Mesoscopic and Continuum Models Linking for Nanoparticles Gas-Phase Synthesis Simulation

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Abstract: In this work results from the new NanoDome model for the simulation of nanoparticle synthesis in a plasma reactor are presented and compared with CFD computations of particle dynamics. The novelty of the NanoDome approach entails the simulation of all the scales involved in the process; the results presented here are obtained by linking the continuum scale with mesoscale calculations. The model can capture correctly the evolution of the nanoparticles and matches well with the CFD calculations.

Keywords: Nanoparticles, Synthesis, Multiscale, Plasma,

1. Introduction

Nanoparticle synthesis processes have been developed for a wide range of materials such as pure metals (e.g. Si, Ni, W), oxides (e.g. ZnO, TiO2) or alloys (e.g. Au-Cu).

However, precisely control of properties such as particle size distribution, composition, purity and dispersibility in a reliable and reproducible way, and at the same time guarantee a high-volume, continuous production at attractive cost/benefit ratios remains an issue. Wet-phase methods produce nanoparticles with very well-defined size and morphology, but they often lack scale-up capabilities and cost-effectiveness. On the contrary, GP synthesis processes, such as plasma processes, provide a good balance between precision synthesis and production scale, even though accurate control of particle properties is still a big challenge.

The H2020 NanoDome project is aimed to solve some of these issues by providing an open source modelling tool to improve existing nanoparticle gas phase synthesis process design capabilities, at research and industrial level. The novel approach proposed by the project is to provide a tool for simulating nanoparticles dynamics at mesoscopic scale and couple this simulation with data provided by the atomistic level for describing the behaviour of different species in the GP and on the other hand, elaborate the data provided by the CFD simulating the reactor, covering the complete processing route, in fact proposing a full multiscale model. The preliminary results presented here are promising, not only regarding the mesoscopic simulation itself but also for the linking process with the CFD. In this poster, we present the results obtained for Si nanoparticles synthesis in a plasma reactor.

2. Multiscale Approach

The NanoDome model describes the phenomena occurring at all the length scales involved in the nanoparticle synthesis process as depicted in Fig. 1, from individual atoms to macroscopic reactor scale flow, using a multiscale approach. At each scale simulations are performed to extrapolate meaningful data for the nanoparticles formation. All these data are elaborated by the mesoscopic simulation for mimicking the nanoparticles behaviour.

Atomistic scale: Atomistic modelling (MD) is performed with the aim to provide fundamental understanding and data for setting up the basic mechanisms of formation (nucleation) and growth (condensation) and inter-particle interaction (sintering and aggregation).

Mesoscale: The coarse grained mesoscopic model for the description of nanoparticles behaviour and aggregate formation, including homogeneous and heterogeneous nucleation, coagulation, coalescence and sintering. Nanoparticles and aggregates mutual interaction and formation is predicted using different approaches model like Langevin dynamics, Moments method and Population Balance method.

Continuum scale: Continuum reactor models elaborate the environmental condition in which the nanoparticles dynamics take place (i.e. p, T, species concentration).

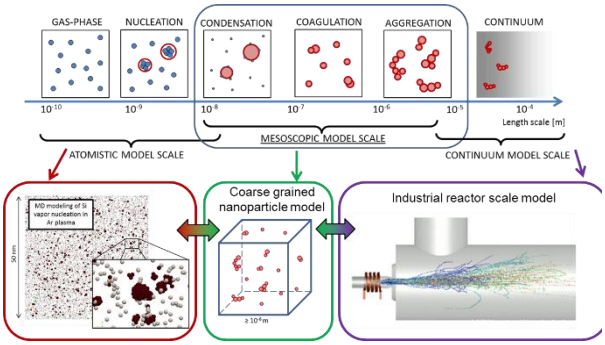

Figure 1: NanoDome multiscale approach.

Chemical kinetics: Chemical kinetics for the continuum and the mesoscopic model are developed using DFT and statistical thermodynamics.

Interfacing: For interfacing the mesoscopic simulation environment two main approaches have been considered:

- Linking or loose coupling: the data coming from the CFD (e.g. a streamline) are used to guide the mesoscopic simulation.
- Strong coupling: The data provided by the CFD are elaborated by the mesoscopic simulation and the results are used as input for the next iterations of the continuum simulation.

