AGGLOMERATION IN PRATSOLIS PROJECT


PRATSOLIS Project:

Ecole des mines Saint Etiene (France)
Technische Universität Berlin (Germany)
Technische Universiteit Delft (The Netherlands)
Politecnico di Torino (Italy)

Abstract

The aim of this paper is to give an overview of the state of art in the agglomeration studies, and an introduction to the work carried out in this field, both from the numerical and the experimental point of view, by the European Network PRATSOLIS (PREcipitation and Agglomeration in Turbulent SOLid/LIquid Systems).

1. Introduction

In powder technology and industrial crystallization, agglomeration is known as an essential step because of its influence on the particle size and morphology. According to the desired quality of products or to possible process requirements, agglomeration should be prevented or promoted. For instance, agglomeration can be used to concentrate solid particles initially dispersed in a liquid medium, in order to make their withdrawal easier. Agglomeration, however, often appears as a step which should be avoided, especially when a suspension of a large population of very fine particles is to be produced. Meanwhile the understanding and mastering of agglomeration is an important challenge for technology and engineering. In this respect, several points deserve to be emphasized:

- Particle structure which induces particular geometrical, fluidodynamic, mechanical and optical properties.
- At all scales agglomeration involves a big variety of phenomena like solid particles interactions, morphology and mechanics of the agglomerates, fluidodynamic and chemical interactions between the flow and the agglomerates.
- The whole process of agglomeration is characterized by aggregation where the particles form cluster with a relatively loose structure, followed, in a supersaturated system, by crystal
growth in the contact points that gives solidity to the aggregates structures.

- The morphological aspects are particularly important in agglomeration. First models of agglomeration assimilated the clusters to compact spheres, whereas in most cases, they have a porous or ramified structures. Agglomeration models that consider this complex structures should be validated and integrated into existing or to-come computational fluid dynamics (CFD) codes.

In spite of the existence of several valuable experiments, models and simulations applicable to the separate aspects of the phenomenon, so far, relatively few comprehensive approaches have been able to describe the turbulent agglomeration of polydisperse particles in physico-chemical and fluiddynamic interaction in a real industrial reactor. Such an enterprise can probably be only undertaken in a multidisciplinary framework because of the variety of competences involved.

Taking advantage of the research training network PRATSOLIS (Precipitation and agglomeration in turbulent solid liquid systems, financed RTN of the fifth European framework programme of research and development), four academic and two industrial research groups have joined their competencies and human and technological potential to re-visit the agglomeration topic.

The aim of this paper is to describe the state-of-art of the agglomeration problem, while insisting particularly on the main difficulties and presenting the first results or investigation tracks of the network partners.

2. Basic Mechanism

From a general point of view, agglomeration includes several aspects [49] which should be properly taken into account in models at the local (i.e. at the crystal or agglomerate) scale:

- collisions between solid particles;
- physicochemical interactions between particles;
- agglomerate morphology;
- agglomerate fragmentation.

In what follows, we give a brief presentation of each item.

2.1 Collision between solid particles

Agglomeration is the consequence of collision between solid particles or collision between particles and already formed agglomerates. The mechanism which brings particles into close proximity results from the fluidynamics of the suspension. The \textit{agglomeration kernel} $K_i$ gives the number of collisions per unit volume and time between particles of size $i$ and
particles of size \( j \). According to the type of flow and the particle size, *Brownian* kernels or *turbulent* kernels should be considered. To express them, the relevant parameters are \( \beta_1 \), the ratio of the particle size to the *Kolmogoroff microscale* and \( \beta_2 \), the ratio of the particle size to the *Levich critical diameter* \( d_L \) [33].

For \( \beta_1 > 1 \), models of highly turbulent suspensions should be applied [1].

For \( \beta_1 < 1 \) and \( \beta_2 > 1 \), the classical turbulent models (which in fact assume a local shear flow in the Kolmogoroff’s eddies) can be used.

For \( \beta_1 < 1 \) and \( \beta_2 < 1 \), the Brownian contribution is no more negligible. In this case, Adachi et al. [2] propose to express \( K_{ij} \) as the sum of two contributions:

\[
K_{ij} = (K_{ij})_{Br} + (K_{ij})_{turb}
\]

in which \( (K_{ij})_{Br} \) is the Brownian kernel and \( (K_{ij})_{turb} \) the turbulent kernel.

The problem is to describe the conditions of collision of two interacting particles brought into close proximity by a viscous fluid. At this scale, physicochemical interactions (van der Waals, double-layer,...) have an influence on the particle trajectories. Another, purely fluiddynamic, effect should be considered too. In fact, particles on intersecting trajectories will collide only if the liquid between them can be drained off to allow the contact. This results in a repulsive force (lubrication force) which can reduce or prevent agglomeration.

2.1.1 Brownian motion

Following the pioneering works of Smoluchowski [52], several authors [16,54] expressed the agglomeration flow \( J_{ij} (R) \) of particles of radius \( a_j \) which collide with the sphere of radius \( R \) surrounding a reference particle, of radius \( a_i \):

\[
J_{ij} = -4\pi R^2 G(R) \left[ (D_i + D_j) \frac{\partial N_j}{\partial R} + \frac{N_j}{G\pi \mu} \frac{a_i + a_j}{a_i a_j} \frac{\partial N_j}{\partial R} \right] \tag{1}
\]

\( G(R) \) (global collision efficiency) is a function of \( R, a_i \) and \( a_j \). \( D_i \) is the Brownian diffusion coefficient of a sphere of radius \( a_i \):

\[
D_i = \frac{k_B T}{6\pi \mu a_i} \tag{2}
\]
\(k_b\) is the Boltzman constant, \(T\), the temperature, \(\mu\) the dynamic viscosity; \(N_j\) is the number of particles of radius \(a_j\) per unit volume; \(V_T\) is the total interaction potential.

