1. For control purposes, a descriptive model such as the one-dimensional population balance presented in Chapter 4 can be sufficient. For predictive purposes it is inadequate. (Chapter 4 of this thesis).

Voor regeldoeleinden kan een beschrijvend model, zoals het één-dimensionale populatiebalans model van hoofdstuk 4 van dit proefschrift, toereikend zijn. Een dergelijk model is echter niet geschikt om mee te voorspellen. (Hoofdstuk 4 van dit proefschrift)

2. Multi-dimensional population balances are the only sensible way forward in order to construct models that describe the physical behaviour of a granulation process. (Chapter 5 of this thesis)

Meer-dimensionale populatiebalansen zijn de enige zinnige weg voorwaarts teneinde modellen te ontwikkelen die het achterliggende fysische gedrag van een granulatieproces kunnen beschrijven. (Hoofdstuk 5 van dit proefschrift)

3. When working with pilot scale equipment, one becomes painfully aware of how many more things can go wrong than originally held possible.

Als men experimenten uitvoert op proeffabriekschaal wordt men op pijnlijke wijze bewust van hoeveel meer dingen fout kunnen gaan dan men aanvankelijk voor mogelijk hield.

4. "Granules do not carry a stopwatch around". (Professor Mike Hounslow on the time dependence of the kinetic constants in the population balance.)

"Granules dragen geen stopwatch. (Professor Mike Hounslow over de tijdsafhankelijkheid van de kinetische constanten in een populatiebalans.)

5. A priori prediction of the growth rate and behaviour of granules is the Holy Grail of granulation research.

Het van te voren voorspellen van de groeisnelheid en het groeigedrag van granules is de Heilige Graal van granulatie-onderzoek.

6. Newton’s First Law of motion applies also to peoples’ reluctance to change.

De Eerste Wet van Newton is ook van toepassing op de traagheid waarmee mensen veranderen.


(Of all these [Gauls] the Belgians are the bravest.)

(Van al deze [Galliërs] zijn de Belgen het dapperst.)
8. "There is an art, or rather a knack, to flying. The knack lies in throwing yourself at the ground and miss." (D. Adams, The hitchhiker’s guide to the galaxy)

9. To appreciate home one has to be elsewhere.
   Om thuis te leren waarderen moet men elders zijn.

10. Finishing any enterprise is always harder than starting. So is it with a promotion.
    Het afronden van een onderneming is altijd moeilijker dan het aanvangen ervan.
    Dit geldt ook voor een promotie.
Modelling and Mechanisms of Granulation

Proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus prof. ir. K.F. Wakker,
voorzitter van het College van Promoties,
in het openbaar te verdedigen op maandag 11 juni 2001 om 16.00 uur

door

Philippe Alfons Lodewijk WAUTERS

scheikundig ingenieur
geboren te Utrecht.
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Dr. ir. G.M.H. Meesters heeft als begeleider in belangrijke mate aan de totstandkoming van het proefschrift bijgedragen.
Voor Pa en Ma ...
Summary

Modelling and Mechanisms of Granulation

Granulation is the generic term for particle size enlargement processes. The granules possess various advantages compared to the powders which they are composed of, such as improved flow properties, a reduced risk of segregation and improved product homogeneity. Despite more than four decades of research, both in industry and at universities, granulation processes are still notoriously difficult to model and control and therefore high recycle ratios and plant shutdowns are not uncommon. The performance of the process relies heavily on the expertise of the operators. It is imminent that there is a desire for adequate models that can lead to an improved process performance or design. In this thesis, experimental data is generated that is used in two ways: first it is adopted for gaining an improved understanding of the process in a qualitative sense. Consequently, this understanding is then used for extending and improving already existing population balance models. Thus, the understanding of the process in the quantitative sense is augmented.

Experiments were conducted with a rotating drum, operated batch wise, using copper concentrate (chalcopyrite) and water as starting materials. It was found that this material exhibited induction type behaviour (Iveson and Litster (AIChe J., 44 (1998) 1510-1518). Induction behaviour is characterised by an induction period which follows immediately after the binder addition stage. The induction stage is a period during which the particle size does not change. It can last up to several hundreds of drum revolutions. Usually strong granules that do not deform much on impact exhibit an induction stage. It is thought that during the induction period, these granules are compacted until the binder liquid in the pores is squeezed onto the granules' surface (Iveson and Litster (AIChe J., 44 (1998) 1510-1518). At this point, the granules appear to be surface wet and the liquid layer at their surfaces allows them to coalesce with each other. This leads to rapid growth. An increased amount of binder will lead to a shorter induction stage. If more than a certain critical amount of binder is added, the induction stage is not entered and the process exhibits rapid growth. Another critical boundary exists and when less binder is added than this critical amount, the induction stage lasts for an indefinite time.

Two types of experiments were conducted: experiments in which the binder and the powder were pre-mixed and pushed through a 2 mm sieve, ensuring a constant size distribution of the nuclei and experiments in which the binder was sprayed onto the powder
bed. The former experiments were used to test the growth and compacting behaviour of the material and the latter experiments were used to assess the effect of the method of liquid addition and liquid distribution. It was found that during the induction stage the porosity of the granules decreased and that, at the start of the rapid growth stage, the granules had become surface wet. In addition, it was found that an increased amount of binder liquid resulted in a shorter induction stage. These findings were all in accordance with the literature. However, the results from the spray-on experiments provided evidence for a modified mechanism of induction type behaviour. It was found that the nuclei that are formed during the liquid addition stage consist of larger granules which contain more binder liquid and of smaller granules which contain less binder liquid. This can be attributed to the pattern of the nozzle that was used to spray the binder liquid onto the powder. Binder flow rates are higher in the centre of the spraying zone than on the perimeter of the spraying zone. Therefore, the liquid distribution is not uniform which results in areas of powder that receive more binder than other areas. Naturally, larger granules are formed in the former areas. It was found that during the induction stage, the fraction of smaller granules decreases linearly in time and the rapid growth starts immediately after the smaller granules have disappeared. Selective removal of the smaller granules resulted in a significant reduction of the duration of the induction stage.

It was concluded that the mechanism of induction behaviour is as follows: During the liquid addition stage nuclei are formed. Due to the fact that the liquid is not added homogeneously, some regions receive more binder liquid than others. Inevitably, this leads to the formation of large and relatively wet nuclei and smaller and drier nuclei. After the liquid addition stage, an induction stage is entered. During this induction stage, the granules are compacted. The large and wet granules continuously become surface wet, but as soon as patches of liquid appear at their surface, small and dry granules stick to the liquid at the surface. This results in a lower binder content of the large granule. Therefore, the granules do not appear to be surface wet. When there are no more smaller granules present, further compaction of the large granules produces large, surface wet, granules that remain surface wet since they cannot pick up small and dry granules. At this stage, the large and surface wet granules coalesce with each other resulting in a sharp increase in the growth rate. This transition is the rapid growth stage. The binder liquid is then homogeneously distributed among the granules. This illustrates that the induction stage can also be regarded as a stage of liquid redistribution.

In addition, it was shown that the distance from the nozzle to the powder bed had a significant influence on the process. A larger distance resulted in a more homogeneous distribution of the binder liquid. This reduced the time required for the liquid redistribution and therefore the induction time. Varying the flow rate, however, had no effect within the range of flow rates studied. Therefore, it can be concluded that the nozzle height is a crucial parameter in controlling the growth behaviour of the granulation process.

An existing set of data, which was published before (Hoornaert et al. (Powder Technol., 96 (1998) 116-128), from a high shear mixer was simulated using a one-dimensional population balance model, i.e. a population balance model which uses one granule prop-
erty, in this case particle volume, as an internal co-ordinate. A sectional method, such as the one described by Hounslow et al. (AIChE J., 34 (1988) 1821-1832) was adopted. Based on an analysis of the experimental data, the granulation process was divided into three separate stages: nucleation, induction and coalescence growth. These three stages were then simulated separately with good results. It is possible to construct a kernel that can fit both the induction stage as well as the coalescence growth stage. Modelling the nucleation stage proved to be more challenging due to the complex mechanism of nucleus formation. It was concluded that a one-dimensional population balance can be used effectively to simulate existing data with an empirical kernel and therefore it can be applied to process control, provided that the process is operated within certain boundaries. It is expected that the model will not predict the behaviour well if the process is operated outside of these boundaries, i.e. the model can not be extrapolated.

In order to make the model more physically based, it is necessary to include other particle properties, such as porosity and moisture content. The experimental data had already revealed the importance of these properties. Others (Anapragada and Neilly, Powder Technol., 89 (1996) 83-84, and Iveson, Control of Particulate Processes 6, Fraser Island, Australia, 1999) have also stressed the relevance of including these properties in a population balance. Therefore a multi-dimensional population balance was derived in which three particle properties were included: the volume of solid, the volume of liquid and the volume of air in each granule. When two granules coalesce, these properties can be simply added in order to obtain the properties of the new particles and properties such as porosity, liquid content and pore saturation can easily be derived from the volumes of the three different phases.

By incorporating the results from the experiments conducted on the rotating drum, a kernel for the multi-dimensional population balance was derived that was based on the mechanism of induction behaviour. A Monte Carlo method was adopted to solve the multi-dimensional population balance. Monte Carlo methods have been applied to one-dimensional population balances before and they have been shown to be very well suitable for modelling particulate processes in which discrete size changes occur. It was found that the Monte Carlo method was also very well suited for multi-dimensional population balance simulations. It remains to be seen whether other numerical methods are capable of performing these kind of simulation with the same speed and accuracy.

The results from the multi-dimensional population balance model matched the experimental data well. Both the size changes as well as the changes in binder liquid content in the simulation followed those of the experiments. It is evident that multi-dimensional population balance modelling has great potential for modelling granulation processes since it is more physically based than a one-dimensional population balance. The results presented in this thesis support this finding.

P.A.L. Wauters
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Chapter 1

Introduction

1.1 Granulation

Granulation is a generic term for particle size enlargement processes. Granules are larger, relatively permanent masses in which the original particles can still be distinguished [1]. In general, granules have a size of a few hundred microns up to a few millimeters and they consist of particles ranging in size from a few microns up to a few hundred microns. There are several reasons why granules rather than smaller particles, i.e. powders, are preferred, e.g. [2]:

1. Improved flow properties: in general, coarser powders have better flow properties than fine powders. Powders with better flow properties are easier to meter and dispense.

2. Prevention of segregation: when granules of a certain size are produced they can be mixed with other particles of the same size. This mixture will not have a tendency to segregate.

3. Increased bulk density: this will reduce storage volume and cut costs of transportation.

4. Improved dusting behaviour: granules do not have a tendency to become airborne as opposed to fine powders. In addition, when produced properly, granules have sufficient strength to resist attrition, which ensures that potentially harmful dust is not released into the atmosphere.

5. Production of mixtures with a uniform composition: often granules are produced that consist of an active component, such as a drug or an enzyme, and a filler. When for example tablets are produced from such granules, rather than from a powder mixture the variation in composition of these tablets is much smaller.

6. Improved product appearance: by adding a dye or by producing granules/tablets of a certain shape.
CHAPTER 1. INTRODUCTION

7. Improved solubility: powders can be more difficult to dissolve due to their tendency to form lumps. This does not happen with granules.

8. Improved performance: for example by incorporating certain powders in granules that improve the disintegration of tablets or instants.

Granulation is applied in a wide range of industries. These include the pharmaceutical industry, the food and feed industry, but also bulk industries such as metal ore processing industry, the fertilizer industry and the plastics industry.

A number of techniques are available in order to achieve the desired particle size enlargement. Sherington and Oliver made a classification of the different techniques [3] which is shown in Figure 1.1.

![Granulation Diagram](image)

**Figure 1.1:** Subdivision of the field of granulation, according to Sherington and Oliver [3].

Sherington and Oliver indicated that there was (and is) an inconsistency in the literature with regard to the nomenclature used. This is due to the widespread use of granulation in various industries. It is therefore possible that *agglomeration* in a rotating drum is sometimes referred to as *balling* or as *pelletization* or simply *granulation*. One can thus conclude that their system of nomenclature was merely an attempt to create a logical subdivision of the different techniques, but by no means is this subdivision absolute.

