_3 nanoparticles by SiO_2 films [93], b) a mesoscale model of an agglomerate of polydisperse primary particles (courtesy of Max Eggersdorfer, ETH Zürich) [109], c) molecular dynamics of TiO_2 nanoparticles undergoing sintering to full coalescence [52] and d) a schematic representing quantum mechanics used to calculate the electronic structure of materials.

Figure 4.

a) Simulated temperature fields of a turbulent laboratory-scale diffusion flame with oxygen flow rates of 12, 15.3 and 20 l/min (Courtesy of Arto Gröhn, ETH Zürich). b) Comparison of primary particle diameter predicted by the model [50] shown in a) and experimental data [92] as function of oxygen flow rate.

a) Direct Numerical Simulation, fully resolved turbulence

Instantaneous temperature field

b) Large Eddy Simulation, large-scale resolved turbulence

Figure 5.

The instantaneous temperature of a turbulent jet for nanoparticles synthesis as obtained from a) fully resolved turbulence in Direct Numerical Simulations (DNS) and b) large-scale resolved turbulence in Large Eddy Simulations (LES). It can be seen that LES captures the large motions of the fluid quite well while DNS also tracks the evolution of the turbulence features at smaller scales. Courtesy of Sean C. Garrick (University of Minnesota).

Figure 6.

Evolution (from the left to the right) of the fractal-like structure of an agglomerate (blue) undergoing sintering to a fully coalesced sphere (red) simulated with a mesoscale model representing the primary particles as spheres that overlap and increase their diameter during sintering [51]. Reprinted and adapted with permission from [51]. Copyright 2011 American Chemical Society

a) $t = 0$ b) $t = 3 \text{ ns}$ c) $t = 300 \text{ ns}$ **Figure 7.**

Cross-sections of two TiO_2 nanoparticles ($d_p = 3.5 \text{ nm}$, $T = 1800 \text{ K}$) with Ti and O atoms initially ($t = 0$) colored green and red (bulk atoms) or yellow and blue (surface atoms), respectively, at a) $t = 0$, b) 3, c) 300 ns [52].