The effect of these interactions is characterized by the stability factor \(W_{ij}\), defined as:

\[
W_{ij} = \frac{J_{ij}^0(R)}{J_{ij}(R)}
\]

\(J_{ij}^0(R)\) denotes the \(J_{ij}(R)\) value in the absence of interactions. Spielman [54] has proposed a determination of \(W_{ij}\) which takes into account the attractive and repulsive interactions and also the effect of the viscosity via a corrected mobility coefficient. The models derived from previous equations assume that agglomeration takes place through Brownian motion. Brownian agglomeration is important for submicronic particles. However, when their size becomes larger, the particles are submitted to the action of the flow and other agglomeration mechanisms take place.

More recent studies [58;65;22] take into account the different types of interactions in a shear flow. Their authors introduce the capture efficiency coefficient \(\alpha_{ij}\) between two particles of radius \(a_i\) and \(a_j\): \(\alpha_{ij}\) is the ratio of the calculated particle collision flow to the flow value predicted by Smoluchowski \((\alpha_{ij} = W_{ij}^{-1})\). The model of Van de Ven and Mason [58] includes attractive, repulsive and fluiddynamic interactions in the case of equally sized particles, whereas the model of Higashitani et al. [22] can be applied to any pair of spherical particles, however in the case of attractive and fluiddynamic interactions only.

2.1.2 Turbulent flow

The case of agglomeration in turbulent flows has been little investigated. For particles smaller than the Kolmogoroff microscale, agglomeration is assumed to take place in the smallest eddies in local shear flow conditions. This makes possible the use of models like the one from Saffman and Turner [48] De Boer et al. [9] or Higashitani et al.[22]. In this type of models \((K_{ij})_{turb}\) is derived from one of the classical turbulent models and is commonly expressed in the form:

\[
(K_{ij})_{turb} = \frac{4}{3} \cdot \gamma \cdot \left( a_i + a_j \right) \alpha_{ij} : \quad \gamma = \frac{e_m}{\nu}
\]
in which $a_i$ and $a_j$ are the respective radii of particles $i$ and $j$ (supposed spherical) and $\alpha_{ij}$ the collision efficiency (see below). An important parameter both in the agglomeration and the breakage kernel calculations is the velocity gradient $\gamma$ which itself depends on the energy dissipation rate per unit mass $\varepsilon_m$. This is a local value but to get a rough approximations many expressions are found in the literature for the mean value of $\varepsilon_m$, for instance:

$$\varepsilon = \frac{N_p \omega^3 D_s^5}{V} \quad (5)$$

in which $N_p$ is the power number, $D_s$ the stirrer diameter, $\omega$ the rotation rate of the stirrer and $V$ the volume of the suspension. This type of expression should be used with precautions because, $\varepsilon_m$ is not uniform in a stirred vessel. This will be an essential subject of interest for the PRATSOLIS joint programme to get more realistic expressions for $\varepsilon_m$ based on CFD computations, taking into account the local variations and the presence of solid particles in the flow.

### 2.2 Physico-chemical interactions between solid particles

The trajectories of the particles just before their encounter, the collision efficiency and the agglomerate cohesion, depend on the different interactions between solid particles. Two of them shall be discussed here:

- **London-Van der Waals attractive interactions**
  These forces have their origin in interactions between instantaneous induced dipoles. For two spheres of radii $a_i$ and $a_j$ separated by distance $h$, an attractive interaction potential $V_A$ can be calculated [21]. For instance, in the case of two identical particles of radius $R$, the interaction force $F_w$ is given by:

$$F_w = \frac{AR}{12h^2} \quad (6)$$

in which $A$ is the Hamaker constant of the particle in the medium.

- **Double layer repulsive interactions**
  A solid particle located in an electrolyte generally shows a surface charge and is surrounded by a layer of dissolved ions [59]. The zeta potential is the only characteristic parameter of this double layer which is experimentally
available; it is currently assimilated to the surface potential $\zeta_0$ in the case of dilute liquid media. When two particles get into contact, the interactions of their respective double layers result in a repulsive potential $V_R$. Van der Waals and double layer interactions are taken into account in the DLVO theory [11, 59]. However, more recently, experimental studies proved the existence of other interactions between particles, for instance short-range attractive forces and long range attractive forces (in the case of hydrophobic particles, see [47]).

### 2.3 Agglomerate morphology

The morphology of the agglomerates both depends on the physicochemical and fluiddynamic conditions of their formation as well as on their intrinsic mechanical properties. However, the agglomeration dynamics also depends on the morphology of the colliding particles. Most of the recent experiments show that agglomerates have a fractal structure [4; 32]. An agglomerate containing $i$ primary particles of radius $a_i$ is characterized by the fractal dimension $D_f$, the outer radius $a_i$, the fluiddynamic radius $a_H$. As the structure of the agglomerates is non-uniform, their volume density $\phi(r)$ depends on the distance $r$ from the centre of mass of the agglomerate; the average volume density is denoted $\bar{\phi}$. These different characteristics are linked by the following relations [18]:

$$a_i = a_i \left( \frac{i}{S} \right)^{\frac{1}{D_f}}; \quad \phi(r) = \frac{S}{3} D_f \left( \frac{r}{a_i} \right)^{D_f - 3}; \quad \bar{\phi} = S \left( \frac{a_i}{\bar{a}} \right)^{D_f - 3} \quad (7)$$

where $S$ is a structure factor.

The various authors differ in the way they express the ratio between the fluiddynamic radius and the outer radius. This ratio is either assumed to be constant [57; 4] whereas, according to Kusters et al. [32], it depends on the agglomerate volume density. However, for fractal dimensions close to 2, the two models are in agreement.

From computer simulations, Gmachowski [18] has found the following relation between $S$ and $D_f$:

$$S = 0.42 D_f - 0.22$$

Modelling of large fractal-like agglomerates can be considered as relatively satisfactory with respect of their geometry, their fluiddynamic behaviour and their optical properties. In particular, many experimental results validate the assumption of fractal-like structure. In case of weak aggregation, however, particularly in vigorously stirred or little concentrated systems, or at the
beginning of the agglomeration process, clusters are small and contain a few tenths of particles, even less; in this case, the fractal assumption is no more valid as well as the “macroscopic” models of large agglomerates.