In Table 1.1 an overview is given of the different types of granulating equipment available. This thesis is mainly concerned with agglomeration techniques and most notably granulation in rotating drums and high shear mixers.

### 1.2 The granulation process

Figure 1.2 presents a schematic representation of a continuous granulation process which is applied, for example, in the production of fertilizer. In the granulator, the dry powder
### 1.3. AIM AND THESIS OUTLINE

**Table 1.1:** Types of granulating equipment and their characteristics.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Type of technique</th>
<th>Granule size</th>
<th>Granule strength</th>
<th>Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluidized bed</td>
<td>agglomeration</td>
<td>0.1-1 mm</td>
<td>+/-</td>
<td>0.5-5 ton/h</td>
</tr>
<tr>
<td>granulation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rotating drum</td>
<td>agglomeration</td>
<td>1-5 mm</td>
<td>+/-</td>
<td>5-100 ton/h</td>
</tr>
<tr>
<td>Rotating pan</td>
<td>agglomeration</td>
<td>1-5 mm</td>
<td>+/-</td>
<td>5-100 ton/h</td>
</tr>
<tr>
<td>High shear mixer</td>
<td>agglomeration</td>
<td>0.3-0.8 mm</td>
<td>+</td>
<td>0.5-50 ton/h</td>
</tr>
<tr>
<td>Prilling</td>
<td>globulation</td>
<td>0.5-1 mm</td>
<td>+/-</td>
<td>0.5-50 ton/h</td>
</tr>
<tr>
<td>Roll compaction</td>
<td>compression</td>
<td>1.5-10 mm</td>
<td>++</td>
<td>0.5-5 ton/h</td>
</tr>
<tr>
<td>Tabletting</td>
<td>compression</td>
<td>any shape &gt; 2mm</td>
<td>++</td>
<td>&lt; 2 ton/h</td>
</tr>
<tr>
<td>Screw extrusion</td>
<td>extrusion</td>
<td>1-10 mm</td>
<td>++</td>
<td>0.5-5 ton/h</td>
</tr>
</tbody>
</table>

is wetted by the binder liquid and consequently agitated. Thus granules are formed. These are dried and screened. Off-spec material is recycled back into the granulator (the oversize fraction is crushed first). Recycle ratios of up to 5:1 are not uncommon [1]. These large recycle streams have a profound effect on the stability of the process but also on the economy of the process, since it requires large granulators and dryers, but it also means that a substantial amount of material is dried and consequently wetted again in the granulator. In particular in the fertilizer and metal ore industries, where the profit margins are small, a reduction in the recycle stream is therefore desirable. In addition, improved process stability is also desirable since plant shut down occurs frequently [4].

The pharmaceutical industry faces the difficulty of having to find the optimum formulation (i.e. the mixture of solids and liquids) and the optimum process conditions (e.g. the type of granulator, the load of the granulator, the speed of the agitation etc.). This is often done by trial and error. These experiments require large amounts of the active component, which is not yet available in large quantities, since at that point the production process is under development. A more fundamental approach, based on small scale tests which can be readily scaled up to production scale, would reduce the amount of material and time spent on the development of the production process.

### 1.3 Aim and thesis outline

The previous section has illustrated the need for an improved understanding of the granulation process. Existing plants can perform better when such knowledge is applied. In addition, improved understanding can also be used during the development and/or commissioning of new plants. This understanding can be in the form of some (population balance) model but also of a more qualitative nature.
The aim of this thesis, in a broader sense, is to improve the understanding of the granulation process. This is achieved in the following manner:

- Conduct granulation experiments during which the three stages of a granulation process are studied. These three stages are: nucleation (the formation of the first granules, or nuclei), compaction (the densification of the granules) and coalescence (sticking together of granules). This aids in the building of qualitative models.

- Apply the acquired knowledge into existing population balance models. Thus, the qualitative insights are utilized in the development of an improved population balance that describes the three stages of a granulation process more adequately.

This thesis is set up in the following manner: first, the existing models that describe granule behaviour are discussed in Chapter 2: Mechanisms. The next chapter, An experimental study of induction type behaviour, describes a number of experiments that were conducted in a rotating drum, using a material that exhibits induction type growth (for a description of induction type growth, see Section 2.3.5). The interpretation of the results of these experiments contribute to the improved understanding of the granulation process in the qualitative sense. The second part of the thesis covers population balance modelling of the granulation process, in other words, the quantitative understanding. Chapter 4, One-dimensional population balances, introduces the concept of population balances and how they are applied in particulate processes where size changes occur. In the same chapter an example is given of how one-dimensional population balances can
be applied to a granulation process. The performed simulations are compared to existing granulation data from a high shear mixer. The next chapter, **Multi-dimensional population balance modelling**, discusses the application of multi-dimensional population balances, i.e. population balances that incorporate more particle properties apart from its size. The insights gained from the experiments described in Chapter 3, **An experimental study of induction type behaviour**, are applied in the multi-dimensional population balance. Thus, the **existing model is improved by applying the acquired fundamental understanding of the granulation process**. Finally, conclusions are drawn and recommendations for further research are made.

---

**A word of warning:**
In a few cases, a figure or an equation is repeated. This should allow the reader to carry on reading, avoiding having to go back and forth between two sections. However, figures and equations always reappear with the number they originally appeared with. Readers are not to be confused by what seems to be a discontinuity in the numbering of the figures and equations.
Chapter 2

Mechanisms

This chapter will start with an overview of different studies on growth mechanisms. Beginning with the groundbreaking work of Newitt and Conway-Jones [5] in 1958 through to the present day, all major models of granule growth will be discussed. This chapter will focus on both the micro and macro-scale models.

2.1 Early work on mechanisms of granulation

In 1958, Newitt and Conway-Jones laid the foundation for granulation research [5]. They performed a number of batch experiments in a rotating drum in which they studied the effects of a large number of parameters on granule growth rate, granule porosity and granule strength. Their paper mainly focused on how the internal structure of granules affects their behaviour. First, they reported the effects of moisture content, rotational speed of the drum, drum loading and the initial particle size distribution on the granule growth. Granulation occurred only when the moisture content was between a minimum and maximum boundary. Below the minimum value, there was excessive cake formation, and only a limited number of large and weak granules were produced. Above the maximum value, the growth rate was excessive and the granules were weaker. In between the two boundaries, increasing the amount of binder resulted in a higher growth rate. As for the drum load, they stated that a minimum load was required in order to achieve tumbling motion of the granules. For high drum loads, the growth rates were excessive due to cascading. The effect of the initial particle size distribution could be explained by studying the deformability of the granules. They stated that granules consisting of smaller particles are less deformable and therefore had lower growth rates. On the other hand, when the particles were too large, it was not possible to make granules at all, due to their low strength. In addition, granules produced from particles with a wide initial size distribution also proved to be stronger.

Newitt and Conway-Jones then proceeded to explain these phenomena by studying the structure of the granules. Three states of water content were defined, see Figure 2.1. When not much binder liquid is present, discrete lens shaped rings of water bind the
particles together. This is called the pendular state. When more binder liquid is present, a continuous network of liquid, interspersed with air is present in the granule. This is called the funicular state. Increasing the binder content will result in a granule that has all its pores filled with binder. This is the capillary state. Through calculations and experimental data, Newitt and Conway-Jones showed that the strongest granules were in the capillary state. In this state the binder menisci are withdrawn into the surface waists of the granule. The curvature of these menisci causes a pressure deficiency which holds the granule together.

![Diagram](image)

**Figure 2.1:** Three states of binder content. "A" represents the pendular state, "B" the funicular state and "C" the capillary state. From Newitt and Conway-Jones [5].

They stated that granules had to be compacted from the pendular/funicular state to the capillary state in order to make growth possible. Their proposed mechanism of growth was that granules can only coalesce when they are surface wet, i.e. when the pores are saturated and excess binder liquid is present on the surface. When the granules are surface wet, they have a certain degree of surface plasticity and this allows the formation of a large area of contact upon collision. Furthermore when surface wet granules are strained, the excess moisture is withdrawn into the granule and then the granules are in the capillary state, making them stronger.

Kapur and Fuerstenau performed a study of drum granulation of pulverized limestone in 1964 [6]. They divided the granulation process in three regions: nuclei growth region, transition region and the ball growth region, each having its own distinct mechanism, see Figure 2.2.

Prior to an experiment, Kapur and Fuerstenau mixed their limestone with water and rubbed the wet mass through a 3.3 mm sieve. This yielded highly porous and loose flocs. During the nuclei growth region, the tumbling motion of the drum caused the particles inside these flocs to rearrange themselves and it compacted the flocs as well. The flocs were thus transformed into stable nuclei. These nuclei consisted of three phases: solid, liquid and air. In the transition region, the granules were gradually compacted until the air in the pores was driven out. Further densification then caused binder liquid to be squeezed onto the surface of the granules, yielding surface-wet granules. According to Kapur and
2.1. EARLY WORK ON MECHANISMS OF GRANULATION

Figure 2.2: The average diameter of the granules as a function of the number of drum revolutions. The results of four repeat runs are represented in this graph. From Kapur and Fuerstenau [6].

Fuerstenau, these surface-wet granules were much more reactive, i.e. they coagulated readily with other particles. As not all granules reached the surface-wet stage at the same time, the granules which were surface-wet were able to grow at a much higher rate, leading to a widening of the granule size distribution. After the granules had become surface-wet, the ball growth region was entered. In this region, the main growth mechanism was dubbed coalescence by Kapur and Fuerstenau. Coalescence occurred when two surface-wet granules collided and stuck together, forming a clump, which was subsequently deformed to form a larger spherical granule. There were also other mechanisms occurring in the ball growth region, such as abrasion transfer, where small parts of the surface of one granule are transferred onto the surface of another granule by the rubbing together of two granules, but the contributions of these mechanisms were only minor.

In 1965, Capes and Danckwerts reported a study on the drum granulation of uniformly sized silica sands [7]. Their aim was to describe the mechanism of granule growth and they conducted experiments similar to those of Newitt and Conway-Jones [5]. They found that there are several stages of granule growth. Firstly, the moistened feed (referred to as ‘crumb’) forms spherical granules. During this stage, which is called the nucleation stage of growth, the loose aggregates of particles in the crumb are kneaded into granules by the kneading action of the rotating drum. Due to the tumbling motion of the drum, particles are compacted and therefore their pore volume is reduced. If sufficient liquid is present in the initial feed, the pores of the granules are almost completely filled with liquid. As Newitt and Conway-Jones pointed out before, such granules are very deformable and form a large area of contact upon collision with another granule, forming a dumbbell which is
subsequently kneaded into a spherical granule. After the granules had reached a certain size, they no longer grew according to this random mechanism. Capes and Danckwerts performed experiments with small granules made from different colored sands. From these experiments, they concluded that once granules reach a critical size, their growth mechanism changes from a random mechanism to a crushing and layering mechanism. Capes and Danckwerts found that when two granules of different sizes collide, the smaller granule is crushed and the fragments that are formed are then layered onto the surface of the remaining granules. They drew this conclusion from the observation that granules consisted of a core of one colour and a layer around that core of a different colour.

Linkson et al. [8] addressed the seemingly contradictory results of earlier studies, concerning the type of growth mechanism. Some of these earlier studies claimed that granules grew by crushing and layering [7], others claimed that granules grew by coalescence [5, 6]. They performed a series of batch drum experiments with different initial size distributions. By using tracers, they were able to see how granules grew under certain conditions. They found that primarily the width of the initial size distribution of the material had a profound effect on the type of granule growth mechanism that occurred. With a narrow initial size distribution, granulation proceeded according to the crushing and layering mechanism. The granules were quite weak and the smaller granules were crushed and their fragments were picked up by the larger ones. Also, granule growth continued throughout the experiments, not reaching a maximum value. Linkson et al. also noted that the larger the initial particles, the weaker the granules that were formed. Above a certain size of the initial particles, no granules could be formed. With a wide initial size distribution, granulation proceeded according to the coalescence mechanism. This was due to the fact that strong and dense (i.e. with a low porosity) granules were formed, which did not break. A maximum size was reached and after that, granules exhibited abrasion transfer-type growth, which did not alter the size distribution significantly. It is interesting to note that Linkson et al. also mentioned the influence of the initial size distribution (and therefore the growth mechanism) on the shape of the granules. Granules that grew according to the crushing and layering mechanism were spherical and granules that grew according to the coalescence mechanism were spheroidal. This was attributed to the fact that the granules that were formed by the crushing and layering mechanism possessed low surface strength and were therefore easily rounded off, whereas the granules that grew according to the coalescence regime formed dumbbells. These were stronger and therefore did not round off easily. Additionally, these dumbbells were likely to roll about the longest axis of the granules, so that the spheroidal shape persisted even if the granules were still fairly plastic.

