

# The Coalescence of Aerosol Nanoparticles by Molecular and Computational Fluid Dynamics

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## Introduction

Inorganic nanoparticles produced by combustion processes often grow by coagulation and sintering. The basic sintering mechanisms can be investigated by molecular dynamics allowing to extract particle sintering rates for continuum scale simulations. Here multi-scale simulations are conducted for an example case of nanoparticle production by a flame spray pyrolysis (FSP; Mädler et al., 2002). FSP has been shown to be a versatile and economic process (Wegner et al., 2011). It relies on inexpensive metal-containing liquid precursors, which are atomized by a dispersion gas and ignited to form a spray flame. Following spray droplet evaporation and precursor conversion nanoparticles grow by nucleation, coagulation, sintering and/or surface growth. The objective of this work is the development of a computational fluid-particle dynamics model covering all important process steps to provide insight into the evolution of nanoparticle characteristics.

## Method

The sintering or coalescence of nanoparticles is elucidated by monitoring the detailed motion of the atoms with accelerated molecular dynamics (Buesser et al., 2011). Spray, fluid, combustion and aerosol dynamics are integrated in a computational fluid dynamics solver to predict product nanoparticle properties without adjustable parameters or need of experimental input data. By assuming immediate particle formation on precursor oxidation and a self-preserving particle size distribution a robust and computationally feasible description of the process could be constructed (Gröhn et al., 2011). Fourier-transform infrared spectroscopy, Phase-doppler anemometry and nanoparticle sampling in-situ the flame are employed for characterizing the temperature, velocity and particle growth profiles of the flame reactor and are used for validation of the computational code (Gröhn et al., 2012).

## Results and Discussion

It is revealed that sintering by surface diffusion dominates the initial growth of nanoparticles with minimal displacement of inner atoms (sintering by grain boundary diffusion). This is in stark contrast with classical ceramics where compacts of particles are used in sintering studies. In addition, a long-standing question on the significance and sequence of these two sintering mechanisms is resolved contributing a quantitative expression for the accelerated sintering rate of nanoparticles that beautifully converges to that of much larger ones at only about 5 nm instead of 10 or 20 nm. This expression can be readily used in phenomenological sintering models for the design, scale-up and optimization of gas-phase manufacture of nanoparticles. Furthermore it is extended to metal nanoparticles and multi-particle structures exploring the role of geometry in deciphering sintering mechanisms and extracting their sintering or coalescence rates.

The predicted product primary particle size is strongly influenced by the description of sintering as revealed by comparing three literature expressions for the solid-state diffusion coefficient, showing that an adequate description of sintering is required for the development of accurate aerosol synthesis models. A simple and robust model describing flame spray synthesis of nanoparticles has been developed that does not rely on experimental input data and is well suited for process design, reactor optimization and scale-up of the widely-used FSP process for synthesis of a broad spectrum of nanostructured materials.

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## Introduction

A multi-scale approach to describe formation of inorganic nanoparticles by combustion is presented for an example case of flame spray pyrolysis (FSP) aerosol reactor.

- Nanoparticle growth in flames takes often place by coagulation and sintering
- Process simulations by computational fluid dynamics are sensitive to the sintering rate of nanoparticles
- Molecular dynamics can be employed to extract a characteristic sintering rate
- Simulation results are compared to experiments

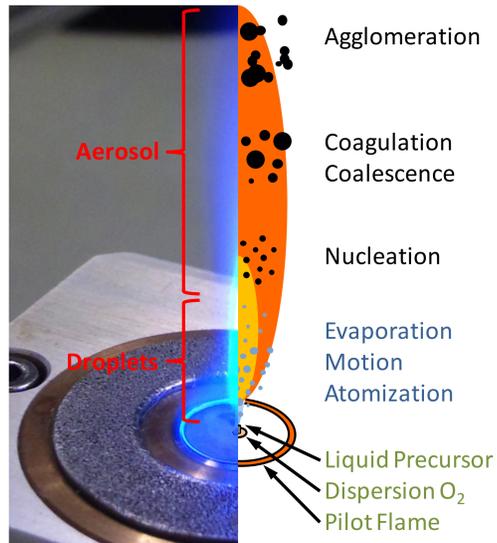


Fig. 1. Schematic of the FSP reactor.