2.4 Agglomerate fragmentation
The occurrence of break-up depends on the balance between the disagglomeration effects due to the action of the fluid and the overall cohesion of the agglomerate due to the interactions between primary particles. The fluiddynamic effects are of different nature if it is that the agglomerate is larger or smaller than the Kolmogoroff microscale. In the latter case, a shear stress originating from the local velocity gradient acts on the agglomerate. The different authors do not agree on the way to express the competition between the desagglomeration and the cohesion effects. According to the models, the relevant parameter is either the ratio $\frac{E_t}{E_c}$ or the ratio $\frac{\sigma}{\tau}$; $E_t$ and $E_c$ are respectively the agglomerate cohesion energy and the turbulent energy acting on this agglomerate; $\sigma$ is the mean mechanical strength of the agglomerate and $\tau$ is the mean shear stress. 

[53;4;32;36]. The breakage rate is proportional respectively to $\gamma e^{-\frac{E_t}{E_c}}$ and to $\gamma e^{-\frac{\sigma}{\tau}}$. Another discussion is related with size of the fragments produced by breakage. Two cases are currently envisaged:
- erosion of single or small groups of particles from the agglomerate surface;
- production of fragments with sizes of about one fourth of the agglomerate diameter.
In all cases, the breakage rate depends on the fluiddynamic conditions of the flow, via $\varepsilon_m$ and $\mu$ and on the characteristics of the agglomerates: outer radius, fractal dimension, primary particle radius and cohesion force between two primary particles. This last parameter is calculated differently according to the nature of the bond between the particle and the rest of the agglomerate:
- in the case of purely physical interaction, it is equal to the van der Waals interaction;
- in the case of supersaturated solutions, crystalline bridges grow around the contact points, reinforce the aggregate cohesion and decrease the break-up probability [42];
• in the case of hydrophobic particles, gas bridges are formed around the contact points and reduce the possibility of fragmentation, too [47].

3. New challenges for study of agglomeration dynamics
Validation of previous models or test of new theoretical approaches require experimental tools permitting study of fast agglomeration in turbulent medium. Qualitative analysis of suspension samples shows that agglomerates in a stirred tank are generally small (with \( i_{\text{mon}} = 100 \)) and not very porous [32]. There are two difficulties:
• morphological description of a population of small agglomerates which cannot be considered as fractal,
• estimation of physical properties of the agglomerate, required for analysis of agglomeration experiments

3.1 Small agglomerate morphology
Standard relations (Equation 7), which express the relationship between the size and the number of monomers they consist of, have to be carefully used. For small agglomerates, alternative approaches can be attempted. One [19] consists in building an agglomerates set type \( (i = 1, 2, 4, 8, 16, 32 \ldots) \). For instance, a set of agglomerates with small porosity may consist of doublets \((i=2)\), tetrahedrons \((i=4)\), cubes \((i=8)\), etc. These agglomerates are not fractal-like. The set of integers (defined by \( i = 2^j \)) is suitable for the chosen agglomerate classes for agglomeration modelling. Most developments in agglomeration theory and optical properties modelling (used for experiments analysis) correspond to spherical particles. In these two fields, the relevant parameter is the projected area \( Sp \) of the sphere on a plane. Thus, we define radius \( a_{\text{e}} \) of the equivalent sphere for an agglomerate as:

\[
\pi a_{\text{e}}^2 = < Sp >_O
\]

(8)

where \( < Sp >_O \) is the average projected area according to all agglomerate orientations. Then, the average volume density is \( \bar{\phi} = i \left( \frac{a_1}{a_{\text{e}}} \right)^3 \). Neverthelesss, it is possible to associate a fractal dimension to a well-built set by assuming that a given set element has the same average volume
density as the fractal agglomerate with the same primary particles number. Then, we may characterize a given agglomerates set by the previously defined and weak (in the mathematical meaning of the word) fractal dimension $D_{wf}$. This new definition can be only applied to agglomerates with high (quasi spherical) symmetry. The so-defined agglomerates contain accurately located primary particles. Hence, this description is more realistic than an enlargement of a fractal one to small agglomerates. During an agglomeration process, small and large agglomerates are present. If $i < i_{\text{lim}}$, agglomerates are assumed to belong to a given agglomerates set characterised by a weak fractal dimension $D_{wf}$; if $i > i_{\text{lim}}$, agglomerates are considered as fractal with the same fractal dimension. So, Gruy [19] defines several hierarchical families (sets) of agglomerates, each one characterised by its weak fractal dimension $D_{wf}$.

Another way to build agglomerate sets [20] consists of achieving computer simulation of agglomeration process: primary particles are randomly located on nodes of a cubic network and are allowed to move according to the shear flow; so, an agglomerates set is built. As the aim of these simulations is not the precise study of the whole agglomeration process or the particle size distribution determination at each time step, reasonable computer time is needed. As previously, a weak fractal dimension will be assigned to this agglomerates set.

### 3.2 Physical properties of small agglomerates

Each agglomerate is also characterised by its gyration radius, fluiddynamic radius, porosity, permeability, all physical parameters needed for modelling phenomena as sedimentation and agglomeration. Up to now, fluiddynamic behaviour of small (rigid or not rigid) agglomerates are not well understood. Recently Gruy [20] undertook to measure the sedimentation velocity of small agglomerates. They consist of a rigid set of glass beads (1mm in diameter). Various structures have been built: linear, planar or three-dimensional. The primary particles number per agglomerate is in the range (2-100). Settling was performed in glycerol in order to keep Reynolds number inferior to 0.1. So, we show that the fluiddynamic radius is equal to equivalent radius calculated from average projected area whatever is the orientation of the falling agglomerates.