Sastry and Fuerstenau conducted tracer experiments as well and from the results they were able to propose the basic five mechanisms of granulation [9]. Drawing a parallel between granulation and crystallization, they divided the granulating mass into a phase consisting of discrete, well-formed, granules and a continuous phase consisting of the feed particles, i.e. fines. The five mechanisms defined by Sastry and Fuerstenau are (see also Figure 2.3):

1. **Nucleation.** This the formation of new granules, i.e. well-formed particles, from
2. **Coalescence.** This is the clumping together of two granules, i.e. two well-formed particles, leading to the formation of a larger granule.

3. **Breakage.** The formation of smaller granules from one larger granule. Sastry and Fuerstenau demonstrated experimentally that the breakage of a granule does not yield fines, but rather a limited number of smaller granules.

4. **Abrasion transfer.** This occurs when the surfaces of two granules come into contact and a certain part of each granule is transferred onto the surface of the other one.

5. **Snowballing (or layering).** The layering of fines (new feed) onto already existing granules.

![Diagram](image)

**Figure 2.3:** Graphic representation of the five basic granule growth mechanisms, according to Sastry and Fuerstenau [9]. A: Coalescence, B: Breakage, C: Abrasion Transfer, D: Nucleation and Snow-balling (Layering).
2.2 Micro-scale modelling

The studies presented in the previous section focused on macro-scale phenomena. In this section, studies of granulation mechanisms at the micro-scale are presented.

Rumpf [10] continued Newitt and Conway-Jones's analysis of granule strength. Rather than focusing on the experimental determination of granule strength, Rumpf did a thorough theoretical study of the strength of all types of bonds that can exist in granules as well as testing his theory with experiments.

Rumpf started his analysis with an overview of the different types of bonding mechanisms in granules:

1. **Solid bridges** can be formed by sintering, melting, a chemical reaction or by the crystallization of dissolved materials. The latter occurs during drying of moist granules in which the binder contains dissolved material.

2. There are, according to Rumpf, three types of **movable liquid bridges**, similar to the distinction that Newitt and Conway-Jones made (see Figure 2.1): pores that are partly filled by the binding liquid (called the pendular state by Newitt and Conway-Jones), pores that are completely filled (called the capillary state by Newitt and Conway-Jones) and a state in which the binding liquid completely fills the pores and envelopes the solid (called the droplet state by Newitt and Conway-Jones).

3. **Not freely movable liquid bridges** such as viscous binders and adsorbed layers of liquid.

4. **Attraction between solid particles** due to van der Waals forces and electrostatic charges can be significant, but only if the separating distance between the particles is small or if there is no chance of charge equalization.

5. **Form closed bonds** occur when particles interlock. This type of bond can exist when the particles have an irregular shape and with suitable motion and compression.

From here on, Rumpf calculated the tensile strength of granules for each of the bond types he listed. Rumpf argued that the tensile strength should be investigated for two reasons: first of all, tensile stresses often lead to failure when brittle granules are sheared, as these granules cannot withstand the volume expansion that occurs due to shearing. Only very moist granules are not brittle. Secondly, it was possible to theoretically derive the tensile strength of granules and then compare it to experimental results.

Rumpf assumed the granules to consist of spherical, mono-sized, particles. Furthermore, he assumed a homogeneous structure of the granules. The results of his theoretical analysis are summarized in Figure 2.4.

In Figure 2.4 there is a broken horizontal line, dividing the range of theoretical strengths into two regions. Below the line is the tensile strength of granules with salt bridges and above it the tensile strength of granules that have solid bridges formed during
briquetting, i.e. by very high pressures. As the line is horizontal, it would indicate that
the tensile strength of granules having these solid bonds does not depend on the size of
the particles, but Rumpf stated that, in practice, granules consisting of smaller particles
are stronger. The strength of electrostatic bonds, which is also independent of particle
size is far below the range plotted in Figure 2.4.

Region A in Figure 2.4 represents the strength of van der Waals forces. This strength
depends on the size of the particles and on the separating distance of the particles. Particles
with adsorbed layers are much stronger. These particles fall in region B. Lines 1, 2a,
2b and 2c cover the range of tensile strengths due to capillary forces. It can be seen from
these four lines that granules with their void volumes completely filled with binder are
stronger and that granules made from particles with a wide size distribution are stronger.
Finally, even stronger granules can be made by sintering, which is represented by region D.
Obviously, wet granules obtain their strength from the liquid bonds, not from electrostatic
or Van der Waals forces.

Following his theoretical analysis, Rumpf tested his findings by making a number of
granules and measuring the tensile strength of the granules while they were still moist. This was by no means a trivial task. However, Rumpf managed to demonstrate that the tensile strength of his granules coincided reasonably well with the strength for movable liquid bridges which he predicted. In all cases, the measured strength was lower than the theoretical strength of granules with completely filled voids. Rumpf attributed this to the fact that air may have been trapped inside the granule and inhomogeneities in the granule structure.

Rather than focusing on the strength of granules, Ouchiyama and Tanaka theoretically derived the probability of a successful collision between two granules, i.e. the chance of two granules sticking together after they collide [11]. They made their analysis for rotating drums and pans and divided these granulating devices into two zones: a constant angular velocity zone and a tumbling zone. In the constant angular velocity zone, a compressive force acts on a pair of granules, leading to an increase of the contact surface area, which results in the formation of a dumbbell. This compressive force is independent of the granule size. In the tumbling zone, there are forces acting on the newly formed dumbbell, which may separate the two granules. These forces were assumed to be a function of the size of the two granules. Ouchiyama and Tanaka carried out an extensive analysis of all the forces that are involved in the process and from this, they calculated the probability of the coalescence of two granules. Although Ouchiyama and Tanaka introduced a number of empirical constants and empirical relationships between the separating forces and the size of the granules, they found that when the size difference of the two granules is large, the probability of coalescence is high and when the two granules are of the same size, the probability of coalescence is lowest. This led them to conclude that granules growing according to the balling mechanism can grow indefinitely, whereas granules that grow by coalescence have a maximum attainable size. Unfortunately, Ouchiyama and Tanaka did not study the kinetics of granulation as they only investigated the probability of coalescence when two granules collide and not the frequency with which two granules collide.

Kristensen et al. assessed the deformability of moist granules [12, 13], as they recognized that granule deformability is ‘one of the principal factors that govern granulation mechanisms and granule growth’. Rumpf had already shown that the strength of moist granules is derived from their mobile liquid bonds [10] and that an increasing amount of liquid binder will further increase the strength of these bonds. However, Rumpf used mono-sized spheres for his analysis, whereas in practical applications materials of different sizes and shapes are used. The strength of granules made from these polydisperse, non-spherical, powders deviate from Rumpf’s theoretical model in two ways: their tensile strength is much greater and increasing the amount of binder liquid reduces the strength. Kristensen et al. demonstrated this by measuring the tensile strength of cylindrical pellets made from glass ballotini with a narrow size distribution (almost mono-sized spheres) and lactose and dicalcium phosphate (polydisperse, non-spherical, powders) [12].

As stated before, pellets made from polydisperse powders possessed a much greater strength than what Rumpf’s model predicted. Kristensen et al. attributed this deviation from Rumpf’s model to particle-particle interactions. There was another deviation from Rumpf’s model: an increased amount of binder liquid leads to a reduction of the strength
of the pellets. This was explained by the fact that the binder liquid acts as a lubricant and increased amounts of binder therefore reduce friction, i.e. particle-particle interactions [12].

Kristensen et al. then formulated a theory for the mechanism of granulation [13]. They stated that after the formation of the initial nuclei, coalescence only occurred when these nuclei had sufficient strength. Another requirement for coalescence was that the granules were also deformable. After their formation, the granules were still brittle, but as the granules were densified, their saturation increased and at a certain critical saturation, the granules changed from brittle to plastic. They derived the following equation that describes granule deformation:

$$\sigma_{cr} = C_1 \frac{j^3}{\delta^{2/\alpha_0}}$$  \hspace{1cm} (2.1)

Here $\sigma_{cr}$ is the critical stress, $l_{cr}$ the critical strain, $\delta$ the limiting size of coalescence and $C_1$ and $\alpha_0$ are constants. Kristensen et al. stated that the granule growth rate was related to the limiting size of coalescence. The limiting size was related to the porosity and saturation in the following manner:

$$\delta^{2/\alpha_0} = C_2 \frac{l_{cr}^3 \epsilon^{1+C_3}}{1 - \epsilon \alpha_0 - C_4 S}$$  \hspace{1cm} (2.2)

Here $\epsilon$ is the porosity, $S$ the saturation, $\alpha_0$ the intrinsic interaction parameter describing the work required to separate particles at zero saturation and $C_2$, $C_3$ and $C_4$ are constants. $l_{cr}$ was also a function of the porosity and saturation, but the functional relationship was not known.

It is clear from Kristensen’s et al. analysis that there are a number of competing mechanisms: the granules require a certain minimum strength in order to survive the stresses in a granulator, but granules that are too strong do not deform sufficiently in order for them to coalesce. Densification causes a decrease in the porosity, which results in lower deformability and lower growth rates. On the other hand, densification also causes an increase in saturation, which increases the deformability and therefore the granule growth rate. Kristensen et al. concluded from Equation 2.2 that the effect of the critical strain on the growth rate is the dominating factor. The critical strain is determined mainly by the saturation. At a certain critical saturation, varying between 90 % and 100 %, depending on the material used, the critical strain increases dramatically, giving rise to coalescence. This was demonstrated by the fact that the correlation between mean granule size and granule saturation was almost unaffected by process parameters (see also Kristensen et al. [14]).

In addition to their theoretical analysis, Kristensen et al. investigated the influence of feed particle size and size distribution experimentally [13]. Using four different grades of dicalcium phosphate, they demonstrated that granules produced from small particles were stronger than granules produced from larger particles. In addition, they showed that wide particle size distribution produced granules that were much stronger. These findings were underlined by the fact that the granule growth rates of the formulations with the small particles and the wide size distribution were much lower.
Ennis et al. studied the influence of the viscosity of the pendular bond [15]. They conducted an analysis of the forces that are present when two granules with a liquid layer on their surface approach each other and collide, as shown in Figure 2.5. When these two granules approach one another, the liquid surface layers form a dynamic pendular bond. The strength of a dynamic bridge differs from a static bond since the liquid in the bond is moving. Therefore, the Laplace-Young equation, as used by Rumpf [10] underestimates the strength of the dynamic bridge because it does not take into account the viscous dissipation of the liquid layer. In fact, in an earlier publication, Ennis et al. showed that the viscous forces exceed the capillary forces by at least one order of magnitude [16].

![Figure 2.5](image_url)

**Figure 2.5:** Two approaching granules of radius $a$ with a liquid layer of thickness $h$. From Ennis et al. [15].

Ennis et al. derived a criterion for granule coalescence by stating that the relative kinetic energy of two colliding granules should be completely dissipated by the liquid layer at their surfaces. They calculated how the relative velocity of the granules changed from the moment their liquid layers came into contact during their approach, until the granules rebounded after they had collided. When that velocity was reduced to zero, two granules had coalesced. Ennis et al. defined two Stokes numbers as follows for their criterion: the viscous Stokes number,

$$St_v = \frac{8 \rho u_0 a}{9 \mu} \quad (2.3)$$

Here $St_v$ is the viscous Stokes number, $\rho$ the density of the granules, $u_0$ the initial velocity, $a$ the granule radius and $\mu$ the viscosity of the liquid layers (see also Figure 2.5); and the
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critical viscous Stokes number:

\[ St_v^* = \left(1 + \frac{1}{e}\right) \ln \left(\frac{h}{h_a}\right) \]  (2.4)

Here \( St_v^* \) is the critical viscous Stokes number, \( e \) the coefficient of restitution, \( h \) the thickness of the surface liquid layer and \( h_a \) a characteristic length of the surface asperities. Ennis et al. then proceeded to state that for a successful collision between two granules to occur, the viscous Stokes number had to be less than, or equal to, the critical viscous Stokes number.