## Molecular Dynamics

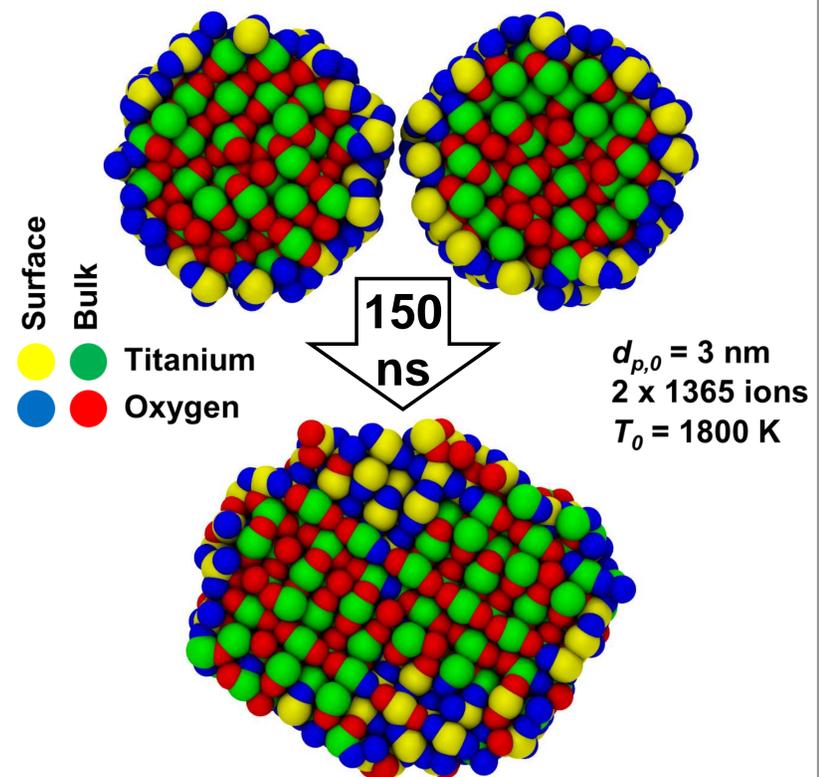


Fig. 2. Sintering of nanoparticles by molecular dynamics.

## Computational Fluid Dynamics

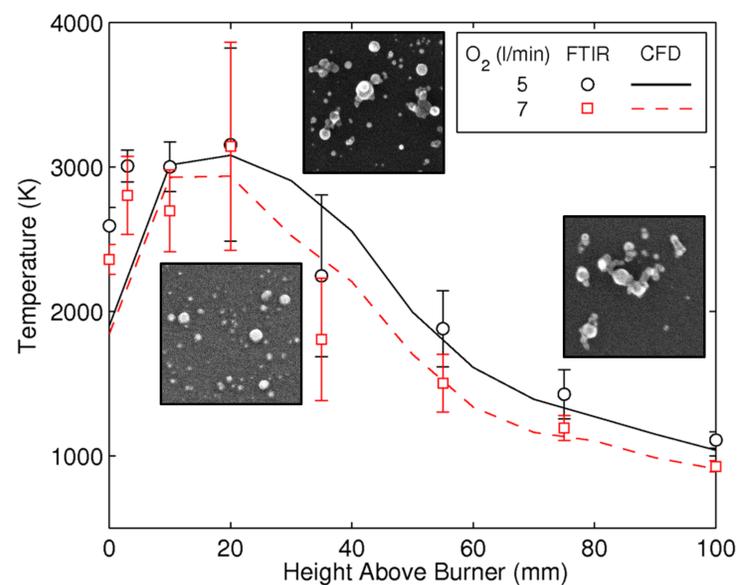


Fig. 5. Comparison of FTIR measured (symbols) and simulated (lines) line-of-sight average temperatures of the 4 ml/min ethanol and 5 (black, continuous line) or 7 (red, broken line) l/min dispersion O<sub>2</sub> flame. TEM micrographs from thermophoretic sampling show how spherical particles are formed by rapid coalescence in the high temperature region while coagulation produces more agglomerated structures higher up in the flame.

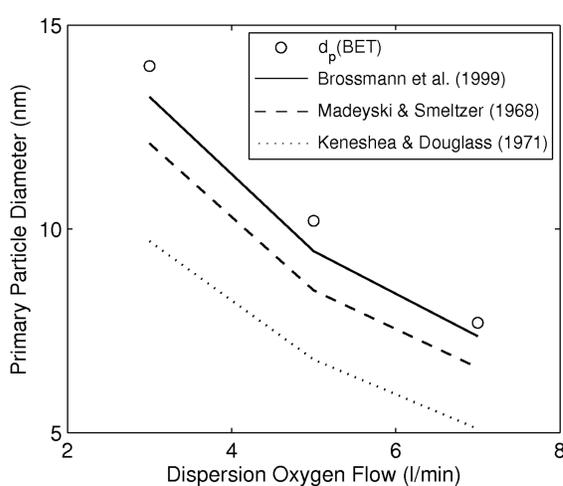


Fig. 6. Effect of sintering rate on the predicted particle diameters for 4 ml/min of 0.5 mol/l Zr precursor. Grain boundary diffusivity of Brossmann et al. (1999) gave best agreement with experiments.