Another important physical parameter for agglomerates is related to their experimental characterisation during agglomeration process. Characterisation of agglomerates population during agglomeration process is a difficult task. Unfortunately, no separation methods exist in order to classify a given population of loose agglomerates produced in a
stirred tank. Only the agglomerate set and not a selected agglomerate size class can be analysed.

Optical methods, based on static light scattering, are particularly suitable for characterisation (in situ or on line) of agglomerates composed of submicronic and micronic particles:

- spectral turbidimetry
- analysis of turbidity fluctuations
- analysis of backscattered light
- laser diffraction

For instance, turbidity $\tau$ of a monodisperse suspension of spherical particles (radius $a$) is given by the Mie theory [60]:

$$\tau(\lambda) = N C_{\text{sca}}(m, 2\pi a/\lambda)$$  \hspace{1cm} (9)

$N$ and $C_{\text{sca}}$ are respectively the number concentration of particles and their light scattering cross section. $\tau$ and $m$ are respectively the light wavelength and the ratio of particle refractive index to surrounding medium refractive index. The turbidity of a polydisperse suspension includes the contribution of each size class $i$ of particles ($1 \leq i \leq n$):

$$\tau(\lambda) = \sum_{i=1}^{n} N_i C_{\text{sca},i}$$  \hspace{1cm} (10)

Hence, the time evolution of a suspension due to agglomeration can be studied by spectral turbidimetry. Particle size distribution ($N_i; 1 \leq i \leq n$) can be deduced by mathematical inversion if light scattering cross section values of agglomerates are known.

To our knowledge, accurate calculation of agglomerate scattering cross-sections is not yet completed for any primary particle size. Nevertheless, calculations were achieved when primary particle is a Rayleigh or Rayleigh-Debye-Gans (RDG) scatterer. Two kinds of modelling are used to calculate optical properties of porous materials:

- effective refractive index method
The easiest way to determine the optical properties of an agglomerate is to calculate its effective refractive index $m_a$ [14]. The equation derived by Maxwell-Garnett has proven to be suitable:

$$\frac{(m_a^2 - 1)}{(m_a^2 + 2)} = \phi \frac{(m^2 - 1)}{(m^2 + 2)} \quad (11)$$

$m$ and $m_a$ are the relative refractive indices respectively for primary particles and agglomerates.

Given the diameter and the effective refractive index of an agglomerate, the Mie theory allows to calculate the scattering cross section $C_{sca}$ for a given wavelength.

- interferences method

Generally, the object (primary particle, agglomerate ...) can be divided into smaller identical parts (elements). Each element is polarisable. In the presence of a variable electric field, the element becomes an oscillating dipole, which itself creates an electromagnetic field. When an object is illuminated by an electromagnetic wave, each element receives the incident electric field and the one coming from the other elements. Thus, the object emits an electromagnetic wave (scattered wave), which includes the contribution of each oscillating dipole.

Most often, the incident wave is randomly polarised and the object (scatterer) can randomly orientate. Thus, the optical properties are obtained after calculating an average over all the wave polarisation states and object orientations.

Table 1 presents several models, each one characterised by the polarisable element, the object, the calculation type. If the object is an agglomerate, the element may be either the whole primary particle or a part of the primary particle. The Khlebtsov procedure, similar to Percival-Berry [6] one, has been applied to agglomerates of many particles (fractal agglomerates).

For instance, agglomeration of silica suspension has been studied [19]. The $m$ value (silica in water) is close to 1 ($m - 1 << 1$). Depending on the primary particle size, two cases are possible:
• the primary particle size is small compared to the wavelength \( \frac{4\pi}{\lambda} a_i (m-1) \ll 1 \). So, primary particles are Rayleigh-Debye-Gans scatterers and Khlebtsov procedure can be applied.

• The primary particle size is very large compared to the wavelength. Then, anomalous diffraction occurs [60]. In the Rayleigh-Debye-Gans domain, there is interference of light waves which are independently scattered by all small volume elements. In the anomalous diffraction domain, there is straight transmission and subsequent diffraction. In this case, the scattered intensity is concentrated near the original direction of propagation and the scattering cross section obeys the relation:

\[
C_{\text{scat}} = 2 \int \left( 1 - \cos \frac{2\pi}{\lambda} \delta (m-1) \right) dS_p
\]  

(12)

Integration is performed over the object projected area \( S_p \) on a plane perpendicular to propagation direction. \( \delta \) is the path travelled through the object. This calculated path is a function of the projection coordinates.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Element</th>
<th>Object</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percival-Berry</td>
<td>Rayleigh scatterer</td>
<td>Any</td>
<td>A+MFA</td>
</tr>
<tr>
<td>Draine-Flatau</td>
<td>Electric dipole</td>
<td>sphere, doublet</td>
<td>S</td>
</tr>
<tr>
<td>Mulholland</td>
<td>Electric/magnetic dipole</td>
<td>Agglomerate</td>
<td>A+S</td>
</tr>
<tr>
<td>Khlebtsov [27]</td>
<td>RDG scatterer</td>
<td>Agglomerate fractal-like or not</td>
<td>A+MFA</td>
</tr>
<tr>
<td>Xu [65]</td>
<td>Mie scatterer</td>
<td>Agglomerate</td>
<td>A+S</td>
</tr>
</tbody>
</table>

Table 1: Different models of agglomerate optical properties

A : analytical  
S : simulation  
MFA : mean field approximation

3.3 Main results

The agglomeration of metallic oxides as alumina [49], titania [56] and silica [19] powder in water has been experimentally studied by turbidimetry. The
agglomeration was carried out in a stirred tank under physicochemical conditions corresponding to attractive inter-particle forces. The effect of different primary particle sizes and stirring rates on agglomeration dynamics has been studied. Agglomeration has been studied by using:

- Kusters's approach for collision efficiency calculation [32]
- Brakalov's approach for agglomeration-fragmentation dynamics at high time [7].