3. CFD Modelling

Plasma torch and reactor have been simulated using a CFD model described in [1]. To simulate the nanoparticles growth and transport an improved version of the method of moments approach as described in [2], with new terms for the prediction of dissolution and evaporation, has been used. Vapors production from solid micrometric precursors has been modelled using a lagrangian discrete particle models as done in [3].

The 2D computational domain is presented in Fig. 2, and comprises a PL-50 plasma torch and a generic axisymmetric reaction chamber with a radial quench injections. Two axial inlets for the working gas and one inlet for the injection of the precursory powders are included at the head of the torch and one radial inlet for quenching at the entrance of the chamber. Plasma torch geometry and operating conditions are taken from [4]. Operating gas is pure Ar and Si powders with 10 μm diameter have been used as precursors.

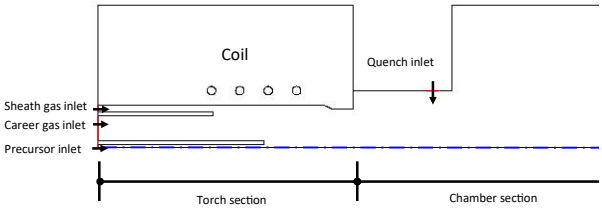

Figure 2 - Torch and quench region geometry.

4. Mesoscopic Simulation

Phenomena occurring at mesoscopic scale can be simulated adopting different models. The key factors that discriminate these approaches are the detail in the simulation of the dynamics during the particles formation and the computational effort required. The NanoDome framework is designed to provide a complete toolbox with different models, depending on the aspects that are investigated by the user. Each model is implemented exploiting a solid and versatile C++ classes structure that allows an agile development of the source code as described in [5]. However, in this paper results coming from a mesoscopic Population Balanced Model (PBM) are shown. The PBM has been proposed by [6], it has been applied in different cases in material science and nanoparticles synthesis. The model chosen in NanoDome is the one in [7]. The population balance equations are numerically solved using a stochastic approach, allowing to extend the model with specific quantities at particle level. More in detail, the interaction between the Gas Phase and the Particle Phase is modelled by means of the operator splitting technique as described in [8]. The coagulation among nanoparticles is modelled using collisional kernels related to a given fractal dimension. PBM, compared with the moments method, allows to get more information regarding other particles characteristics like sintering level of each aggregate. Moreover, a particle size distribution is not given, and is retrieved by the evolution of the system. Form the computational point of view is affordable for problem with a high number of particles and for long simulation times. Each nanoparticle is treated like a single entity, with specific quantities (e.g. mass, position, surface area, chemical composition). The nanoparticles, seen as an aggregate of primary particles connected by bonds representing the distance among particles. Each primary particle considers also surface condensation from the free molecular regime. The sintering process is characterized by the modification of the distance between the centres of mass of the coagulated particles and is driven by the thermodynamic quantities of the specific material.

5. Linked Simulation

The novelty of this approach is to retrieve the Gas Phase quantities like temperature, pressure and species concentration without using a specific solver but extracting these data from the CFD model simulating the reactor. This data is exported as a set of streamlines characterized by their own temperature history, pressure and species concentration in a specific part of the reactor domain. Each parameter is sampled and the resulting values are imported into the mesoscopic environment and interpolated. At each timestep of the mesoscopic simulation, the CFD quantities are retrieved and used for computing all the parameters of the Gas Phase. These parameters are directly involved in the simulation of phenomena like nucleation, motion or surface condensation inside the Particle Phase. The aim of this approach is to predict the structure and the thermo-physical characteristics of the nanoparticles moving across the reactor. This soft-coupling approach neglects the interactions that the mesoscopic scale has on the continuum one, in fact can be also called “one-way” linking.

6. Results

Fig. 3 shows details of the thermo-fluid dynamic field inside the torch and the chamber obtained with the CFD simulation whilst Fig. 4 presents the solution for the distribution and size of the nanoparticles as predicted by the method of moments. From these fields, it is possible to extrapolate the data to be fed into the NanoDome model, as explained above. Temperature and molar fraction of silicon obtained from the streamline lying on the central axis are shown in Fig. 5 and 6.

