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Modelling of strongly coupled particle growth and aggregation

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Abstract. The mathematical modelling of the dynamics of particle suspension is based on the population balance equation (PBE). PBE is an integro-differential equation for the population density that is a function of time *t*, space coordinates and internal parameters. Usually, the particle is characterized by a unique parameter, e.g. the matter volume *v*. PBE consists of several terms: for instance, the growth rate and the aggregation rate. So, the growth rate is a function of *v* and *t*. In classical modelling, the growth and the aggregation are independently considered, i.e. they are not coupled. However, current applications occur where the growth and the aggregation are coupled, i.e. the change of the particle volume with time is depending on its initial value v_0, that in turn is related to an aggregation event. As a consequence, the dynamics of the suspension does not obey the classical Von Smoluchowski equation. This paper revisits this problem by proposing a new modelling by using a bivariate PBE (with two internal variables: *v* and v_0) and by solving the PBE by means of a numerical method and Monte Carlo simulations. This is applied to a physicochemical system with a simple growth law and a constant aggregation kernel.

1. Introduction

Particle or crystal synthesis involves several stages: nucleation, growth and aggregation. It is of great importance to model these phenomena in order to manage the dynamics of the particle formation.

At a given time one considers a population of particle. Each particle is characterized by its radius or its matter volume. The population can evolve by growth of particle, i.e. by mass transfer from the surrounding medium to the particle and by aggregation or coalescence, i.e collision of particles possibly followed by merging. Generally it is assumed that the growth law of the particle is a function of the radius or the matter volume:

$$\frac{dv}{dt} = G(v) \tag{1}$$

The coalescence is a particular case of aggregation phenomena. So, a particle with a volume *v* is coming from the collision between a particle with a volume $\bar{v}$ and another one with a volume $v-\bar{v}$. Let us introduce the population density $n(t,v)$. Its change with time obeys the Von Smoluchowski equation [1]:

$$\frac{\partial n}{\partial t} = \frac{1}{2}\int_0^v K\left(\bar{v}, v-\bar{v}\right) n\left(\bar{v}\right) n\left(v-\bar{v}\right) d\bar{v} - n(v)\int_0^\infty K\left(v,\bar{v}\right) n\left(\bar{v}\right) d\bar{v} \tag{2}$$

$K\left(\bar{v}, v-\bar{v}\right)$ is a kinetic constant or kernel that is a function of the volume of the colliding particles. If one takes into account at once the growth and the coalescence, the equation (2) becomes:

$$\frac{\partial n}{\partial t}+\frac{\partial\left(G(v)n\right)}{\partial v}=\frac{1}{2}\int_0^v K\left(\bar{v}, v-\bar{v}\right)n\left(\bar{v}\right)n\left(v-\bar{v}\right)d\bar{v}-n(v)\int_0^\infty K\left(v,\bar{v}\right)n\left(\bar{v}\right)d\bar{v} \qquad (3)$$

It has to be underlined that the growth rate only depends on the particle volume at the given time. There is no memory effect. Equation (3) assumes that the growth and aggregation are independent phenomena. However there are several cases where the growth rate at a given time explicitly depends on events that have previously took place. So, the growth law is allowed to depend on the actual volume v and the initial volume v_0 of the particle.

$$\frac{dv}{dt}=G\left(v, v_0\right) \qquad (4a)$$

If the growth is linked to the coalescence, then the growth rate will change at each coalescence event, i.e. at the birth of a new particle. As a consequence, the dynamics of the particle population does not obey the equation (3). For instance, if the colliding particles are facetted crystals, the resulting crystal has a surface area smaller than the sum of the initial crystals surface areas because some crystalline face is shared as a contact area. In this case, the growth law obeys the expression:

$$\frac{dv}{dt}=B\left(A-\alpha A_0\right)=C\left(v^{2/3}-\alpha v_0^{2/3}\right) \qquad (4b)$$

B and C are functions of the physicochemical parameters (solute concentrations, temperature …) depending on the intrinsic growth mechanism. α is a dimensionless constant within the [0; 1] range. Higher the α-value stronger is the effect of the face joint.

