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 model nanoparticles dynamics. This approach has been used as a foundation by the Authors to developed 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). 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. all, 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 Montecarlo 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 bath 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 model 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. Model

In this section, we first define the entities and the connections among them, then we present the definitions of the different phenomena (motion, agglomeration, sintering) exploiting the new framework proposed.

2.1 Terminology

The basic entities that are taken into consideration in this approach are:

- 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.

In Figure 1 we depict the entities that the model can describe.

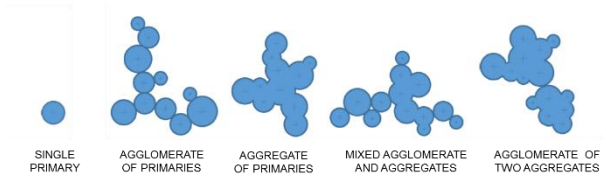

Figure 1: Nanoparticles structures.

2.2 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 micrometers.
- 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).

2.3 Mesoscopic System

The mesoscopic system MS can be defined as a particle phase P composed by a set of particles $p_i$with $\mathrm{i} \in \{1,2,\dots,\mathrm{N(P)}\}$ 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 $\mathrm{p_j} \in \mathrm{P}$ constitute the basic discrete objects of the mesoscopic model. A nanoparticle NP is a collection of $N(NP)$particles $p_i \subset P$ connected together by weak bonds due to interparticle potential (agglomerate) or hard bonds by sintering 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 $\{p_j\} \subset NP$ 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.

2.4 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 $s \in [1,\dots,S]$, 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. Si-H, Si-O, 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. 2).

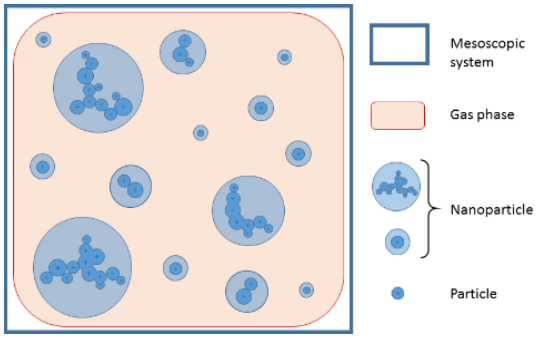

Figure 2: Mesoscopic System.

2.5 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 $\{\eta_s\} = \{\eta_1, \eta_2, \dots, \eta_S\}$ with $S$the number of molecular species in the system. Particles are assumed to be of spherical shape. Follows that $N(p_i) = \sum_{s=1}^{S} \eta_s$ and the particle mass $m(p_i)$ is defined as $m(p_i) = \sum_{s=1}^{S} m_s \eta_s$ 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, in particular 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.

2.6 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 together 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 Walls) 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 not reversible process, and may lead in time to complete sintering. Instantaneous sintering between two particles is called coalescence.

2.7 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 $NP_m = NP_k \cup NP_j$.

2.8 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 τ is the characteristic fusion time, A the aggregate surface area and A_f the final value upon complete coalescence. When the sintering process between two particles is over the 95% we can call it coalescence.

2.9 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 quantity that characterize mainly the aggregate is the fractal dimension defined as:

$$D(AG) = \frac{\ln N_r(AG)}{\ln\left(\frac{d_c(AG)}{d_{p,av}(AG)}\right)}$$

where N_r is the reduced number of particles, 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].

3. 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 (Langevin, DLA, BLA, etc…). 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 like mass, volume, surface area, etc… . 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 in a 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.

3.1 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 a distance of approximately 1.0 Angstrom. 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.

4. Computational Results

In this section, we report the computational results of the three methods implemented in the framework based on the proposed model: Langevin Dynamics, Population Based Method and Moments Method, simulating a plasma gradient.