In Fig. 7 and 8 a comparison is presented between the results obtained with CFD and those obtained with the PBM model used in NanoDome, for the evolution of the particle density and the mean diameter along the streamline. For the particle density, the value predicted with the NanoDome model at the end of the streamline

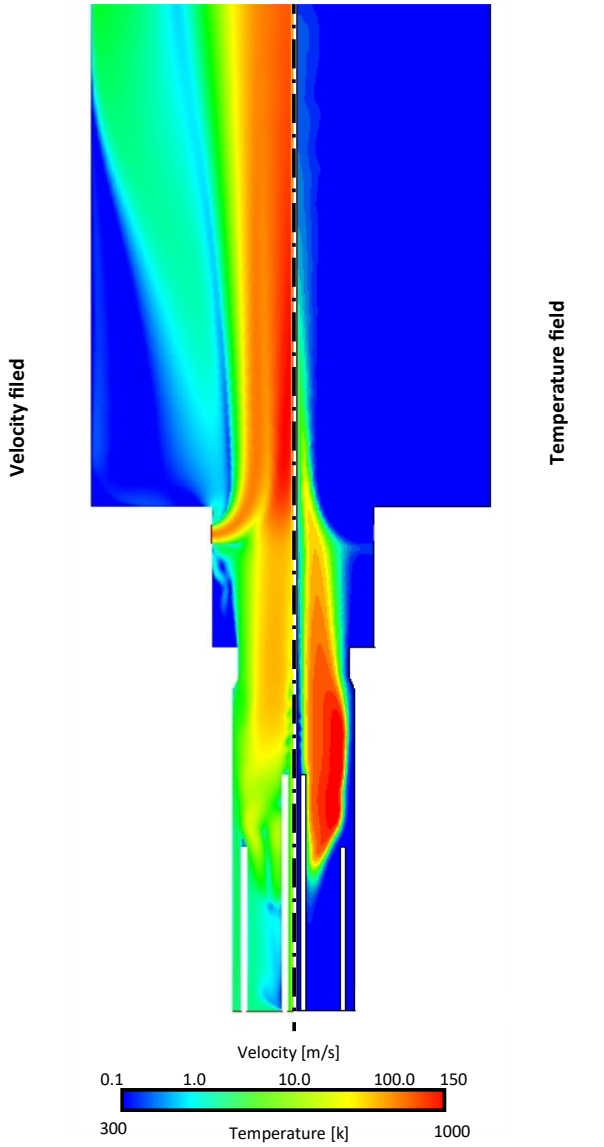

Figure 3 - Velocity (left) and temperature (right) fields.

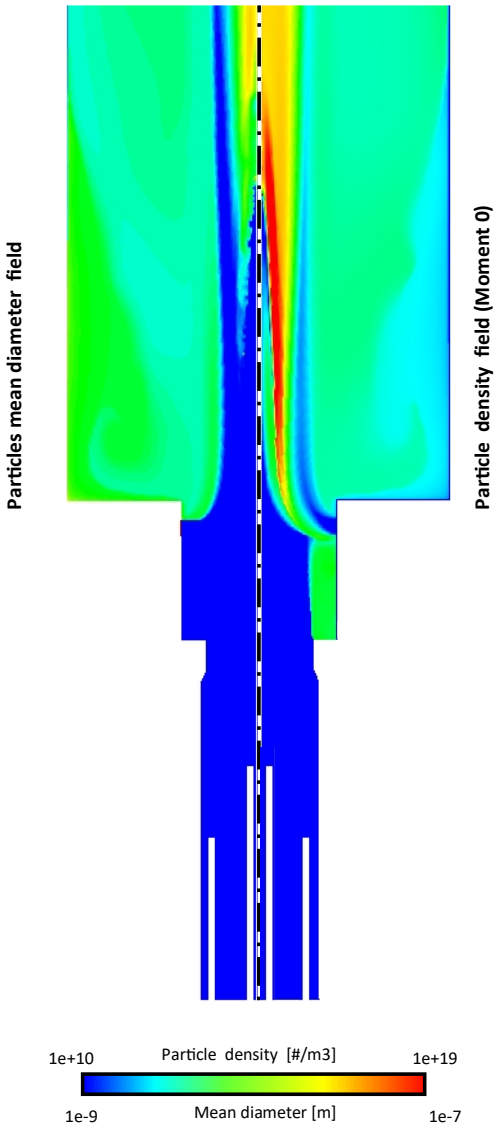

Figure 4 - Particle mean diameter (left) and density (right) fields.