Ennis et al. derived expressions to estimate \( u_0 \) in fluid beds and rotating drums. They then proposed three regimes of granulation: the non-inertial regime, the inertial regime and the coating regime. In the non-inertial regime, all values of \( St_v \) \(^1\) are lower than \( St_v^* \). All collisions between granules therefore lead to coalescence. As granule size increases, so does \( St_v \) and at some point the maximum value of \( St_v \) is approximately equal to \( St_v^* \). This is the inertial regime. In this regime, the granule kinetic energy and binder viscosity will dictate whether a collision will be successful or not. As granules grow even larger, there will be a point where the average value of \( St_v \) is equal to \( St_v^* \). In this regime, the coating regime, most collisions will be unsuccessful. Ennis et al. conducted a number of fluid bed granulation experiments that confirmed the existence of the three mentioned regimes. In addition, they used previously published drum granulation data from Newitt and Conway-Jones [5] and they showed that the process proceeded directly from the non-inertial regime to the coating regime. They explained this by pointing out that there is a narrow distribution of \( St_v \), as all the granules experience the same collision velocity, which is in the order of the revolution speed of the drum.

Ennis et al. only considered the viscous dissipation by the surface liquid layer of the granules and not the energy dissipated by the plastic and elastic deformation. On the other hand, Ouchiham and Tanaka considered the granules to be surface dry and deformable. Liu et al. extended the work of Ennis et al. by incorporating granule deformation [17]. They divided a binary granule collision in four stages: the approach stage, during which the granules are moving towards each other but are not yet in contact. The liquid layer is being squeezed out. The approach stage is followed by the deformation stage, where the granule surfaces are in contact and the granules still have kinetic energy, which is being dissipated by plastic and elastic deformation. After the relative velocity of the granules has been reduced to zero, the stored elastic energy is converted to kinetic energy, which is simultaneously being dissipated by the binder liquid layer. This is the initial separation stage. If the kinetic energy is not completely dissipated by the binder liquid layer, the granules will rebound. This is called the final separation stage. These stages are depicted graphically in Figure 2.6.

Like Ennis et al., Liu et al. stated that, for a successful collision to occur, the kinetic energy had to be dissipated completely. Through a thorough theoretical analysis, they proposed a criterion for coalescence, using the same granule properties as Ennis et al. (see

\(^1\)As the granules experience different conditions in a granulator, there is a distribution of values of \( u_0 \) and hence a distribution of values of \( St_v \).
Equations 2.3 and 2.4) and introducing the granule Young’s moduli, Poisson ratios and yield strengths, as the deformation of the granules was also taken into account. Liu et al. divided coalescence into two types, using the four stages as described above. Type I coalescence indicates that the kinetic energy of the granules is dissipated completely before the deformation stage. In other words, the kinetic energy is completely dissipated by the liquid binder and granule deformability has no influence. Ennis’ et al. theory can be applied to type I coalescence. Type II coalescence occurs when the kinetic energy is dissipated after the deformation stage. For type II coalescence, granule deformability plays an important role.

Liu et al. assessed the sensitivity to formulation and process properties, such as the amount of binder and the process intensity (which is represented by the relative velocity $u_1$ in the model). They found that for strong granules the amount of binder liquid had a profound influence on the coalescence probability. For weak, i.e. relatively deformable granules, this influence was much less pronounced. However, they found that weak granules can have a higher coalescence probability when the granules have a larger relative velocity, which is the opposite of what Ennis et al. predicted. The theoretical results were related to macroscopic granulation behaviour and they found that granules that exhibit induction type growth (see Section 2.3.5) fit type I coalescence. These are strong granules that only grow when they have a liquid layer on their surface. Ennis’ et al. model therefore also applies to induction type growth. Deformable granules that grow according to the steady growth (see Section 2.3.5) mechanism follow type II coalescence. Clearly Ennis’ et al. theory can not be applied here.

Simons et al. took yet another approach [18]. Unlike Ennis et al., they focused on
the strength of the liquid pendular bond due to the surface tension and the hydrostatic pressure due to the curvature of the pendular bond. Simons et al. calculated the energy required to rupture such a bond numerically and then derived an analytical approximation to the numerical solution. They argued that their work could be applied in the modelling of the deformation and fracture of bulk particulate materials. In a later publication, Fairbrother and Simons experimentally verified the rupture energies of pendular bonds [19]. They found that for systems with a zero contact angle the experimentally determined rupture energy was in excellent agreement with the approximation to the theoretical value, but for systems with a non-zero contact angle, the theoretical value was higher than the experimental value. Fairbrother and Simons attributed this to the fact that in the latter case, the pendular bond was not toroidally shaped.

2.3 Macro-scale modelling

Unlike the studies discussed in the previous section, many studies have focused on the macro-scale phenomena. Often these studies consisted of experiments conducted in laboratory scale or pilot scale equipment and usually the influence of certain process parameters on macroscopic properties such as the particle size distribution or particle porosity was investigated. In some cases statistical techniques such as factorial design were employed [20]. If conducted well, these experiments provide qualitative insight into the mechanisms of granulation as they occur in the granulator. However, the findings are not generally applicable because different formulations and granulating devices have been used. This may lead to seemingly contradictory results. In this section an attempt will be made to give an overview of the most important studies of macro-scale granulation behaviour.

2.3.1 The influence of process parameters

Amount of binder liquid

In many studies, the influence of the amount of binder liquid is studied. It is generally accepted that granulation can occur between two boundaries, e.g. [21, 22, 23]. When less than the minimum amount of binder is added, a wet powder with no clearly distinguishable granules will be formed and when more than the maximum amount of binder is added, an overwet paste will be formed [22]. Between these two boundaries, an increased amount of binder will give rise to more rapid growth and larger granules (e.g. [5, 6, 7, 20, 21, 24, 25, 26, 27, 28, 29, 30]). Although it is known that, in order for granulation to be successful, the amount of added binder must be such that the pores of the granules are filled with liquid 2, it is not possible to a priori predict the required amount of binder [21, 22, 23], since the pore saturation depends on the porosity which is a complex function of the size distribution and shape of the primary particles as well as the mixing intensity and the deformability of the granules.

2In other words: the pore saturation (see Equation 3.6) must be roughly equal to unity.
Primary particle size

Newitt and Conway-Jones discussed the profound effect that the primary particle size has on the granulation process [5] (see also Section 2.1). These can be briefly summarized as follows: granules consisting of small primary particles are stronger than granules consisting of larger particles. This caused the growth rates to be smaller for granules produced from finer powders. There was an upper limit on the size (in their case 209 μm) of the primary particles that could be used to produce granules. In addition, they also stated that powders with a wide size distribution produced strong granules, as the small particles are able to fit in the voids between the larger particles. Linkson et al. supported these findings [8] (see also Section 2.1), particularly the effects of the width of the distribution. In his theoretical analysis, Rumpf found a decrease in strength with increasing particle size [10] (see also Section 2.2), but he did not address the effect of the width of the size distribution since he only calculated particle strength of spherical, mono-sized particles. Finally, Kristensen et al. measured the deformability of granules consisting of powders with different size distributions [12, 13]. Their observations coincided with the ones described above.

Keningley et al. studied the effects of both binder viscosity as well as constituent particle size [22]. They granulated several grades of calcium carbonate with different silicone fluids as binder, thus covering a wide range of particle sizes and binder viscosities. All the experimental results were tested to determine whether granules were formed or not. The experimental results are summarized in Figure 2.7. It can be seen that formulations with small constituent particles readily form granules but when larger particles are used a viscous binder is required in order to produce granules. The data was tested against the theory of Newitt and Conway-Jones (see Section 2.1) and Ennis et al. (see Section 2.2). Newitt and Conway-Jones stated that the main parameters contributing to the strength of a granule were the binder surface tension and the constituent particle size. When Keningley et al. applied the theory they found that the critical size (i.e. the maximum particle size that can produce granules) was smaller than 8 μm, irrespective of viscosity. This is represented by the dashed vertical line in Figure 2.7. Ennis’ et al. theory indicated that there was a minimum viscosity (indicated by the dashed horizontal line in Figure 2.7) below which granule cannot be formed. However, Keningley et al. were able to produce granules with constituent particles larger than the critical size predicted by Newitt and Conway-Jones and with binders with a lower viscosity than the minimum viscosity predicted by Ennis et al. This clearly indicated the deficiencies of both models and demonstrated that both particle size as well as binder viscosity are crucial parameters which should be taken into account. Through a rough theoretical estimation, Keningley et al. were able to demonstrate that the impact strength of granules was the critical factor which determined whether granules would fracture or not. This determined whether or not a formulation formed granules or a paste. Keningley et al. found that the impact strength was determined by the forced viscous flow within the granules which depended mainly on the viscosity of the binder fluid and the pore size. The pore size is closely related to the constituent particle size. This theoretical analysis underlined their experimental findings.
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![Graph showing binder viscosity vs. median size of constituent particles.](image)

**Figure 2.7:** Experimental results from Keningley et al. [22]. The larger dots represent the formulations which produced granules, the smaller dots represent the formulations which produced a paste.

Mixing intensity

The mixing, or process, intensity of different granulation devices will be dealt with here. In drum granulation, the rotational speed of the drum determines the mixing intensity and in high shear mixers, the mixing intensity is determined by the impeller speed and the chopper speed, when a chopper is present.

Newitt and Conway-Jones conducted at several experiments at various rotational speeds in a batch rotating drum. They found that below a certain speed, the granule growth rate scaled linearly with the rotational speed. This is not surprising, since the granules grow by colliding with one another and the frequency of collisions is proportional to the rotational speed. When plotting granule size versus number of revolutions, the growth curves of experiments performed at different rotational speeds all collapsed onto one curve. Therefore, they used number of drum revolutions instead of time as the abscissa. This made it possible to compare results from different drums.

The influence of the impeller and chopper in a high shear mixer is less straightforward. For instance, Knight conducted experiments with sodium sulphate in a vertical high shear mixer [25]. This mixer was equipped with an impeller rotating on a vertical axis as well a tulip-shaped chopper fitted to the side of the mixer. He found a linear increase of the particle size with time, i.e. steady growth (see Section 2.3.5). The influence of the rotational speed of the impeller was tested by performing experiments at four different
speeds. Knight found that there was a strong correlation between the rotational speed of the impellers and the frequency of collisions and therefore there was a strong correlation between the rotational speed of the impellers and the growth rates:

$$k \sim 17.5N + 7.5N^2$$  \hspace{5em} (2.5)

In Equation 2.5 $k$ is a proportionality coefficient determining the number of binary collisions per unit time and $N$ is the rotational speed of the impellers. Knight also determined the effect of the chopper speed by performing identical experiments with the chopper either switched on (at a constant rotational speed) or off. He found that when the chopper was rotating the size distribution of the granules was narrower. Knight postulated that this was due to the fact that the chopper preferentially breaks larger granules. When Knight extended this hypothesis he concluded that the growth rates should be lower when the chopper was rotating. However, this was not the case. In fact, there was no notable difference between the course of the median size versus time for experiments with the chopper rotating or stationary (with all other settings identical). Knight concluded that the “neutral effect of the chopper on [the] granule growth rate [was] fortuitous.” He made speculations as to what neutralized the disintegrating action, but provided no proof.

Schaefer et al. found similar effects of the impeller speed [31]. They performed a number of factorially designed experiments on both a vertical as well as a horizontal high shear mixer. Growth rates (expressed per unit time) were higher at the high level of rotational speed in all cases. However, they attributed this effect to fact that the granules were compacted more densely at high impeller speeds. This resulted in a higher pore saturation and therefore a larger particle size. When they plotted granule size versus pore saturation rather than processing time, the effect of a higher rotational speed disappeared [31]. Their conclusion is somewhat different from that of Knight [25] who stated that the increased growth rates were due to the increased frequency of collisions between granules, whereas Schaefer et al. attributed the increased growth rates to higher rates of densification.