The second section of the paper is dedicated to the modelling of such coupled growth and aggregation. The third section describes a numerical method to solve the corresponding population balance equation. The fourth one presents a comparison of the results coming from this numerical method and Monte Carlo simulations.

2. Modelling

In order to take into account the new form of the equation (4a) one considers two internal variables v and v_0 instead of the unique v. Then one defines the two population densities: $N\left(t, v, v_0\right)$ and $n\left(t, v\right)$ with:

$$n\left(t, v\right)=\int_0^v N\left(t, v, v_0\right)dv_0 \qquad (5)$$

and

$$N\left(t, v<v_0, v_0\right)=0 \qquad (6)$$

One introduces:

$$J_{v0}=\frac{1}{2}\int_0^{v0} K\left(\bar{v}, v_0-\bar{v}\right)n\left(t,\bar{v}\right)n\left(t, v_0-\bar{v}\right)d\bar{v} \qquad (7)$$

The population balance equation is written as:

$$\frac{\partial N\left(t, v, v_0\right)}{\partial t}+\frac{\partial G\left(v, v_0\right)N}{\partial v}=\delta\left(v-v_0\right)J_{v0}-N\left(t, v, v_0\right)\int_0^\infty K\left(v,\bar{v}\right)n\left(t,\bar{v}\right)d\bar{v} \qquad v\geq v_0 \qquad (8)$$

In order to avoid the use of the Dirac function in the equation (8), this one is transformed into [2]:

$$\frac{\partial N\left(t, v, v_0\right)}{\partial t}+\frac{\partial G\left(v, v_0\right)N}{\partial v}=-N\left(t, v, v_0\right)\int_0^\infty K\left(v,\bar{v}\right)n\left(t,\bar{v}\right)d\bar{v} \qquad v>v_0 \qquad (9)$$

With the boundary condition:

$$G\left(v_0,v_0\right)N\left(t,v_0,v_0\right)=J_{v0} \tag{10}$$

If the growth law G does not depend on v_0, one can check that the integration of equation (8) between v_0 =0 and $v(-)$ leads to the equation (3).

3. Numerical method

Among several numerical methods [3] a finite difference method has been selected and fitted. The finite difference scheme is based on upwind derivative for the convection term, and simple rectangle method for the evaluation of the integrals. The hyperbolic integro-differential equation holds on a triangular two dimensional space ($v \geq v_0$). The flux $G\left(v,v_0\right)N(v,v_0)$ is directed in the v direction. The coupling in the v_0 direction occurs through the source term, and the boundary conditions on the line $v=v_0$. The numerical mesh (figure 1) covers a triangular domain, half of a square: $(v,v_0)\in\left[0,v_{\max}\right]\times\left[v_0,v_{\max}\right]$ divided into squares of side length δv, indexed by $(i,j)\in(1...p)\times(1...p)$. $N_{i,j}^k \approx N(t_k,v_i,v_{0j})$ is the discrete population density, and thus $n_i^k=\sum_{j=1}^{p}N_{ij}^k$. $G_{i,j}\approx G(v_i,v_{0j})$ is the discrete growth function, $K_{i,l}\approx K(v_i,v_l)$ is the discrete kinetic constant. The time step and volume step are noted δt and $\delta v(=\delta v_0)$.

The numerical scheme based on equation (8) can be written as:

$$N_{i,j}^{k+1}=N_{ij}^k+\frac{\delta t}{\delta v}\left(N_{i-1,j}^k G_{i-1,j}^k-N_{i,j}^k G_{i,j}^k\right)+\delta t\left(\delta v\right)^2\left(-N_{ij}^k\sum_{l=1}^{p}K_{i,l}n_l^k+\frac{1}{2}\delta_{ij}\sum_{l=1}^{i-1}K_{l,i-l}n_l^k n_{i-l}^k\right) \tag{11}$$

where δ_{ij} is the Kronecker symbol. The initial condition is set to : $N_{ij}^1=0$ except for i=j=1: $N_{11}^1=N_0^1$. The algorithm is of p^2 complexity since it goes trough the couples of cells for the coalescence process.