As we can see, the three methods are in good agreement predicting quantities like aggregates average diameter (Fig. 3) and aggregates density (Fig. 4). Moreover, PBM and Langevin methods are in good agreement for predicting the average number of primary particles for each aggregate (Fig. 5). The Langevin method is aligned with the literature results, predicting an average fractal dimension of 1.5 for each aggregate.

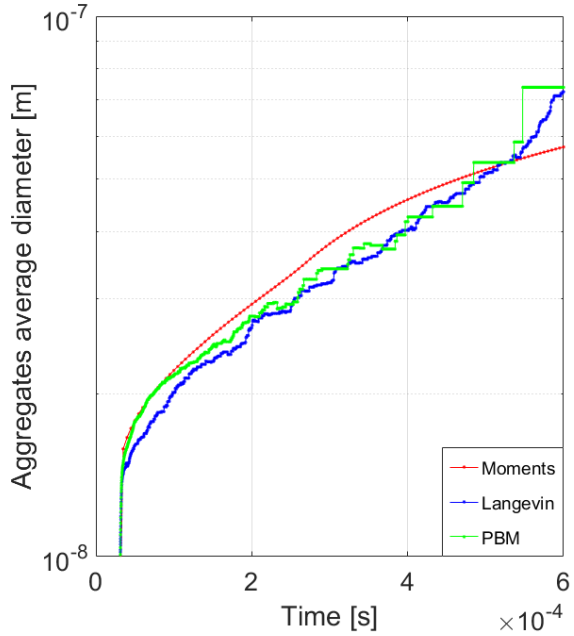

Figure 3: Aggregates mean diameter [m] evolution in time.

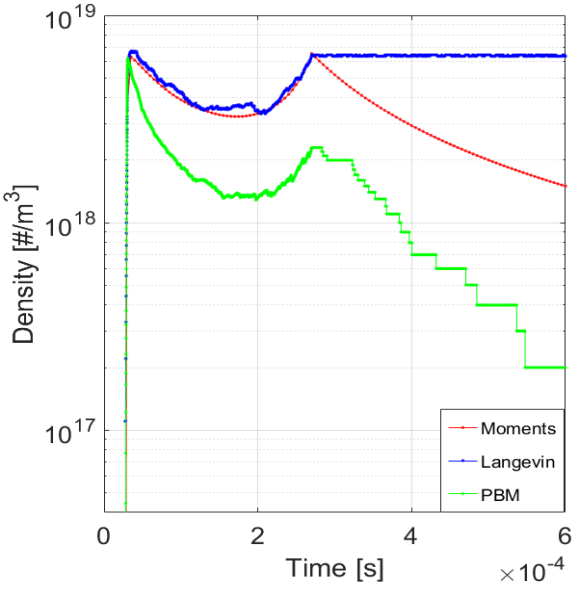

Figure 4: Aggregates density [#/m^3] evolution in time.

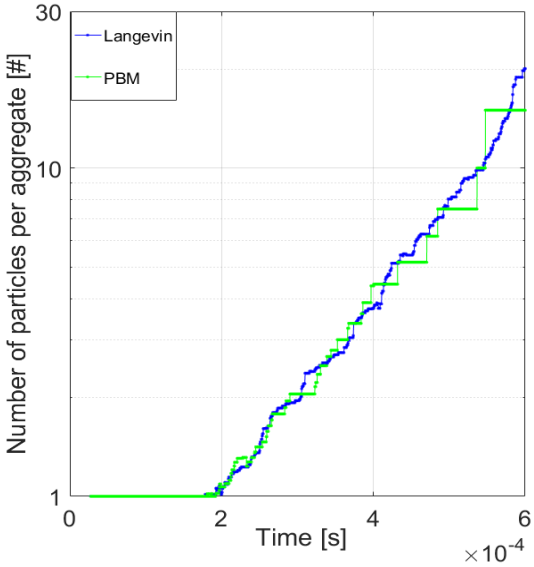

Figure 5: Average particles cardinality per aggregate in time.

5. 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 actual 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.

6. Acknowledgements

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7. References

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