In contrast with the findings of Knight, Hoornaert et al. observed a strong influence of the chopper [29]. They granulated a mixture that mimicked enzyme containing granules for the detergent industry in a pilot scale Lödige high shear mixer with a horizontal axis. Their formulation exhibited induction behaviour (see Section 2.3.5) and they observed that when the chopper was switched off the granules were not compacted sufficiently as there was no appreciable growth of the granules after the liquid addition stage over a two hour period. This led Hoornaert et al. to conclude that only the chopper was capable of compacting the granules to the required level. Wauters performed similar, factorially designed, experiments on the same apparatus [20]. He found that at high rotational speeds of the impeller, there was more attrition at the end of a two hour experiment. He postulated that the chopper was responsible for attrition and that the main function of the impeller was to bring the granulating mass in contact with the chopper. Following the logic of this postulation, it was expected that a higher impeller speed should shorten the induction time (see Section 2.3.5). This hypothesis was tested by Menon, who conducted experiments at three different impeller rotational speeds [32]. The results of his experiments were inconclusive regarding the influence of the rotational speed
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of the impeller. However, Menon also conducted a number of experiments in order to test the influence of the chopper. The results of these experiments were in agreement with those of Hoornaert et al. In one case, Menon switched the chopper off during the rapid growth stage which followed the induction stage and growth ceased immediately. This was strong evidence of the function of the chopper in this particular case. The function of the impeller was less clear. Iveson et al. reasoned that “the ploughshare only serves to bring granules into contact with the chopper which causes consolidation and coalescence” and that “there must be a critical minimum [impeller rotational] speed, below which it becomes important, otherwise at zero [impeller rotational] speed no granules would enter the chopper zone [33].” In summarizing the difference between the results regarding the effect of the process intensity in high shear mixers, Iveson et al. concluded that there no such thing as a “generic high shear mixer [33].” Apart from the fact that the size of the high shear mixer may play a role, as well as the fact whether the rotating shaft was horizontal or vertical, the formulation used may show a different dependency on the process intensity. This may further complicate an attempt to derive the general effect of process intensity in a high shear mixer on the granule growth behaviour.

Liquid distribution

Knight et al. conducted experiments in a high shear mixer with three grades of calcium carbonate with molten polymer (polyethylene glycol) as a binder [28]. They studied the effect of the method of liquid addition by using three methods: “pour-on”, where the binder liquid was simply poured onto the stationary powder bed, “spray-on”, where the liquid binder was atomized over the agitated powder mass and “melt-in”, where the binder was added as a solid flake and mixed with the powder. The solid melted within three minutes of subsequent processing. With all three methods of binder addition, Knight et al. observed similar behaviour: immediately after binder addition, a bimodal distribution existed. In most cases, this bimodal distribution changed to a monomodal distribution, as the finer particles grew due to coalescence and the large particles that were initially formed fragmented because they were relatively porous. The major difference between the three methods of liquid addition were the size and the amount of the large particles formed after liquid addition. In the case of the pour-on experiments, the large particles were around 2000 μm in size and they amounted up to approximately 15 % of the granular mass. However, in the case of the spray-on experiments, the size of the large granules was around 1000 μm and their amount was less than 10 %. Lastly, melt-in resulted in a fraction of large granules that were around 500 μm and amounted to less than 5 %. Apparently, a better dispersion of the binder (assuming that binder dispersion is improved in the following order: pour-on, spray-on, melt-in) results in smaller fraction of large particles, or lumps, and that the size of these lumps is also reduced by improved binder distribution. The occurrence of a bimodal distribution after liquid addition is, as Knight et al. stated, “an intrinsic feature of processes in which liquid is mixed into a fine solid.”

Holm et al. [34, 35] conducted factorially designed experiments in a high shear mixer in which they studied the effect of the method of liquid addition, along with other variables.
They used two levels of atomization of the binder, resulting in smaller droplets with a geometric mean size of 71 $\mu$m and larger droplets with a geometric mean size of 162 $\mu$m as well as no atomization, i.e. the binder was pumped directly into the mixer. It was found that when the binder was finely atomized, the liquid distribution was homogeneous. When the binder was not finely atomized, a homogeneous distribution was obtained during the wet massing of the granular mass through the action of the chopper and impeller. This was explained by the fact that the initial inhomogeneous liquid distribution was caused by the presence of lumps with a higher moisture content. Schaefer et al. conducted similar experiments in high shear mixers and their observations were identical [31].

2.3.2 A more modern division of granulation mechanisms

Recently, Ennis and Litster adopted a more modern approach for dividing the granulation mechanisms [1]. One can argue that the boundary between particles belonging to the “fines” phase and the “well-formed” phase as proposed by Sastry and Fuerstenau (see Section 2.1) is rather arbitrary. If one considers all particles to be of one phase, then snowballing and coalescence are the same mechanism. Ennis and Litster therefore divided the granulation process into three fundamentally different mechanisms. Every granulation process starts with the addition of a liquid binder to the dry powder, forming the first granules, or nuclei. This mechanisms is referred to as wetting and nucleation. These granules then collide with other granules, which can lead to coalescence as well as to densification of the granules. This is referred to as growth and consolidation. Finally, the competing, size-reducing, mechanism is referred to as breakage and attrition. Figure 2.8 shows a graphical representation of these three mechanisms.

![Figure 2.8](image-url)

**Figure 2.8:** The three basic mechanisms of granule growth (A: Wetting & Nucleation, B: Growth & Consolidation, C: Breakage & Attrition) according to Ennis and Litster [1].

In the following sections, nucleation and wetting as well as breakage and attrition will be discussed briefly, since the rest of this chapter is almost entirely devoted to growth and consolidation.
2.3.3 Wetting and nucleation

Although wetting and nucleation are crucial in a granulation process, since the size distribution of the nuclei and the binder distribution among the nuclei have a profound effect on the entire granulation process, it has not often been investigated separately [36]. However recently it is gaining more attention from various research groups worldwide.

Nucleation and wetting can be envisaged as consisting of three different stages:

- Wetting. The stage in which the binder and powder first come into contact and the binder spreads over the powder or vice versa.

- Nuclei formation. During this stage, the nuclei are actually formed.

- Binder dispersion. The stage in which binder is further distributed throughout the powder due to mechanical forces.

Wetting is determined by thermodynamic properties, such as the contact angle between the binder and the powder and the surface tension of the liquid, but also by kinetic properties that can retard the binder penetrating the powder bed. Examples of the latter are the size of the droplet, the viscosity of the binder, the porosity of the powder bed and the size of the pores through which the binder has to progress. The wetting stage can be put in quantitative terms with the use of the theoretical penetration time, which describes the time required to penetrate a powder bed for a single droplet. Denesuk et al. found [37]:

\[
\tau_{CDA} = \frac{2V_0^2}{\pi^2 \epsilon_S^2 \epsilon_d^4 R_{pore} \gamma_{LV} \cos \theta} \frac{\mu}{\pi^2 \epsilon_S^2 \epsilon_d^4 R_{pore} \gamma_{LV} \cos \theta}
\] (2.6)

Here \(\tau_{CDA}\) is the theoretical penetration time in the case where the projected area of the drop on the surface is constant (this is one limiting case), \(V_0\) is the total volume of the droplet, \(\epsilon_S\) is the surface porosity, \(\epsilon_d\) is the radius of the footprint of the drop on the powder surface, \(R_{pore}\) is the effective pore radius based on cylindrical pores, \(\mu\) is the liquid viscosity, \(\gamma_{LV}\) is the liquid surface tension and \(\theta\) is the solid-liquid contact angle. Hapgood et al. validated Equation 2.6 by studying the behaviour of droplets on a powder surface and their findings were quite promising [38].

Nuclei formation is also dictated by parameters such as the size of the binder droplet and the spreading behaviour of the binder which is controlled by the contact angle and surface tension. Finally, binder dispersion is controlled by the mechanical forces in the granulator such as the rotating speed of impellers and choppers in a high shear mixer, the fluidising velocity in a fluid bed and (to a much lesser extent) the rotating speed of a rotating drum. It should be noted, however, that the influence of the mechanical forces is less pronounced when the binder is delivered more homogeneously to powder, as will be shown in the following paragraphs.

A number of different nuclei formation mechanisms have been proposed. The most important of these will be discussed here. Schaeffer and Mathiesen performed experiments with a laboratory scale high shear mixer using lactose and molten polyethylene glycol as a binder [39]. Based on their results they proposed two possible mechanisms for nuclei
formation: the distribution mechanism and the immersion mechanism, see Figure 2.9. Schaefer and Mathiesen found that the distribution mechanism gave rise to a more uniform distribution of the binder.

![Figure 2.9: Nuclei formation mechanism. a) distribution mechanism, b) immersion mechanism. From Schaefer and Mathiesen [39]](image)

The relative size of the binder droplets with respect to the particle size determines according to which mechanism the nuclei are formed. When the binder droplets are small compared to the particles, the nuclei are formed according to the distribution mechanism and vice versa. Schaefer and Mathiesen stated that in fluidized bed granulation the immersion mechanism was the main mechanism of nuclei formation due to the lack of mechanical forces. In high shear mixers both mechanisms occur simultaneously since the mechanical forces tend to reduce the size of the binder droplets. Low shearing forces, large binder droplets and a high binder viscosity tend to shift the nuclei formation mechanism to the immersion mechanism and vice versa.

Vonk et al. proposed the destructive nucleation mechanism based on experiments conducted in a high shear mixer [40]. They stated that growth starts with a single droplet of binder. When this droplet comes into contact with the powder, a nucleus is formed. This nucleus was said to be loose, having a high porosity and low tensile strength. According to Vonk et al., this nucleus can then grow by layering until a size of approximately 5 mm is reached, being quite large for granules produced in a high shear mixer. Consequently this nucleus is broken up through attrition or fragmentation. Attrition occurs when the nuclei comes into contact with other nuclei or with the granulator wall and fragmentation occurs when the nucleus comes into contact with the impeller or with the chopper. Obviously the forces that act upon the nucleus are larger when it comes into contact with either the impeller or with the chopper resulting in smaller particles after the break-up. Vonk et al. called the nucleus that was produced by the single droplet of binder the primary nucleus. The particles that were produced after fragmentation were called the secondary nuclei. The secondary nuclei, being able to withstand the shearing forces within the high shear mixer, were then able to grow further by coalescing with other particles, provided they were consolidated sufficiently. These proposed steps were said to occur simultaneously rather than sequentially.
The dimensionless spray flux and the nucleation regime map

In order to develop a more generalized picture of nucleation and to quantify the influence of process parameters, Litster et al. proposed a dimensionless spray flux [41] and Hapgood et al. constructed the nucleation regime map [42]. Both of these will be discussed in this section.

The dimensionless spray flux is an equipment independent parameter that describes how the binder droplets interact with the dry powder. One can envisage that when a dry powder bed is wetted by droplets of binder from a spray, two extreme cases exist:

1. Each droplet is separate and forms one nucleus after it hits the bed. Each nucleus is formed from one droplet only. This is droplet controlled nucleation.

2. Droplets of binder come into contact with powder that has already been wetted, i.e. the footprints of the droplets overlap. In extreme cases the surface of the powder will cake.

In the spray zone, which is the zone where binder and powder are brought into contact, the projected area of drops by the nozzle per unit time equals:

\[ \dot{a}_d = \frac{3V}{2d_d} \quad (2.7) \]

Here \( \dot{a}_d \) is the projected area of drops by the nozzle per unit time, \( \dot{V} \) is the volumetric spray rate and \( d_d \) is the diameter of the droplet. When Equation 2.7 is combined with the rate at which the surface of the dry powder bed is renewed, this yields:

\[ \Psi_a = \frac{3V}{2Ad_d} \quad (2.8) \]

Here \( \Psi_a \) is the dimensionless spray flux and \( \dot{A} \) is the powder flux through the spray zone. The dimensionless spray flux can now be used as an indication of how well dispersed the binder droplets are. Litster et al. conducted experiments where a dry powder surface was once passed through a spray zone. The formed nuclei were then analysed. From their results, Litster et al. concluded that for \( \Psi_a < 0.1 \), nucleation is in the drop controlled regime and for \( \Psi_a > 0.5 \), much of the bed surface cakes. A low value for \( \Psi_a \) alone is not sufficient to guarantee drop controlled nucleation. The time a droplet of binder requires to penetrate the powder bed also determines the type of nucleation mechanism. Hapgood et al. constructed a nucleation regime map [42], which included both these parameters, see Figure 2.10. The concept of the nucleation regime map is similar to that of the regime map for granule growth, which is presented in Section 2.3.5.