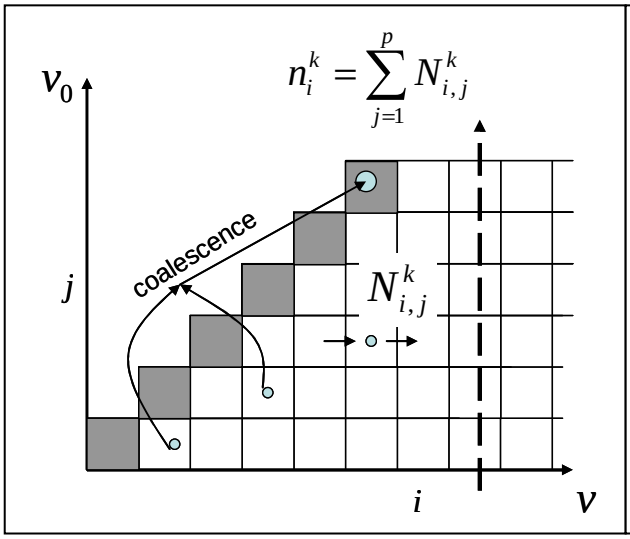

Figure 1: Numerical mesh

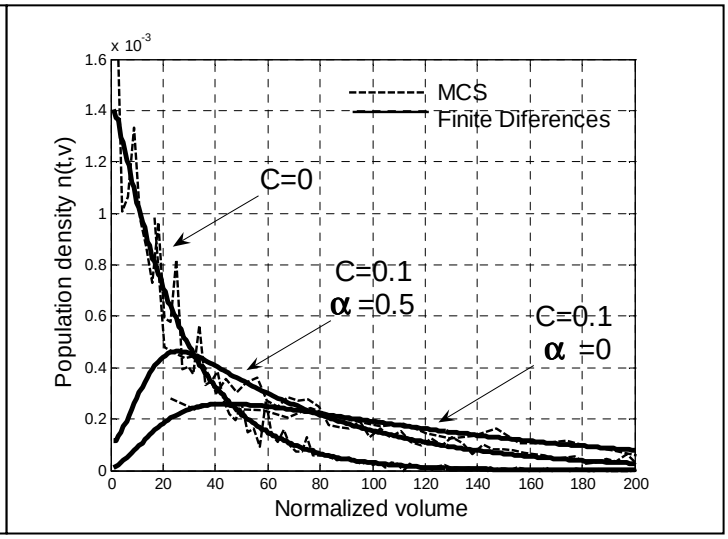

Figure 2: Population density versus volume, Time = 0.1

4. Results

In order to study the consistency of the modelling (equations (8), (9) and (10)) we have compared its numerical solution with Monte Carlo Simulations (MCS). The latter are based on the direct application of the involved elementary processes, i.e. growth and aggregation. Here we use the algorithm suggested by Tandon and Rosner [4] when they studied aggregation coupled with surface area reduction. In our case, the sintering kinetic law was replaced by the matter volume expansion law. The aggregation kernel has been taken as a constant. The choice of the time step in the MCS needs a particular consideration. As a consequence we used a refined method proposed by Smith and Matsoukas [5] in which the number of particles is kept constant. To start the simulations we consider a set of N (N=5000) particles, each of unit volume. During aggregation each aggregate is characterized by v and v_0.

Figure 2 shows the comparison between MCS and finite difference method. The kinetic parameter was constant: K=0.5. The growth law (4b) was applied, with different values for parameters C and α. MCS and finite difference method are in agreement. This shows the consistency of the equations (8), (9) and (10) to represent these strongly coupled growth-aggregation processes. As expected the growth of particles shifts the population density to the large volume values whereas the coupling, as in equation (4b), delays the shift.

5. Conclusion

Strongly coupled growth and aggregation processes have been studied by MCS and by a finite difference method applied to the equations of a dedicated model. Results show the validity of the modelling. Nowadays the authors are investigating various coupled growth-aggregation processes for which the kinetics are available: perikinetic and orthokinetic aggregation, growth in presence of impurity or adsorbed polymer. The next step of this work will be to apply this methodology to other phenomena that strongly depend on the collisions, e.g. restructuring or morphological dynamics of aggregating particles [6].

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