It has been showed that:

- agglomerates are small in a stirred tank (primary particle number per agglomerate smaller than 100)
- small agglomerates are slightly porous. Several agglomerates sets and their equivalent or weak fractal dimension $D_{wf}$ have been defined, which is found in the range (2.4-2.5). This is also verified for the beginning of Brownian agglomeration.
- agglomeration process is characterised by $D_{wf}$ and agglomerate limit size $L$.
- $D_{wf}$ (respectively $L$) is a weakly increasing (respectively decreasing) function of the stirring rate or of the shear rate.

4. Population Balance
The simulation of a dispersed system often requires the solution of the population balance, that is, a budget equation (or set of equations) for the particle distribution function, which accounts for all the processes that generate, enlarge or remove particles from the population [25]. In the population balance particulate properties are represented by a set of internal and external coordinates. External coordinates refer to the spatial location of the particles and internal coordinates to their intrinsic properties, such as size, surface area, void fraction, shape factor, etc. Mathematically the population balance equation is expressed by an integro-differential equation for continuous populations or by its discrete counterpart, if the population is discrete (as it may occur for aggregation-breakage processes in the absence of particle growth). For populations of small particles, as those normally present in turbulent precipitation processes, it can be assumed that the particles have exactly the same velocity as the fluid. In this case the population balance for an inhomogeneous turbulent system with particle size as the only internal coordinate becomes:
\[ \frac{\partial n}{\partial t} + \frac{\partial}{\partial x_i} \left( \bar{u}_i n \right) + \frac{\partial}{\partial L} \left( G(L) n \right) = \frac{\partial}{\partial x_i} \left( \Gamma \frac{\partial n}{\partial x_i} \right) + B(L) - D(L) \quad (13) \]

Here \( n(L, x; t) \, dx \, dL \) is the number of particles with size between \( L \) and \( L + dL \) contained in volume \( dx \), \( u_i \) any component of fluid velocity, \( \Gamma \) the turbulent diffusivity. The growth rate \( G \) depends on the size of the particles \( L \) as well as on the concentration of the solutes in the liquid phase. The birth and death rates of the particles of size \( L \), \( B = B_n + B_a + B_b \) and \( D = D_n + D_b \), include several contributions. Nucleation affects only the birth rate of particles of size \( L_0 \) (nuclei) through the nucleation rate \( J \), that depends on local solute concentration:

\[ B_n (L, x; t) = J(x; t) \, \delta(L_0) \quad (14) \]

Aggregation depends on collision between particles and is expressed through the aggregation kernel \( K \):

\[ B_a (L, x; t) = \frac{L^2}{2} \int_0^L K \left( \frac{(L^3 - \lambda^3)^{1/3}}{(L^3 - \lambda^3)^{2/3}} n(L^3 - \lambda^3, x; t) n(\lambda, x; t) \right) d\lambda \quad (15) \]

\[ D_a (L, x; t) = \int_0^L K(L, \lambda) n(\lambda, x; t) d\lambda \quad (16) \]

Finally breakage depends on the breakage kernel \( b \) and on the fragment distribution function \( a(L, \lambda) \):

\[ B_b (L, x; t) = \int_L^\infty a(\lambda) b(L, \lambda) n(\lambda, x; t) d\lambda \quad (17) \]

\[ D_b (L, x; t) = a(L) n(L, x; t) \quad (18) \]

With the exception of few simple systems, analytical solutions are not available and one must normally solve the population balance numerically. Different strategies are available for this task, the most commonly employed being moment methods, method of classes, and Monte Carlo simulation.
The choice depends on a number of factors: number of internal coordinates, complexity of the mechanisms of aggregation, breakage and growth, computational load, role of non-homogeneity in the system, ease of implementation. In the following the three methods will be shortly reviewed, in order to illustrate the proper field of application of each one.

4.1 The moment method
In the standard moment method (SMM) the internal coordinate is integrated out and the population is described in terms of its moments:

\[ m_j = \int_0^\infty n(L) L^j \, dL \quad (19) \]

In this way the integral properties of the population are an immediate outcome of the method: the zeroth moment giving the total particle number, the second one being related to the total surface area, the third one to the total particle volume or mass. This type of information may be sufficient for many purposes and, if this is the case, the moment method can be very effective.

In order to obtain an equation for the \( j \)-th moment, Eq. (1) is multiplied for \( L^j \) and integrated over \( L \). The resulting equations have the same structure as the scalar transport equations of Computational Fluid Dynamics and thus they can be coupled easily with CFD codes, as done, for instance, by Marchisio et al. [39] in their study on barium sulphate precipitation. The main advantage of the method is that the number of equations required (and therefore of calculated moments) is very small, usually from 4 to 6. The disadvantage is that these equations form a closed set only if the rate of growth and the aggregation and breakage kernels are size-independent. The problem has been recently overcome by the Quadrature Method of Moments (QMOM), proposed originally by McGraw [37]. Here particular quadrature formulas are used that make it possible to express the growth, birth and death rate appearing in the budget equation of each moment in terms of lower order moments only. The QMOM has been recently applied to processes of aggregation and breakage and has shown to be able to give very accurate predictions of the main integral properties of a population, even for conditions at which more computationally intense sectional methods fail [39].

4.2 Method of classes
Sectional methods divide the size range in a number of sections and apply a balance equation to each of the formed intervals. As evidenced by Kumar and Ramkrishna [46], sectional methods can be derived through a
procedure of lumping of the population balance equations in which the mean value theorem is applied either on number density or on event frequency. The general framework for the former case was proposed by Gelbard et al. [17], while in the latter situation a general procedure was proposed by Kumar and Ramkrishna [30;46]. In addition to these general approaches a number of other methods have been derived, either by approximate modelling of the physical process (Batterham [5]; Marchal [40]) or by prescribing the forms of the equations and the conservation of some peculiar quantity (Hounslow [24]; Litster [35]). The behaviour of a number of such methods has been discussed by Kostoglou and Karabelas [28] for aggregation-growth processes and by Vanni [61] for aggregation-breakage processes.