The nucleation regime map features the dimensionless spray flux, \( \Psi_a \), as the abscissa and the drop penetration time, \( t_p \), (made dimensionless by the particle circulation time, \( t_c \)) as the ordinate. When the dimensionless spray flux is small (< 0.1) and the penetration time is short, nucleation occurs within the drop controlled regime where each droplet of binder liquid forms one individual granule. When either the penetration time is long or
the dimensionless spray flux is large, nucleation occurs within the mechanical dispersion regime, where mechanical forces are mainly responsible for the eventual size distribution of the nuclei. At present, the nucleation regime is still in need of validation but the concept has great potential. The findings presented in Section 2.3.1 are supporting the nucleation regime map albeit in a qualitative way.

2.3.4 Breakage and attrition

This section will focus on the breakage and attrition of wet granules, i.e. of particles which are still present in the granulator as opposed to breakage of dried granules, which is beyond the scope of this thesis.

There are very few reports in the literature that focus on breakage of wet granules [36].
Sometimes breakage is part of a mechanism and consequently it receives some attention. One good example is the destructive growth mechanisms as proposed by Vonk et al. [40], see also Section 2.3.3. The mechanical dispersion regime in the nucleation regime map is similar to the destructive growth mechanism. This indicates that breakage can be an important mechanism in controlling the granule size distribution. It is therefore important to know under what conditions breakage occurs and, if it occurs, at what rate. Knowledge of such matters is limited. There is enough qualitative evidence, however, that an increased impeller speed and/or chopper speed in a high shear mixer leads to a reduction in particle size [36]. Tardos et al. have found that for a Stokes’ deformation number (see Section 2.3.5) larger than 0.2, granules break [23]. Keningley et al. found a relationship between the size of constituent particles and the minimum binder viscosity required to form granules with particles of that size [22] (see also Section 2.3.1). If a formulation with either larger constituent particles or a lower binder viscosity was used, no granules were formed, or rather, the granules that were formed were too weak to survive in the granules. This also served as an indication under which circumstances breakage occurs. It must be stated, however, that both Tardos et al. as well as Keningley et al. used rather simple models for their systems and therefore their results serve mainly as quantitative indications.

2.3.5 A regime map for granule growth

In Section 2.2 two different concepts describing granule growth are explained. On the one hand, Ouchiyama and Tanaka [11] and Kristensen et al. [12, 13] consider granulation to occur when plastic granules deform on impact and a contact area is created. On the other hand, Ennis et al. [15] consider granulation to occur when the liquid binder layer at the surface of the granules is able to dissipate the relative kinetic energy of two colliding granules. There are two types of granules growth which follow these two theories (see Figure 2.11), being Steady Growth and Induction Type Growth.

Weak, deformable, granules form a large contact area upon collision and these exhibit steady growth behaviour. This is marked by a steady increase of the particle size in time. Strong granules that consolidate slowly exhibit induction behaviour. During the induction time, these granules slowly consolidate until they are surface wet and the growth rate is approximately zero. After the induction stage, the granules are surface wet and are able to coalesce upon collision. This is accompanied by rapid growth. Apart from steady growth and induction type growth, Iveson and Lister defined five other growth regimes:

- “Dry”, free-flowing powder: at very low liquid contents, no nuclei will be formed.
- Nucleation only: in this regime, there is insufficient binder for the nuclei that have formed during the liquid addition stage to coalesce.
- “Crumb”: when the granules are too weak to withstand the shearing forces in the granulator. No stable granules are produced, leaving a “crumb” in the granulator.
- Rapid growth: when a relatively large amount of binder is present, the growth rate becomes extremely high and uncontrollable.
Steady Growth Behaviour

Granule Size

Increasing Liquid Content

Granulation Time

Induction Behaviour

Granule Size

Increasing Liquid Content

Granulation Time

High Deformation System

Low Deformation System

Figure 2.11: Steady growth behaviour and Induction behaviour. Deformable granules follow steady growth behaviour, which is marked by a steady increase of the granules size in time. Less deformable granules follow induction behaviour, which is marked by an induction period of little growth, followed by a stage of rapid growth. From Iveson and Litster [26].

- Slurry/Over-wet mass: when very large amounts of binder are added, a paste or slurry is formed, rather than granules.

From these descriptions it is obvious that the “Dry/Free flowing” and “Slurry/Over-wet mass” regimes are outside the boundaries of the required binder liquid amount (see Section 2.3.1). These two regimes, together with the “Crumb” and the Rapid growth regime are generally undesirable.

Iveson and Litster attempted to derive a quantitative expression for the location of the boundaries between the regimes mentioned above. In order to do so, they derived two dimensionless numbers, since they recognized that the two main properties were granule deformability and binder amount. Firstly, they derived a deformation number, \( D_{c} \), which
is a measure for the deformability of the granules:

$$D_e = \frac{\rho_g U_c^2}{Y_g}$$ (2.9)

Here $\rho_g$ is the granule density, $U_c$ the representative collision velocity and $Y_g$ the granule dynamic yield stress. Secondly, the maximum pore saturation, which is a measure for the amount of binder, is given by:

$$s_{\text{max}} = \frac{w \rho_s (1 - \epsilon_{\text{min}})}{\rho_l \epsilon_{\text{min}}}$$ (2.10)

Here $s_{\text{max}}$ is the maximum pore saturation, $w$ is the amount of binder liquid (kg/kg), $\rho_s$ the skeletal density of the solid particles, $\rho_l$ the liquid density and $\epsilon_{\text{min}}$ the minimum granule porosity. In a subsequent paper, Iveson et al. used the Stokes’ deformation number, $St_{\text{def}}$, instead of the Deformation number [33]. The Stokes’ deformation number is defined as follows:

$$St_{\text{def}} = \frac{m_g U_0^2}{2 V_p \tau(\dot{\gamma})}$$ (2.11)

Here $m_g$ is the mass of the granule, $U_0$ the velocity of the collision, $V_p$ the volume of the granule and $\tau(\dot{\gamma})$ a characteristic stress, which can be substituted by the yield stress, $Y_g$, assuming the granule is a highly concentrated slurry with a negligible apparent viscosity compared to the yield strength [23]. The Stokes’ deformation number is the ratio between the kinetic energy and the energy required for deformation. It follows from Equations 2.9 and 2.11 that the Deformation number is twice the Stokes’ deformation number. The rationale behind using the Stokes’ deformation number instead of the Deformation number was that Tardos et al. used the Stokes’ deformation number for determining different modes of granule growth. They experimentally determined that for values of $St_{\text{def}}$ higher than 0.2, wet granules do not survive the conditions in the granulator. Therefore, Iveson et al. used this value as the boundary between the “Crumb” regime and the Nucleation only, Steady growth and Rapid growth regimes (see Figures 2.12 and 2.13).

Iveson and Litster performed batch experiments in a rotating drum, using various grades of glass ballotini and binders of varying viscosities in order to cover a wide range of combinations. They measured the granules growth rates as well as granule porosities. The yield stress of the granules was determined by measuring the impact deformation of cylindrical pellets of known porosity and moisture content. From the results of these experiments, they were able to locate the boundaries between the different regimes (see Figure 2.13).

Next Iveson and Litster discussed the influence of several process parameters. They explained how binder liquid amount, process agitation intensity, binder liquid viscosity and surface tension and particle size would influence both the Stokes deformation number and the maximum pore saturation. Although the minimum granule porosity, which directly influences the maximum pore saturation and indirectly influences the Stokes’ deformation number, cannot be predicted beforehand, the regime map proved to be a very powerful tool
in understanding granule growth behaviour. An impressive demonstration of its potential was given by the fact that Iveson and Litster were able to modify the growth behaviour from steady growth, i.e. deformable granules, to induction behaviour, by increasing the binder viscosity.

In a subsequent paper, Iveson et al. validated the regime map by using granulation data from experiments with various raw materials, such as glass ballotini, copper concentrate, iron ore fines and a sodium sulphate/cellulose mixture [33]. In addition, results from experiments in a high shear mixer were also used. This revealed some of the limitations of the regime map. For instance, it was found that estimating the correct value for $U_c$ (see Equation 2.11) was not possible. Only an order of magnitude estimate could be made. In the case of the drum, this was the drum perimeter speed and in the case of the high shear mixer, the average chopper tip speed was chosen. As a consequence it was not possible to use data from both granulation devices for the map. Iveson et al. chose to use the data from the rotating drum, which are shown in Figure 2.13. These results were quite promising, and Iveson et al. concluded that the regime map was a useful tool for comparing the behaviour of different raw materials in the same type of granulator.
However, a theoretical analysis following the work of Liu et al. [17] revealed that apart from the Stokes' deformation number and the maximum pore saturation, binder viscosity must also play a role in the growth behaviour. Therefore, Iveson et al. stated that the regime map "represents only a 2D slice of at least a three parameter space [33]."

![Figure 2.13](image.png)

**Figure 2.13:** Section of the regime map showing the experimental results of a variety of raw materials. The "Chalcopyrite in Drum" data is derived from the data presented in Chapter 3.

## 2.4 Conclusions

In 1968, Sherrington wrote [43]:

[Granulation] has been used for more than thirty years during which time a great deal of process development has been carried out and much process know-how has been accumulated but little attempt has been made to gain a fundamental understanding of the crucial wet granulation stage.
And in 1976, Carstensen et al. wrote [44]:

Granulation technology has been employed for close to a century in pharmacy, yet many aspects are still confined to what is considered art.

Finally, in 1998 Iveson and Litster stated that "in spite of its economic importance and over 40 years of research, granulation is still more of an art than a science [26]."

Does this mean that no advances have been made, despite all the research efforts? This is certainly not the case. For example, deformability has been recognized as a key parameter. When granules deform when they collide, a large area of contact is created which allows them to stick. Therefore, granules require a certain level of deformability in order to be able to grow. On the other hand, granules require a certain amount of strength in order to be able to withstand the shearing forces in a granulator. As a consequence, granulation occurs within a narrow range of deformability where the granules are strong enough to survive yet deformable enough to grow. Granule deformability is dictated by a number of parameters. Newitt and Conway-Jones observed that granules in the capillary state possess the greatest strength. When these granules are compacted further they become surface wet and at that point they are deformable which allows them to coalesce [5]. Kristensen et al. observed that when the pores of the granules become saturated with binder, the granules change from brittle to elastic [13]. They also stated that granules produced from small particles or particles with a wide size distribution are stronger. It is clear from all these finding that the initial particle size distribution, the amount of binder and the porosity dictate the deformability of the granules. Unfortunately, there are no quantitative models available which can predict, a priori, the amount of liquid required for producing granules of a certain desired size. Therefore, the aforementioned findings can only be applied in a qualitative sense.

A great number of studies have been conducted in which the influence of a certain process parameter was investigated. This has created a vast body of empirical knowledge. However, the use of different types of formulations and granulators can obscure results or lead to contradicting conclusions.

The importance of the nucleation stage in the granulation process is recognized. Therefore, in recent years, a growing number of studies have been concerned with nucleation and the method of binder delivery. Research groups are beginning to identify what parameters play a significant role in the formation of the nuclei and how the formed nuclei affect the granulation process. With the concept of the nucleation regime map and the dimensionless spray flux attempts are being made to quantify the influence of crucial parameters, although at present these methods are in the stage of development.

