H2020 NanoDome Project: A Unified Approach for Gas-Phase Nanoparticles Synthesis Modelling

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Abstract: This article presents a unified physical mathematical approach to the modelling nanoparticles dynamic used by the Authors as a foundation to develop a software framework for modelling entities and phenomena occurring at mesoscopic length scale in a generic Gas-Phase (GP) nanoparticle synthesis processes (e.g., plasma, hot-wall and flame reactors) and using Gas-Phase parameters extracted from CFD simulation (linking process). The model considers nanoparticles motion, agglomeration and sintering phenomena and is aimed to provide detailed information about nanoparticles fractal dimension and composition, together with species concentration, consumption rates and particles size distribution. We provide a detailed description of the data structures, the numerical methods and the algorithms adopted to implement the simulation software based on this model.

Keywords: Modelling, Nanoparticles, Synthesis, Multiscale, Thermal Plasma.

1. Introduction

Gas Phase Condensation (GPC) synthesis of nanoparticles is an important link in the manufacturing chain of nanomaterials-based products. This kind of processes enable the production of conspicuous quantities of nanoparticles at several kg/h rates in modern days, leading to an attractive cost/benefit ratio. However, the main issue affecting GPC processes is the difficulty of controlling the precision of the nanoparticles synthesis and to predict which process conditions can lead to products with specific features. Moreover, a better understanding of the link between process conditions and nanoparticle characteristics is also relevant for estimating and control the environmental impact of processes where nanoparticles are an undesired side effect and not the main product. These considerations strongly motivate an increase in theoretical and applied research to understand and predict the mechanisms of nanoparticles and nanostructures formation.

Since sixties, several models have been proposed for describing coarse-grained structures formation and from the beginning of the eighties, exploiting the constant improvement of computational units, more precise models, based on different concepts, arose. The difficulties in providing solid theoretical foundation also for the simplest aggregation processes, pushed the development of different numerical and hierarchical approaches. Diffusion Limited Agglomeration models (DLA) [1], propose the addition of simple primary particles, in the case of particle-cluster interactions, to a growing cluster via random walk paths. The evolution of this approach, the Diffusion Limited Cluster-Cluster Aggregation models (DLCCA), whose intent is to move two cluster via random walk, representing the Brownian motion in a fluid, and make them collide. Another approach, less computational expensive, is the Ballistic Limited Agglomeration Model (BLA) in which two clusters are made collide by linear paths, randomly chosen, like in [2]. Pratsinis et. al, Frencklach and Harris and Gelbard and Seinfeld [3]–[5] proposed models based on the method of moments for describing the evolution in function of time of monodisperse or polydisperse populations in terms of particles size distribution and chemical composition distribution. Other approaches for simulating nanoparticles dynamics are based on coordinated Montecarlo and Molecular Dynamics simulations like in [6]. A valid alternative to Monte Carlo simulations is the Langevin dynamics approach, introduced in [7]. The simulations based on this model are characterized by the solution of the equation of motion for each single particle, adding two forces: a friction force proportional the velocity with a friction coefficient related to the background gas and a Gaussian stochastic term related to the thermal white noise.

Each model presented has its own definitions for the entities taken into consideration and in literature is not present a univocal mathematical physical description of the objects involved in such processes. The aim of our work, indeed, is to provide a common software platform for describing mesoscale systems and entities with a clear and precise mathematical notation, classifying the different structures that can occur during a coarse-grained simulation and, finally, propose a framework based on these definitions.

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.
Figure 1- NanoDome Multiscale Architecture

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).

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. Model
In this section the entities and the connections among them, together with the definitions of the different phenomena (motion, agglomeration, sintering) described within the model, are introduced.

3.1 Terminology
The basic entities that are taken into consideration in this approach are (see Fig. 2):
- Primary particle: the smallest identifiable individual particles, usually in the size range between 5 and 50 nm.
- Agglomerates: assemblies of primary particles and/or aggregates loosely held together by weak bonds.
- Aggregates: assemblies of partially sintered primary particles held together by strong bonds. The surface area of an aggregate is smaller than the sum of all primary particle surface areas.
3.2 Mesoscopic Model

The mesoscopic model is a coarse-grained molecular dynamics model focused on nanoparticles. In this paper, we neglect the atomistic regime underlying the mesoscopic one.