is in good agreement with the results from CFD (Fig. 7). Furthermore, the trend of the evolution of the density is well captured. As for the particle size, the mean diameter predicted by CFD is one order of magnitude larger than the value obtained with NanoDome (Fig. 8). However, given the quite diverse approach used for the two calculations these can be considered acceptable discrepancies.

7. Conclusions

The results obtained with the PBM method implemented in the new NanoDome model for the prediction of nanoparticles formation and evolution were presented and compared with results obtained through CFD simulations. The density of the particles showed a good match between the two approaches and, moreover, the model could correctly capture, at least qualitatively, the evolution of the size of the nanoparticles. Further investigation and validation against experimental data is needed, but the results are promising.

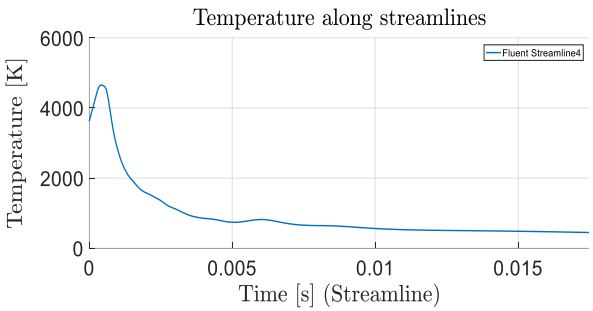

Figure 5 - Temperature evolution along the streamline as function of time.

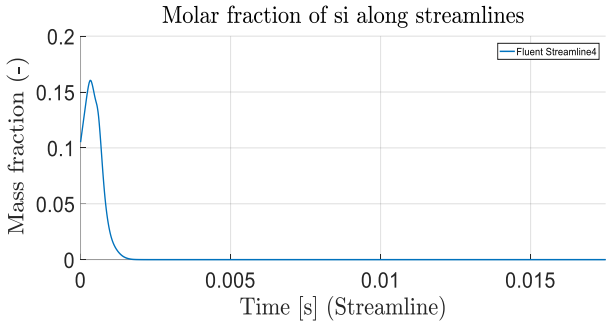

Figure 6 - Silicon molar fraction evolution along the streamline as function of time.

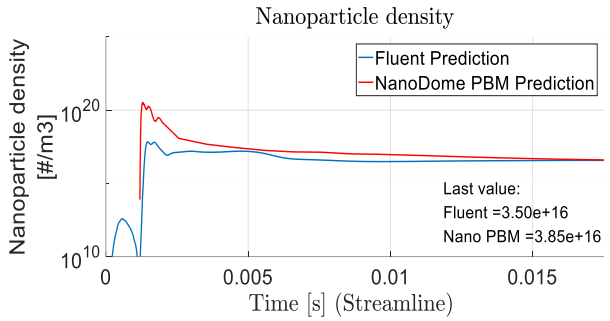

Figure 7 - Nanoparticle density computed evolution in time.

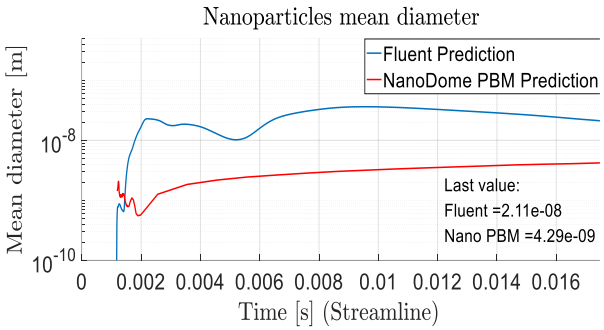

Figure 8 - Nanoparticle density computed evolution in time.

8. Acknowledgements

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9. References

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