In summary, we can conclude that the influence of many parameters on the granulation process is understood, albeit in a qualitative manner in many cases. The observations made during experiments can be explained qualitatively, but to predict granulation behaviour, even qualitatively, is difficult. It seems that if one is interested in finding out how granules behave in a certain granulator, one is forced to adopt a trial and error method of finding the correct settings for the process parameters in order to produce the desired granules.
List of symbols

\( a \)  
granule radius (\( \text{m} \))

\( a_0 \)  
exponent in Equation 2.1

\( A \)  
powder flux through the spray zone (\( \text{m}^2 \text{s}^{-1} \))

\( a_d \)  
projected area of drops per unit time (\( \text{m}^2 \text{s}^{-1} \))

\( C_1 \)  
constant in Equation 2.1 (\( \text{N} \text{ m}^{-2+2/a_0} \))

\( C_2 \)  
constant in Equation 2.2 (\( \text{m}^{2/a_0} \))

\( C_3 \)  
exponent in Equation 2.2

\( C_4 \)  
constant in Equation 2.2 (-)

\( d_d \)  
diameter of the droplet (\( \text{m} \))

\( D_e \)  
deformation number (-)

\( e \)  
coefficient of restitution (-)

\( h \)  
thickness of the surface liquid layer (\( \text{m} \))

\( h_a \)  
characteristic length of the surface asperities (\( \text{m} \))

\( k \)  
proportionality coefficient (-)

\( l_{cr} \)  
critical strain (-)

\( m_p \)  
the mass of the granule (\( \text{kg} \))

\( N \)  
rotational speed of the impellers (\( \text{s}^{-1} \))

\( r_d \)  
radius of the footprint of the drop on the powder surface (\( \text{m} \))

\( R_{porc} \)  
effective pore radius based on cylindrical pores (\( \text{m} \))

\( S \)  
pore saturation (-)

\( s_{max} \)  
maximum pore saturation (-)

\( S t_{def} \)  
Stokes’ deformation number (-)

\( S t_v \)  
viscous Stokes number (-)

\( S t^* \)  
critical viscous Stokes number (-)

\( u_0 \)  
initial velocity (\( \text{m s}^{-1} \))

\( U_0, U_c \)  
representative collision velocity (\( \text{m s}^{-1} \))

\( V \)  
volumetric spray rate (\( \text{m}^3 \text{s}^{-1} \))

\( V_0 \)  
total volume of the drop (\( \text{m}^3 \))

\( V_p \)  
volume of the granule (\( \text{m}^3 \))

\( w \)  
amount of binder liquid (\( \text{kg/kg} \))

\( Y_g \)  
granule dynamic yield stress (\( \text{N m}^{-2} \))

Greek symbols

\( \alpha_0 \)  
intrinsic interaction parameter (-)

\( \gamma_{LV} \)  
liquid surface tension (\( \text{N m}^{-1} \))

\( \delta \)  
limiting size of coalescence (\( \text{m} \))

\( \epsilon \)  
porosity (-)

\( \epsilon_{min} \)  
minimum granule porosity (-)

\( \epsilon_S \)  
surface porosity (-)

\( \mu \)  
viscosity of the liquid or liquid layers (\( \text{Pa s} \))

\( \rho, \rho_g \)  
density of the granules (\( \text{kg m}^{-3} \))
\[ \begin{align*}
\rho_l & \quad \text{liquid density (kg m}^{-3}\text{)} \\
\rho_s & \quad \text{skeletal density of the solid particles (kg m}^{-3}\text{)} \\
\sigma_{\sigma} & \quad \text{critical stress (N m}^{-2}\text{)} \\
\tau_{CDA} & \quad \text{the theoretical penetration time, constant drawing area (s)} \\
\tau(\dot{\gamma}) & \quad \text{a characteristic stress (N m}^{-2}\text{)} \\
\theta & \quad \text{solid-liquid contact angle (-)} \\
\Psi_a & \quad \text{dimensionless spray flux (-)}
\end{align*} \]
Chapter 3

An experimental study of induction type behaviour

In this chapter the mechanism of a granulation process that exhibits induction type behaviour is investigated. Particular interest is paid to the effect of the amount of binder liquid and the method of addition. Finally, a new mechanism of induction type behaviour is put forward.

3.1 Introduction

Systems that exhibit induction type behaviour are characterised by a stage during which little or no growth occurs, the so-called induction stage [26]. During this stage, the granules are compacted and liquid is squeezed from the interior of the granule on to the surface of the granules (See Figure 2.11). Once the pores of the granules are saturated, they become surface wet and the liquid layer at their surface makes further growth possible. Increasing the amount of binder liquid results in a shorter induction period. A more detailed description of induction type behaviour is given in Section 2.3.5.

In the study presented in this chapter, copper concentrate (chalcopyrite) was granulated in a batch-scale rotating drum with water as the binder. In order to elucidate the various mechanisms that occur during granulation, different kinds of experiments were conducted:

1. Experiments in which binder and powder are pre-mixed prior to an experiment. These experiments were conducted in order to determine the kinetics of size enlargement and to determine the minimum and maximum amount of binder with which granules can be produced.

2. Experiments conducted in the same manner as in 1) during which the porosity was determined.

3. Experiments with a liquid addition phase, i.e. the binder was sprayed onto the powder while the drum was rotating. During these experiments the effects of the
liquid addition were determined.

4. Experiments conducted in the same manner as in 3) during which the liquid distribution was measured.

It is obvious from the previous paragraph that the compaction and therefore the deformation of the granules plays a key role. Iveson and Litster studied the deformability of granules [45] and they found that it was controlled by three types of forces: interparticle forces, capillary and viscous forces. The interparticle forces arose from friction between the particles of which a granule is made up. When small particles are used, there are more interparticle contacts and the granules become less deformable. Iveson and Litster found that when a low viscosity binder, in their case water, was used, an increased amount of binder resulted in increased deformability of the granule. This was due to a lubrication effect, which Kristensen et al. also mentioned [12, 13]. However, with a high viscosity binder, such as glycerol, Iveson and Litster observed the reverse. Therefore, they concluded that the effect of binder content on granule deformability cannot be predicted beforehand. The capillary forces were studied by altering the surface tension of the binders. Binders with a lower surface tension produced weaker, more deformable granules, but usually the effect of surface tension was swamped by the effect of viscous forces.

Hancock et al. studied the rheological behaviour of wet masses using a mixer torque rheometer [46, 47]. The rheological behaviour of a wet mass is assumed to be related to the deformability of the granules. Hancock et al. measured the torque as a function of time for a variety of powder/binder formulations [46]. They found that a larger amount of binder liquid resulted in a higher torque measurement. However, at a certain critical binder liquid level, there was an initial torque peak followed by a gradual decrease. This was attributed to the fact that due to mixing action the granules were compacted which resulted in overwet particles which were weaker. Hancock et al. were unable to predict the location of this critical boundary. Apart from the amount of binder liquid, they also tested the influence of other parameters. They found that an increased binder viscosity, by dissolving polymers such as HPMC (hydroxypropylmethylcellulose) and PVP (polyvinylpyrrolidone) into the water, led to an increased torque. The influence of the particle size was less straightforward. In general, smaller particles formed stronger wet masses, expressed by the increased torque, but their shape seemed to have a significant effect as well. The complex effect of particle shape on the rheological behaviour of the wet mass was not discussed by Hancock et al.

Monitoring the porosity of the granules is also paramount. There are a number of studies available in the literature that report the porosity of granules. Iveson et al. [48, 49] studied the consolidation of granules and they proposed a first order model for granule consolidation. They assumed that there is a minimum porosity that granules reach after they have experienced a large number of collisions. The rate of consolidation is proportional to the driving force, which is the difference between the actual porosity and the minimum porosity. In equations, this gives:

\[
\frac{d\epsilon}{dN} = -k(\epsilon - \epsilon_{\text{min}})
\]  (3.1)
3.2. EXPERIMENTAL

Here \( \epsilon \) is the porosity of the granule, \( \epsilon_{\text{min}} \) is the minimum porosity of the granule, \( N \) the number of drum revolutions and \( k \) is the rate constant. Integrating Equation 3.1 yields:

\[
\epsilon = \epsilon_{\text{min}} + (\epsilon_0 - \epsilon_{\text{min}}) e^{-kN}
\]  

(3.2)

Here \( \epsilon_0 \) is the initial porosity. Iveson et al. found that this equation was in good agreement with their experimental data. They also observed that for low viscosity binders (e.g. water) the minimum porosity decreased and the rate constants increased with increasing binder content. They attributed this effect to the reduced particle-particle friction within the granule. However, in a later paper, Iveson and Litster altered their conclusion regarding the effect of binder content on the rate constant \( k \) [49]. They stated that due to the large uncertainty in \( k \), there was no significant effect of the binder content on \( k \). With high viscosity binders, Iveson et al. observed the opposite: with increasing binder content, the minimum porosity increases. This is attributed to the increased viscous dissipation of the binder [48]. Iveson and Litster related the compaction model presented in Equations 3.1 and 3.2 to their study of granule deformation and were able to derive a relationship between \( k \) and the granule deformability, expressed as the yield strength [49]. Capes and Danckwerts also measured granule porosities for a sand-water formulation [7]. They found that with increasing binder content, the porosity at the end of an experiment increased. It must be mentioned however, that they only took three samples during an entire experiment and therefore the data is not suitable for fitting Equation 3.2 but the data does show a trend. Kapur and Fuerstenau measured the porosities of granules produced from limestone and water [50]. Their findings seem to suggest that an increased amount of binder results in a higher minimum porosity and this minimum porosity is reached quicker. However, Kapur and Fuerstenau made no comments about these phenomena. In Section 3.2.4 these seemingly contradictory results will be addressed in more detail.

3.2 Experimental

3.2.1 Materials

For the drum granulation experiments copper concentrate (chalcopyrite, \( CuFeS_2 \)) was used, which was supplied by Mt. Isa Mines Ltd. (Mount Isa, Queensland, Australia). This material had a mass mean diameter of 118 \( \mu \text{m} \) and 50\% of the mass was smaller than 63 \( \mu \text{m} \). Attempts to determine the particle size distribution more accurately with a laser diffraction method were unsuccessful due to the cohesiveness of the material. The skeletal density of the chalcopyrite was 3796 \( \text{kg m}^{-3} \). Tap water was used as the binder, which was assumed to possess the standard material properties for water.

3.2.2 Equipment

The granulation experiments were performed using a stainless steel rotating drum with a diameter of 0.3 m and a length of 0.2 m. It was equipped with six wedge-shaped lifters of
5 mm in height to promote the tumbling motion and a scraper in order to prevent caking on the wall. The front and back of the drum were sealed with detachable Perspex covers, the front cover having a 160 mm orifice which enabled sampling. During an experiment this orifice was covered with a Perspex hatch in order to reduce evaporation. The speed of the drum could be varied, but was set to a constant value of 21.4 rpm during all experiments. A photograph of the drum can be seen in Figure 3.1.

![Photograph of the rotating drum granulator. The front cover has been removed so the scraper and lifters can be seen.](image)

For the experiments in which the binder was sprayed onto the powder, a nozzle and pressure pot system, containing the binder liquid, was used. The nozzle (TP 500017, Spraying Systems Co., Wheaton, U.S.A.) had a fan shaped spraying pattern. The width of the spray as well as the flowrate were determined by the pressure supplied by the pressure pot. In order to characterize the behaviour of the spray, a number of tests were conducted in which the distribution of the binder fluxes was determined at three different pressures. This was done by spraying over an array of 18 by 6 cuvettes (normally used for chemical analysis by light absorption), each having a width of 12.6 mm by 12.6 mm and an opening of 10.0 mm by 10.0 mm. A different nozzle (TP 650017, Spraying Systems Co., Wheaton, U.S.A.), which also had a fan shaped spraying pattern, was also characterized in this manner. This particular spray was tested at different heights, i.e. different distances between the nozzle and the array of cuvettes.
3.2. EXPERIMENTAL

3.2.3 Granulation experiments

Pre-mix experiments

For the "pre-mix" granulation experiments, both the powder, which had been dried for at least eight hours, and the binder were premixed in a plastic bag, after which the mixture was pushed through a 2 mm sieve, in order to obtain an identical starting distribution for all experiments. For each experiment, approximately 1.4 kg of dry powder was used. A total number of 14 experiments were conducted out with binder contents ranging from around 37.0 vol.% to 43.4 vol.% (see also Table 3.3). This method of premixing powder and binder and of creating an identical, narrow sized, particle size distribution of the starting material has been applied before by other workers [5, 7, 24, 51].