The application of the sectional methods differs depending on the presentation of the size distribution as a discrete or a continuous function. In the discrete case (size characterized by the number of included monomers) not all possible states can be described because of the high number of discrete equations in that case and a characteristic selection has to be done. If new particles of a non-selected size are formed they are counted with the nearest selected size giving the problem, that either the total number of particles or the total mass can be preserved but not both. Different possibilities to reduce this error are discussed in literature.

For the continuous presentation (either given by a characteristic length or the mass of the particles) the formation of classes is equivalent to the discretization of the appropriate internal coordinate. Also here each class has a characteristic value and the combination of particles of two characteristic values does not necessarily give an other one but a value in between. If now the amount of the newly produced particles is dedicated partly to the two closest characteristic values the fractions can be computed in a way that number and mass of particles are conserved.

As for the moment approach, the sectional methods give rise to a number of equations (one for each considered size class) with the same structure as the transport equations of any scalar variable, making their implementation in CFD codes possible with a relatively moderate effort. This has been performed for instance by [38] for the same system studied by Marchisio et al. The information on the size distribution makes this method superior to the moment method. In particular it appears promising for the simulation of concentrated dispersions in which the interaction between the fluid and the population of particles is relevant and strongly size dependent. Obviously the higher level of information with respect to the moment method is paid by much higher computational load: while the QMOM adopts 4-6 additional scalar equations, the implementation of the population balance may require up to 50-100 equations in addition to the standard fluid dynamic ones.
4.3 Direct Simulation Monte Carlo method

The methods cited so far consider size as the only internal coordinate. Unfortunately many processes lead to the consideration of two or more internal variables. Occasionally multi-dimensional extensions of the previous methods have been adopted: Xiong and Pratsinis [67] and Jackson [26] for the method of the classes and Wright et al. [65] for the QMOM. Although these papers refer to coagulation processes with simple kinetics and two internal coordinates only, the implementation resulted in a very complex algorithm. Therefore it does not seem practical to extend these approaches to a higher number of internal coordinates.

An alternative is Monte Carlo simulation. In this case an artificial realisation of the studied process is created, by generating a sequence of random events on a computer, which obeys the same statistical laws as the physical system. This technique is often indicated as the DSMC [pope] (Direct Simulation Monte Carlo) method. The DSMC method is based exclusively on the transformation of event rates (i.e. aggregation or breakage rate) in event probabilities, without regarding the actual particle movements or trajectories. Figure 2 shows the outcome of the DSMC approach for the same conditions as Figure 1, evidencing its statistical nature.

Monte Carlo simulations are computationally expensive, since a large number of simulated particles (10⁴ to 10⁶ in a homogeneous system) should be used, in order to obtain accurate results. Due to this fact, at present the method cannot be coupled with classical CFD codes to analyse processes in non-homogeneous systems, whereas a coupling with Lattice-Boltzmann solvers seems to be reasonable.

In comparison with the previous approaches, the Monte Carlo method obviates the need for solving integro-differential equations, which become exceedingly difficult for multivariate number density functions. The implementation of multidimensional systems does not give relevant additional problems to the DSMC approach. Furthermore, since the Monte Carlo method is based on the generation of a sequence of particular events, it is easy to consider complex aggregation or fragmentation mechanisms that, conversely, may be difficult to implement in the analytical form required by the population balance equations.

Another advantage of the DSMC method is that information about the history of the particles is available. This fact makes Monte Carlo simulation a valuable tool to predict the internal structure of the formed aggregates, that is determined by the sequence and the type of the collisions.

If one is interested only in finding the asymptotic or the self-preserving distribution of a population, the precise evaluation of its evolution with time is
not required and one can use relatively simple MC algorithms, such as that proposed by Meakin [41] and used subsequently by Tandon and Rosner [55] for simulating particle aggregation and restructuring with two internal coordinates.

More complex methods should be used to evaluate the time-evolution of a population. They can be classified in two general types. The first one, called time-driven MC, consists in setting a fixed time interval $\Delta t$ and using Monte Carlo to decide which events will take place within this time [34,63,15]. The other approach can be called IQ-based Monte Carlo. At each step the method determines the time interval after which a new event occurs (Interval of Quiescence, IQ) and select the event. In this case the time step adjusts itself to the rates of the various processes [50,52].

5. Influence of aggregation in precipitation processes, experimental results and comparison with CFD computations.

The barium sulphate precipitation is studied in the PRATSOLIS project both experimentally and numerically. Results for a tubular reactor can be presented. But it has to be mentioned that even if in a tubular reactor the geometry is really simple, the small residence time makes an eventual study of agglomeration processes not easy.

The experimental set-up is presented in the Figure 3. The tubular reactor is 2.1 m long and has an internal diameter of 10 mm. The jet is positioned on the reactor axis, and is made of a small pipe (ID=1 mm, OD=1.5 mm). With A and B are indicated the two reactants barium chloride and sodium sulphate, respectively fed in the internal pipe and in the annular zone. Two different series of measurements were performed: on-and off-line. In the first one the reactor outlet was connected with a laser particle sizes analyser (LPSA; Cuolter LS 230), as reported in Figure 3, and the CSD was directly measured on the particles flowing in the outlet fluid. In the second case LPSA were used with a “fluid cell” device. These experiments were carried out because in certain cases the reaction was not complete and would have progressed during sampling and analysis. The table (Tab. 2) gives an overview of the measurements carried out.

Our attention was focused on the concentration ratio effect ($\alpha=\frac{c_B}{c_A}$) on CSD (Crystal Size Distribution) and crystal morphology. Keeping constant the A reactant concentration and increasing $\alpha$ different crystal morphologies were achieved. For values of $\alpha$ less then 0.01 nucleation and growth are quite slow and after sampling the crystal continue to growth and well formed crystal are produced Figure 4. Increasing $\alpha$ up to 1.0, growth becomes diffusion controlled, resulting in a dendritic crystal structure (Figure 4, (b) and (c)). For high values ($\alpha=3$) aggregation plays an important role resulting in a significantly different structure (Figure 4, (d)).
Results of experiments at high concentrations are reported in Figure 5. As it is possible to see, for all values of $\alpha$, the CSDs maintain the same shape, although generally the primary peak decreases and the secondary one (or ones) increases. This is a proof of the high tendency of the precipitate to aggregate also for longer time (30 min). It should be highlighted that in this case also at the reactor outlet CSDs had more than one peak, meaning that aggregation started to occur inside the reactor despite the short residence time.