The model characteristics are:
- Nanoparticles size from 10 to 200 nm,
- A volume with characteristic side length from 1 to 10 μm,
- An estimated number of nanoparticles from 100 to 100,000,
- A simulation time scale from 1 to 100 ms.

The basic discrete physical object of the mesoscopic model (a.k.a. grain, pseudo-atom) is the minimum thermodynamically stable cluster of molecules that is called primary particle. Since free molecules are smaller than a primary particle, they are not included the model as distinct discrete objects; instead they are described using integral thermodynamic quantities (i.e. temperature, species density) and called gas phase (GP).

3.3 Mesoscopic System

The mesoscopic system MS can be defined as a particle phase $P$ composed by a set of particles $p_i$ with $i \in \{1, 2, ..., N(P)\}$ where $N(P)$ is the number of particles in the system, and a free molecules gas phase $GP$ characterized by its thermodynamic properties. Each particle $p_i \in P$ constitutes the basic discrete objects of the mesoscopic model. A nanoparticle $NP$ is a collection of $N(NP)$ particles $p_i \in P$ connected by weak bonds due to interparticle potential (agglomerate), or hard sintering-based bonds (aggregate), and a list of connections $C_{ij}$ between particles storing the information about connection type and sintering evolution. The simplest nanoparticle is composed by a single particle so that a new nanoparticle is created when a particle is formed by nucleation. For two different nanoparticles, the relation $NP_i \cap NP_j = 0$ holds. An aggregate $AG$ is the subset of $N(AG)$ particles inside a nanoparticle $NP$ that are connected by sintering. While agglomeration is a reversible process, sintering is not reversible. The relations $AG_i \subset NP$ and $AG_j \cap AG_j = 0$ always holds.

3.4 Particles Definition

A particle $p_i(x_i,v_i, \eta_i)$ is a collection of $N(p_i)$ molecules and is characterized by its position $x_i$, velocity $v_i$ and the composition in terms of number of each contained species $\eta_i = \{\eta_1, \eta_2, ..., \eta_S\}$ with $S$ the number of molecular species in the system. Particles are assumed to be of spherical shape. Follows that $N(p_i) = \sum_{\eta_i} \eta_i$ and the particle mass $m(p_i)$ is defined as $m(p_i) = \sum_{\eta_i} m(\eta_i)$ while the volume $v(p_i)$ is $v(p_i) = m(p_i)/\rho(p_i)$ with $\rho(p_i)$ that is the bulk density of the material. The reduction of a particle from a cluster of atoms to a simple 0D geometric point leads to loss of information about its internal degrees of freedom, regarding:

- the dissipation phenomena occurring inside the real particle,
- the possibility for a particle to rotate around an arbitrary axis,
- the possibility to oscillate around the shape of minimum surface tension energy (spherical shape).

While these phenomena can affect e.g. the way particles coagulate or the mechanisms of energy transfer, their influence on the model prediction is assumed to be negligible. Liquid/solid phase change and its effect on particle temperature and heat exchange with gas is also neglected, assuming a small concentration of nanoparticles in the gas phase so that nanoparticles follow the local gas temperature (negligible nanoparticle heating inertia). Moreover, the categorization of liquid and solid for particles less than 10 nm is not clearly definable.

3.5 Particles Dynamics and Agglomeration

Interactions among particles occur in the mesoscopic model by means of the interparticle potential and their Brownian driven motion. When particles collide, they connect to form agglomerates of finite size that can contain from 1 to 10,000 particles. The connection of two particles by means of weak forces (e.g. van der Waals) is called coagulation and can be broken if another sufficiently energetic collision occurs. As soon as two particles are connected by coagulation they can irreversibly stick together by sintering, which is a temperature driven irreversible process, and may lead in time to complete sintering. Instantaneous sintering between two particles is called coalescence.

3.6 Coagulation

Coagulation occurs when two particles comes in contact as result of their relative motion (by solving the Langevin equation of motion) or due to collision algorithm (by using a stochastic approach). In our model we assume that sticking of two particles always happen when they collide. When two single particles $p_i$ and $p_j$ coagulate, each one representing a single nanoparticle $NP_k$ and $NP_l$, respectively, a new nanoparticle $NP_m = NP_k \cup NP_l$.