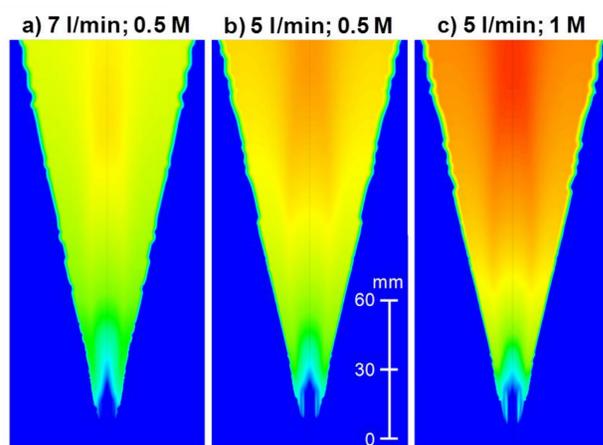


Fig. 7. Simulated primary particle diameter profiles for 4 ml/min precursor at: a) 0.5 M Zr with 7 l/min O<sub>2</sub>, b) 0.5 M Zr with 5 l/min O<sub>2</sub> and c) 1 M Zr with 5 l/min O<sub>2</sub>.

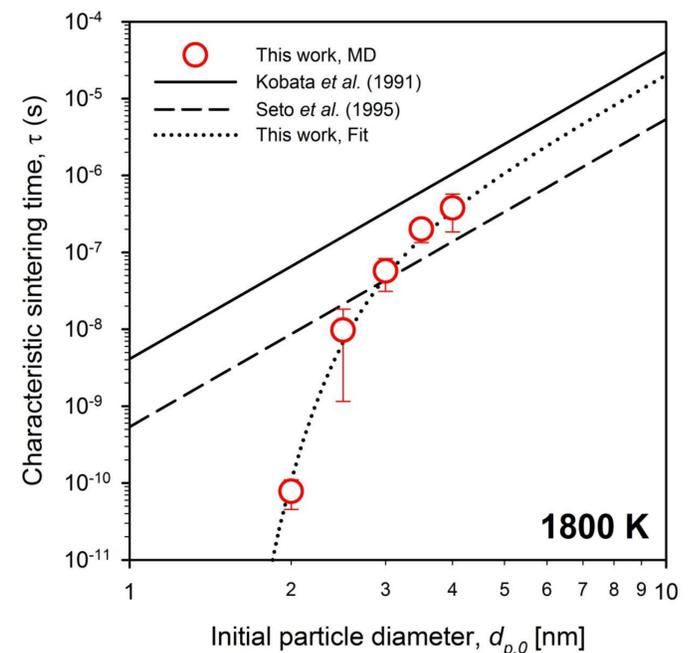


Fig. 3. Characteristic sintering time obtained from molecular dynamics along with that of Kobata et al. (solid lines) and Seto et al. (dashed lines) as a function of initial primary particle diameter at  $T = 1800 \text{ K}$ .

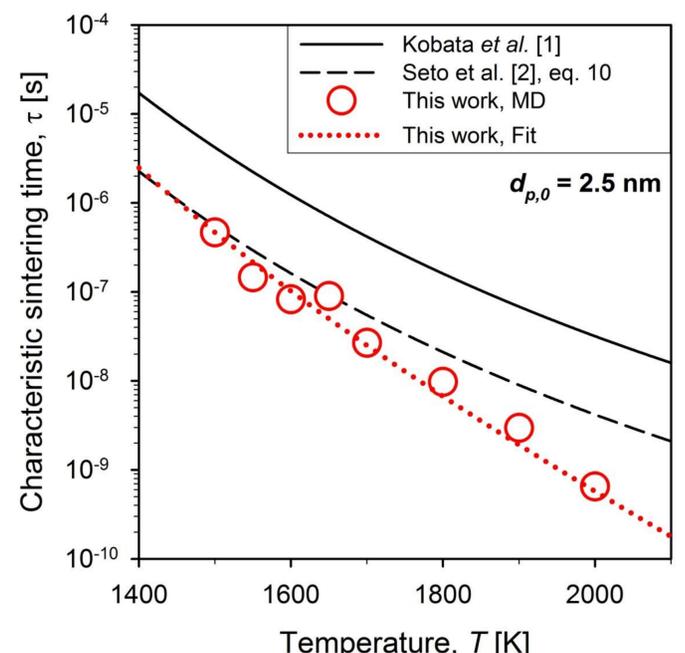


Fig. 4. Characteristic sintering time obtained by the present molecular dynamics simulations as a function of temperature for initial primary particle diameter of 2.5 nm.

## Conclusions

- Fair agreement with experiments is attained for molecular and computational fluid dynamics simulations.
- For small nanoparticles ( $d < 5 \text{ nm}$ ) sintering takes place mainly by surface diffusion. For more agglomerated structures grain boundary diffusion becomes important.

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