The simulation results presented here were gained with commercial codes (Fluent, Star-CD), where the fluid dynamic field is solved via standard $\kappa$-$\varepsilon$ turbulence model already implemented in the code, while the micromixing and the population balance model were introduced via user-defined functions.

After solving the flow field to get mean velocities and turbulence quantities in stationary conditions two methodologies were followed. The first approach is constituted by a set of nine transport equations, in which the convection and the turbulent diffusion were modelled by the CFD code, and a source term must be specified for each scalar. Mixing properties were determined by solving the transport equations for the probability of modes (concentration of the reactant species at the inlet) A and B and for the weighted mixture fraction and high concentration ratio values. The reaction and particles formation were given by solving the transport equation for the reaction progress variable and for the CSD moments the Standard Moments Method was used.

For the second approach to solve the CSD the class method was used with a total number of 40 classes, while the discretization of agglomeration term was done with the method presented in [10] which allows conservation of particles and mass number.

In Figure 6 model predictions at the reactor outlet are compared with experimental data (high concentration, $c_{A0}=34\text{mol/m}^3$, $\alpha=3.0$). The mean crystal size is compared with the model with and without aggregation. In this case only a constant kernel is considered for agglomeration. Comparison shows that for these operating conditions if aggregation is neglected the mean crystal size is significantly underestimated, for $\alpha$ larger than 0.1. The mean crystal size of agglomerates is still higher than model predictions. This could be caused by the fact that turbulent aggregation is not considered. In fact, it has been shown that also for particles smaller than the Kolmogorov scale turbulent aggregation might be important.

Figure 7 shows the normalized integral particle size distribution for the experiments and for the different computations ($c_{A0}=0.0049\text{kg/kg}$, $\alpha=2.05$). This presentation is required because the experimental data are available only in normalized form. It can be seen that even the numerical
curve without agglomeration shows larger particles than the experimental one. Reason for that is mainly the impreciseness in the kinetic expressions for nucleation and growth, but there are also effects of numerical inaccuracy and different references for the characteristic particle size in experiments and simulations. Therefore, consideration of agglomeration does not bring the simulations closer to the experiments. Nevertheless, it can be seen, that assuming turbulent agglomeration the particle size computed is slightly larger than without, even for the small residence times in the tube.

6. Numerical simulation of orthokinetic agglomeration in stirred vessels

In this section of the paper, we numerically investigate the scale-up behavior of agglomeration in agitated tanks (agitation is widely used in industrial crystallization to promote circulation, and enhance heat and mass transfer). For a more elaborate discussion, we refer to the article by Hollander [23]. By considering crystals with a size of the order of 10 µm, the main particle-particle collision mechanism is due to orthokinetic motion. Particles of this size are too big to experience significant Brownian motion. The steps in an agglomeration event (i.e. collision, cementing, and possibly rupture) make the agglomeration rate a strongly non-linear function of the velocity gradient [43]. Along with the non-linear nature of turbulent fluid flow, predicting and/or scaling up agglomeration in stirred vessels is a difficult task.

As a sample system, we consider calcium oxalate monohydrate. For this system, a theoretical agglomeration model is available in the literature [43] that provides a full description of the agglomeration kernel $K$. The model predicts a weak dependency of $K$ on $d$. Furthermore, if chemostatic conditions are assumed (in other words: the consumption of supersaturation by the agglomeration process is considered negligible), $K$ can be considered to be a function of the shear rate only. The functional relation between $K$ and $\dot{\gamma}$ as derived from Mumtaz [43] is depicted in Figure 9. At low shear rates, the agglomeration kernel is dominated by the collision frequency, which is proportional to the shear rate. Here, every collision leads to an agglomerate due to the weak disruptive forces acting on the newly formed agglomerates. The higher the shear rate, the less effective the collisions get, and the more $K$ deviates from linearity with respect to shear.

The basis of our numerical study on agglomeration in stirred tanks is formed by Large-Eddy Simulation (LES) of the turbulent flow in the tank [12], using the simplest subgrid-scale model, the Smagorinsky model [51]. A typical result of an LES of stirred tank flow is depicted in Figure 10. From the vector plots and time-series, the time dependent nature of the flow becomes apparent. The vortical structures of various sizes that can be observed in the snapshot are lost in the time-averaged flow. The availability of local, and
time-dependent flow information in an LES, as demonstrated in Figure 10, is exactly the reason why it has been used in our study on the interaction between agglomeration and turbulence. The non-linear relation between the agglomeration and the shear rate (Figure 8) requires local shear rate information, and not average information, since $K(\tilde{\gamma}) \neq K(\bar{\gamma})$ (where an overbar indicates spatial and/or temporal averaging).

In order to model agglomeration in stirred tanks, the LES code was supplemented with a Monte-Carlo algorithm that solved the transport equation for the number density $n$ [23]. In the transport equation, agglomeration acts as a sink. The local, time-dependent shear rate, necessary to determine the local value of $K$ in the particle number transport equation was estimated from the LES through the deformation rate:

$$\tilde{\gamma}^2 = 2S_{ij}S_{ij} \equiv \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)^2$$

(20)

The size of the particles (typically 10 µm) justifies a one-way coupling assumption (i.e. the crystals feel the turbulent fluid flow, the fluid does not feel the presence of the crystals), since the particles are smaller than the Kolmogorov length scale. The presence of the particles might slightly increase the apparent viscosity of the tank’s content (through the Einstein-relation for suspension viscosities, see also Hollander [23]).