3.7 Sintering

Sintering may occur between two connected (coagulated) particles $p_i$ and $p_j$. According to [8] the driving force for sintering is a minimization of the free energy resulting in a reduction of surface area. The energy gained by surface reduction is dissipated by viscous flow, which sets the time scale for sintering. The dissipated energy would increase the particle temperature, which in practical processes is effectively thermostated or dissipated by the surrounding gas.
According to [9] the evolution of the sintering process can be described by:
\[ \frac{dA}{dt} = -\frac{1}{\tau(A - A_f)} \]

where \( \tau \) is the characteristic fusion time, \( A \) the aggregate surface area and \( A_f \) the final value upon complete coalescence. The characteristic fusion time \( \tau \) is dependent on the particles' diameters and temperature. Details on the law and parameters used in this work can be found in [15]. When the sintering process between two particles is over the 95% we can call it coalescence.

3.8 Aggregates
When two particles stick together by sintering then an aggregate (hard agglomerate) \( AG \) is formed. More particles can then become part of the aggregate by sintering with particles already part of it. An aggregate is defined as a structure of sintered particles, evolving in time and whose particles are subject to sintering progress, surface reactions and growth by heterogeneous nucleation. The main quantity that characterize the aggregate is the fractal dimension defined as:
\[ D(AG) = \frac{\ln N_p(AG)}{\ln (d_c(AG) / d_{p,av}(AG))} \]

where \( N_p \) is the reduced number of particles as defined in [9], \( d_c \) the collision diameter and \( d_{p,av} \) is the average particles diameter. The motion of an aggregate is managed by rigid body motion equation or by means of constrained Verlet-type algorithms [10].

4. Gas-Phase
In this section, the approach adopted for modelling the Gas Phase is described by defining the entities composing the gas phase and the linking process between the mesoscopic models and CFD simulation.

4.1 Gas Phase
The gas phase \( GP \) is constituted by free molecules and atoms which are below the mesoscopic model length scale (minimum stable cluster diameter) and it is characterized by time dependent thermodynamic scalar quantities such as: temperature \( T \), pressure \( p(t) \), the total number of molecules \( N_{gas} \) and species molar concentration \( C_s(t) \), with \( s \in [1, ..., S] \), being \( S \) the total number of species in the system. A species can be an atomic species (e.g. Ar, Si) or a molecular species (e.g. SiH, SiO, ZnO). If the mesoscopic domain is considered as an isolated system (0D reactor), the chemical species concentration is calculated according to the possible reactions between species and their interactions with particles using non-equilibrium or equilibrium chemistry (Fig. 3).

4.2 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.

5. Software Implementation

Our aim is to provide general data structures and classes that can be specialized for implementing different models of motion, aggregation and sintering (e.g. Langevin, DLA, BLA). We start from the definition of a hierarchy of classes for the mesoscopic objects and their basic connectivity structures, then we will describe the algorithms and methods adopted for simulating the system's dynamics. The idea behind classes specialization is to progressively add features needed by different models. The first step is to represent the duality of nanoparticles that are at the same time aggregates of primary particles and particles themselves, described by the same basic information as mass, volume, surface area. We decided to split the physical quantities like mass, volume from the motion information like position and velocity, to provide a flexible framework of data types implementing only necessary data for different approaches. An aggregate, semantically, shares quantities that describes also primary particles and, conceptually, using an Object-Oriented design, particles and aggregates can derive from the same base class. For example: a particle for implementing a population-based simulation does not need to keep track of the positions, on the other hand, in a Langevin based simulation particles positions are necessary but they share the mass or the surface area quantities.

5.1 Collision Detection

Collision detection is a mandatory step to perform for simulating the aggregates formation. We must check if two particles, in an aggregate or not, reach the distance necessary to suppose a coagulation event. In our model we suppose that two particles stick at approximately 0.1 nm. Exploiting the concept expressed before, we create a sphere enclosing the aggregate, we check the distance between the centres of mass, if this distance is equal or inferior the threshold, we can suppose that the two aggregates are colliding. For making the computational cost of the collision detection algorithm affordable, we adopted the Linked-Cell algorithm, shifting the complexity from quadratic to pseudo linear.

6. Computational Results

In this section preliminary results obtained testing the NanoDome tool with different conditions are shown. First, a comparison of the results of the different methods implemented in the framework is presented. Then, the results obtained by linking NanoDome with a CFD simulation are shown and commented.

6.1 Methods Comparison

In this section, we report the computational results of the three methods implemented in the framework, based on the proposed model: Langevin Dynamics [7], Population Based Method [15] and Moments Method [3]. NanoDome has been used as a standalone tool for the simulation of the evolution in time of a control volume with initial predefined species concentrations. Operating conditions and code performances are summarized in Table 1 and are aimed to replicate a steep cooling gradient typical of plasma conditions.

As we can see, the three methods are in good agreement predicting quantities like aggregates average diameter (Fig. 4). Aggregates density (Fig. 5) shows an agreement in the cooling region, up to \( t = 3 \) ms, where results differ of a factor of 2, and can be considered in good agreement. However, in the pure collisional region at \( T = 300 \)K and \( t > 3 \) ms, results differ with a factor of 10, mainly due to the small number of particles used in the Langevin (to limit the computational effort) and the intrinsic differences of the Method of Moments and the PBM. Still, PBM and Langevin methods are in good agreement for predicting the average number of primary particles for each aggregate (Fig. 6). Moreover, the Langevin method is aligned with the literature results, predicting an average fractal dimension of 1.6 for each aggregate [9].

6.2 Linking Results

Plasma torch and reactor have been simulated using a FLUENT based CFD model described in [11]. To simulate the nanoparticles growth and transport an improved version of the method of moments approach as described in [12], with new terms for the prediction of dissolution and evaporation, has been used. Vapours production from solid micrometric precursors has been modelled using a Lagrangian discrete particle models as done in [13]. The CFD model has been validated against experimental results in [11] and can be used as reference to check the NanoDome results.

| Model     | Species (equimolar fraction) | Central Volume [m³] | Aggregates [Å] | Pressure [Pa] | Start – end Temperature [K] | Temperature gradient [K/sec] | Simulation time [sec.] | Execution time [sec.] | Fractal dimension |
|-----------|------------------------------|---------------------|----------------|--------------|-----------------------------|-----------------------------|------------------------|----------------------|------------------|
| Moments   | Si/Ar (25%-75%)              |                     |                |              |                |                            |                         |                      |                   |
| PBM       | Si/Ar (25%-75%)              | 2.0 × 10⁻⁷⁰       | 2000           | 1.0          | 3000-500       | -1.0 × 10⁵               | 0.0006                 | ≈ 5.0                | ≈ 1.6 (input)     |
| Langevin  | Si/Ar (25%-75%)              | 2.0 × 10⁻⁷⁰       | 100            | 1.0          | 3000-500       | -1.0 × 10⁵               | 0.0006                 | ≈ 3500               | ≈ 1.6 (computed) |

Table 1 – Operating conditions for the standalone NanoDome simulation.
The 2D computational domain is presented in Fig. 7 and comprises a PL-50 inductively coupled RF plasma torch and a generic axisymmetric reaction chamber with a radial quench injection. Two axial inlets for the working gas and one inlet for the injection of the precursor 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 [14]. Operating gas is pure Ar and Si powders with 10 µm diameter have been used as precursors.

Fig. 8 shows details of the thermo-fluid dynamic field inside the torch and the chamber obtained with the CFD simulation whilst Fig. 9 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. 9 and 11. While the central axis streamline may be considered as representative of the general conditions at which the nanoparticle synthesis occurs, a more comprehensive set of streamline should be used for reactor with complex flow patterns, and their results combined to obtain a better characterization of the final product. However, this type of reactor is known to present flow recirculation that may lead to streamlines of infinite length. This is a limitation of the linking approach that can be solved only by an eulerian based coupling (e.g. reactor network) between CFD and NanoDome.

In Fig. 12 and 13 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 is in good agreement with the results from CFD (Fig. 12). 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. 13). However, given the quite diverse approach used for the two calculations these can be considered acceptable discrepancies.
Conclusions

The multi-method framework based on the multi-scale mathematical physical model proposed for describing the nanoparticles dynamics provides a functional engineering tool for predicting the formation of nanoparticles in a gas-phase synthesis process at different levels of details. Our aim is to exploit the current framework to extend the spectrum of available methods to Diffusion Limited and Ballistic methods and to a simplified rigid body motion method, for tackling the significant computational effort required by the Langevin method. The results obtained with the PBM method implemented in the new NanoDome model for the prediction of nanoparticles formation and evolution in a linked simulation 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,
Further investigation and validation against experimental data is needed, but the results are promising.

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9. References

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