A sample simulation result is presented in Figure 10. It shows for the specific CaOx⋅H₂O system (with $\beta$ as depicted in Figure 8) the (obviously inhomogeneous) distribution of the agglomeration rate kernel throughout the tank. The time-averaged part of Figure 10 indicates that hardly any agglomeration occurs in the volume swept by the impeller. Apparently shear rates close to the impeller are too high to cause agglomeration. The single-realization shows how the turbulent flow structures translate into a spatial $K$-distribution.

With the numerical tool described above, a large number of cases (25 in total) has been simulated [23]. Three scale-up rules (constant specific power input, constant tip-speed, and constant Reynolds number) have been applied to tanks ranging in size from $10^{-3}$ m$^3$ to 10 m$^3$ equipped with two different impellers (viz. a Rushton turbine, and a 45° pitch-blade turbine with four blades). One number has characterized the result of every individual simulation: the apparent agglomeration rate kernel, which is a measure for the tank-averaged agglomeration behavior. The apparent agglomeration rate kernel $K_{app}$ was determined by fitting the evolution of the tank-averaged particle number concentration in time with the function
\[ n(t) = \frac{1}{\frac{1}{2} \beta_{\text{app}} t + \frac{1}{n_0}} \quad (21) \]

which is the solution of \( \frac{dn}{dt} = -\frac{1}{2} K_{\text{app}} n^3 \) with initial condition \( n(0) = n_0 \). This definition of \( K_{\text{app}} \) corresponds to experimental practice, where the kinetics of agglomeration is estimated from the measured particle number decrease in time in stirred tank experiments.

In Figure 11 we have summarized all numerical results. The symbols in the graph represent the apparent agglomeration rate kernel as a function of the average shear rate in the tank. The latter is estimated as \( \bar{\gamma} = \frac{\sqrt{\bar{\varepsilon}}}{V} \), where the tank-averaged dissipation rate relates to the power inserted by stirring:

\[ \bar{\varepsilon} = \frac{P}{\rho V_{\text{tank}}} \]

Figure 11 illustrates our point of the intricate, non-linear interaction between turbulent fluid flow and agglomeration kinetics: It is impossible to derive the applied kinetic relation (of Figure 9) from the (in this case numerical) "experimental" data that contain the mixed effects of turbulence and kinetics. Similar problems are encountered when trying to predict the scaling behavior of an agglomeration process [23].

**Summary**

Agglomeration is a complex process where different phenomena have to be considered to describe it. Local fluiddynamic conditions mainly determine the collision probability of particles while electrostatic and Van Der Waals forces determine if colliding particles will stick together.

In the mathematical models of the agglomeration process usually have the form of a population balance, where integral expressions in terms of an agglomeration kernel are used. Different approaches for that can be found in literature.

Morphology of the agglomerates formed can be discussed using real or weak fractal dimensions.

With the knowledge about the morphological structure measurements based on the optical properties of the agglomerates can be carried out.

For the solution of the population balance mainly three different techniques can be used: The momentum method; The method of classes; The Monte Carlo method.
The own results presented regard precipitation in a tubular reactor and in a stirred vessel. The tube has been modelled by combining population balance solver with commercial CFD codes, using the momentum method. For the stirred tank Lattice-Boltzmann simulations with LES for the turbulent flow have been combined with Monte Carlo simulations. Apart from focusing a validating and/or determining kinetics, work needs to be done to refine the simulation.

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Figure 1: 1a: Asymptotic PSD for an aggregation-breakage process with fragment mass ratio 4:1. Thick line: prediction of the method by Kumar and Ramkrishna; thin line: rigorous solution. 1b: Asymptotic PSD for the same situation as reported in Figure 1a predicted by a DSMC approach.

Figure 2: The agglomeration kernel $\beta$ (as defined in Equation 1) in simple shear flow as a function of the shear rate, theoretical model due to Mumtaz et al. (1997) for CaOx·H₂O crystals. For reference, the collision kernel $\beta_{\text{collision}}$ is indicated.

Figure 3: Experimental set-up (Politecnico di Torino)

Figure 4: Crystal morphologies: a) tabular crystals (BaCl₂ in the jet $c_{A0} = 34 \text{ mol/ m}^3$, $\alpha = 0.1$); b) dendritic crystals (BaCl₂ in the jet $c_{A0} = 34 \text{ mol/ m}^3$, $\alpha = 1.0$); c) particular of a dendritic crystal in (b) conditions; d) round-shaped crystals (BaCl₂ in the jet $c_{A0} = 34 \text{ mol/ m}^3$, $\alpha = 3.0$); e) round-shaped crystals (Na₂SO₄ in the jet $c_{A0} = 34 \text{ mol/ m}^3$, $\alpha = 3.0$); f) round-shaped crystals (BaCl₂ in the jet $c_{A0} = 341 \text{ mol/ m}^3$, $\alpha = 0.1$).

Figure 5: CSDs for several values of $\alpha$ at the reactor outlet (solid line) and after 30 minutes of gentle stirring (dashed lines).
Figure 3 Left: a snapshot of the flow driven by the Rushton turbine in a vertical plane midway between two baffles. Center: the average flow field (averaging time: 24 impeller revolutions) in the same plane. Right: three velocity time series at different positions in the tank (as indicated in the center figure). The grid size was $180^3$, the Reynolds number amounted to 29,000.

Figure 4: Typical distribution of the agglomeration kernel $\beta$ throughout the vertical plane midway between two baffles in an agitated tank driven by a Rushton turbine. Left: time-averaged values; right: single realization.

Figure 6: Mean crystal size versus $\alpha$ (solid line: model prediction; dashed line: model prediction neglecting aggregation).

Figure 7: Comparison of numerical results with and without agglomeration with experimental one.

Figure 11: Solid line: same as Figure 9, with $\dot{\gamma}$ on a logarithmic scale. Symbols: tank-averaged agglomeration kernels (various tank sizes and impeller geometries) as a function of the tank-averaged shear rate $\sqrt{\frac{\dot{\gamma}}{V}}$. Dashed line: fit through the symbols with the same mathematical expression as used for the solid line.