Samples were taken at distinct intervals by scooping approximately 100 grams of material from the centre of the drum. In order to test the suitability of this sampling method, one experiment was performed where the granulator was stopped after 16 minutes and nine samples were withdrawn from the centre of the drum. After the ninth sample was taken, the drum was empty. By comparing the first sample to the rest of samples it was possible to test the representativity of the sampling method.

The amount of binder in the samples was determined by measuring the weight of the wet samples and their weight after drying. Determining the amount of binder in the samples was necessary since in the earlier stages of the research it was revealed that there was marked discrepancy between the added amount of binder and the amount of binder present in the sample. This was due to evaporation which was caused by the fact that the laboratory which was used for the granulation experiments was not climate controlled. Similar effects were encountered by Iveson [51]. The samples were dried for at least eight hours in an oven at a temperature of approximately 70 °C until they reached a constant mass. Chalcopryite does not form hydrates and therefore it was concluded that all water was removed during drying [52]. After drying, the granule size distribution was determined by sieving, using a $\sqrt{2}$ series, ranging from 250 $\mu$m to 11.2 mm.

Spray-on experiments

For these experiments, the powder was also dried prior to an experiment. The dry powder was hand sieved over a 710 $\mu$m sieve and approximately 1546 gram of the material was placed in the drum. The nozzle was attached to a stand and it was positioned inside the drum through the orifice in the front cover of the drum. It was located in the centre of an imaginary line parallel to the drum axis as shown in Figure 3.2. The nozzle was positioned in such a way that the fan was parallel to the drum axis. In most experiments, the distance between the nozzle and the powder was either 10 or 17 cm.

Prior to an experiment, the flowrate at the set pressure was determined and thus the time required to deliver the desired amount of binder could be calculated. At the start of an experiment, the drum started rotating and the nozzle was switched on. A cup was placed underneath the nozzle which collected the binder. After a short period of time, typically around ten seconds, the fan pattern of the spray was fully developed and the
cup was removed and the timer was started. After the nozzle had delivered the required amount of binder, the cup was placed underneath the nozzle again and the nozzle was switched off and removed from the drum. In this way, binder delivery was controllable in each experiment since only a fully developed spray was used.

Table 3.1 lists all the “spray-on” experiments that were conducted. All experiments were duplicated.

A number of different phenomena were investigated during the “spray-on” experiments, as the last column in Table 3.1 indicates. These were:

- **Growth behaviour**: During these experiments, the attention was focused on the evolution of the particle size distribution and the length of the induction time. After the liquid addition phase, samples were taken at distinct time intervals. The location were these samples were taken from was approximately at one third of the drum width. This had proven to be an appropriate location for sampling by Iveson [51]. The moisture content and particle size distribution were determined in the same manner as the samples taken from the “pre-mix” experiments.

- **Water distribution in axial direction**: During these experiments, particular interest was paid to the moisture content of samples taken at different locations within the drum. For this purpose, the drum was divided into three (imaginary) sections of equal width, as depicted in Figure 3.3. Samples were taken at distinct time intervals
3.2. *EXPERIMENTAL*

<table>
<thead>
<tr>
<th>#</th>
<th>Binder content (vol%)</th>
<th>Binder flowrate (ml/min)</th>
<th>Pressure of atomization (bar)</th>
<th>Distance from nozzle to powder (cm)</th>
<th>Phenomenon studied</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-4</td>
<td>37.8 %</td>
<td>94.0</td>
<td>5.0</td>
<td>10</td>
<td>Growth behaviour</td>
</tr>
<tr>
<td>5-10</td>
<td>37.8 %</td>
<td>94.0</td>
<td>5.0</td>
<td>17</td>
<td>Growth behaviour</td>
</tr>
<tr>
<td>11-12</td>
<td>37.8 %</td>
<td>53.5</td>
<td>2.0</td>
<td>10</td>
<td>Growth behaviour</td>
</tr>
<tr>
<td>13-15</td>
<td>37.8 %</td>
<td>75.0</td>
<td>3.5</td>
<td>10</td>
<td>Growth behaviour</td>
</tr>
<tr>
<td>16-18</td>
<td>41.6 %</td>
<td>94.0</td>
<td>5.0</td>
<td>10</td>
<td>Growth behaviour</td>
</tr>
<tr>
<td>19-20</td>
<td>45.4 %</td>
<td>94.0</td>
<td>5.0</td>
<td>10</td>
<td>Growth behaviour</td>
</tr>
<tr>
<td>21-23</td>
<td>37.8 %</td>
<td>94.0</td>
<td>5.0</td>
<td>10</td>
<td>Binder distribution in axial direction</td>
</tr>
<tr>
<td>24-26</td>
<td>37.8 %</td>
<td>94.0</td>
<td>5.0</td>
<td>17</td>
<td>Binder distribution in axial direction</td>
</tr>
<tr>
<td>27</td>
<td>37.8 %</td>
<td>94.0</td>
<td>5.0</td>
<td>10</td>
<td>Binder distribution among the particle sizes</td>
</tr>
<tr>
<td>28-34</td>
<td>37.8 %</td>
<td>94.0</td>
<td>5.0</td>
<td>10</td>
<td>Effect of smaller granules</td>
</tr>
</tbody>
</table>

*Ignoring evaporation*

*from all three sections* and their moisture content and particle size distribution were analysed.

- Water distribution among the particle sizes: The samples taken from these experiments were frozen using liquid nitrogen immediately after they were drawn from the granulator and they were sieved while they were still frozen. Their moisture content was determined after the liquid nitrogen had evaporated.

- Effect of smaller granules: In three experiments, the experiment was stopped after the liquid addition phase and the contents of the granulator were removed and
riffle split. One portion was immediately placed back into the granulator and the experiment was continued. The other portion was hand sieved over a 710 µm sieve and the oversize was further granulated after the experiment with the first half had finished. In this manner, the effect of the small granules could be studied. In the other four experiments, the granulator was not stopped. Samples of 200 to 300 grams were drawn from the drum and these were hand sieved over a 710 µm sieve and the oversize was immediately placed back in the drum. This procedure was repeated four or five times after which the amount of granules smaller than 710 µm had been reduced significantly.

Figure 3.3: Schematic drawing of the granulator, showing the three sections of the drum: (B)ack, (C)entre and (F)ront.
3.2.4 Porosity measurements

The porosity of the granules was monitored in six experiments, in which the binder level varied between 37.0 vol% and 42.9 vol%. The apparent density of these samples was determined by measuring the weight of the sample and the volume of kerosene it displaced in a 50 ml volumetric flask. Care had to be exercised in order to remove trapped air bubbles between the granules. Iveson et al. have shown that kerosene does not displace binder or air in the intragranular pores. From the apparent granule density, the granule porosity was calculated using the following equation:

$$\epsilon = 1 - \frac{\rho_{gr}}{\rho_s (1 + m\frac{\rho_l}{\rho_s})}$$  \hspace{1cm} (3.3)

Here $\rho_{gr}$ is the apparent granule density, $\rho_s$ and $\rho_l$ are the solid and liquid densities and $m$ is the binder content (m$^3$ of binder/m$^3$ of solid). This technique was also used by Capes and Danckwerts [7]. Although Capes and Danckwerts used benzene instead of kerosene, the method was essentially the same.

At a later stage of the investigation, it became clear that this method of porosity measurement cannot be used to determine the porosity of surface wet granules. During compaction, the volume of the pores is reduced and they gradually become filled with binder liquid. The displaced volume of the granule decreases during this stage. When the pores are completely filled with binder liquid, a further reduction of the pore volume will lead to an expulsion of the liquid on to the granule surface. The displaced volume of the granule will not change as this equals the total volume of binder and solid. Even if the kerosene (or any other immersing liquid) strips the liquid layer off the surface of the granule, it will still displace the kerosene and will therefore not affect the measured porosity. One would expect the measured porosity values to level off after the granules become surface wet and that this constant porosity value is higher when more binder liquid is present as granules with more binder become surface wet at a higher porosity. This may well explain the difference in the observations of Iveson et al. [48] and Capes and Danckwerts [7] since Iveson et al. studied only systems which did not grow, i.e. their granules did not become surface wet. Kapur and Fuerstenau used mercury porosimetry for their porosity measurements [50]. Since this method is fundamentally different from the liquid displacement method, the preceding argument cannot explain the difference in their findings and those of Iveson et al.

3.3 Results and discussion

3.3.1 Spray characterization

In Figure 3.4 an example of a contour plot is shown. This shows how the binder flux varies with position underneath the nozzle. As expected, the fluxes are highest in the centre, i.e. directly underneath the nozzle-tip. Since the nozzle is supposed to produce a fan-shaped spray, the width of the spray is much larger than the depth of the spray.
Figure 3.4: Contour plot of the binder flux distribution in grams of binder per second per square meter. Nozzle: TP500017, pressure: 5 bars (flowrate: 90 ml/min), nozzle height: 13.2 cm. The arrow indicates the direction in which the powder in the drum would move.

In Appendix A the results of the other experiments can be found. From these figures it can be concluded that, in general, at a low pressure, and therefore at low flowrate, a narrower spray is developed. In addition, the maximum binder flux in the centre of the spray is also higher, which could lead to local overwetting in the drum.

To study how the binder flux distribution affects the powder in the drum, the concept of the dimensionless spray flux is adopted (see Section 2.3.3):

$$\Psi_a = \frac{3\dot{V}}{2Ad_d} \quad (2.8)$$

Here $\Psi_a$ is the dimensionless spray flux, $\dot{V}$ is the volumetric spray rate, $d_d$ is the diameter of the droplet and $\dot{A}$ is the powder flux through the spray zone. The dimensionless spray flux is a single number that characterizes the whole spray. Having measured the flux distribution of the spray, it would be more sensible to calculate the distribution of the dimensionless spray flux. In order to do so, the area of the spray is divided into sections, each corresponding to a single column of cuvettes. These columns are parallel to the trajectory of the powder as it traverses the spray zone. This trajectory is indicated by the arrow in Figure 3.4. For each column $i$, the dimensionless spray flux is then calculated according to:

$$\Psi_{a,i} = \frac{3\dot{V}_i}{2A_id_d} \quad (3.4)$$

$\dot{V}_i$ is calculated by summing the flow rates of binder collected in all the cuvettes in one column, $A_i$ is calculated by multiplying the tip speed of the drum with the width of a column, which is equal to the width of the opening of the cuvettes. Finally, the values for the size of the droplets were given by the manufacturer and are shown in Table 3.2. It is expected that the size of the droplets is not uniform and may vary with location within in the spray but since such detailed data is not available the values from Table 3.2 will be used.
Table 3.2: Droplet sizes produced by the nozzle as supplied by Spraying Systems Co.

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>Droplet size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>100</td>
</tr>
<tr>
<td>3.5</td>
<td>80</td>
</tr>
<tr>
<td>5.0</td>
<td>60</td>
</tr>
</tbody>
</table>

The results of these calculations are presented in Figures 3.5 to 3.8.

Figure 3.5: Dimensionless spray flux as a function of position within the spraying zone. Nozzle used: TP500017, nozzle height: 13.2 cm, pressure as denoted in the legend.

From these figures a number of observations can be made. First, at constant height, a higher pressure yields a higher maximum dimensionless spray flux. This observation holds for both nozzles. Second, a higher pressure (at constant height) also leads to a more even distribution of the liquid since the width of the area being wetted is larger. This is also apparent from the figures in Appendix A. Naturally, these observations were to be expected. Thirdly, the nozzle height has a marked influence on the distribution of the dimensionless spray flux. At a low nozzle height, the maximum dimensionless spray flux is markedly higher and the distribution is much less homogeneous. Although the influence of the nozzle height was tested for the TP650017 nozzle, similar results are expected for the TP500017 nozzle, which is the nozzle that was used for the spray-on granulation experiments. Given the fact that a high nozzle height leads to a more evenly distributed
Figure 3.6: Dimensionless spray flux as a function of position within the spraying zone. Nozzle used: TP650017, nozzle height: 13.5 cm, pressure as denoted in the legend.

Figure 3.7: Dimensionless spray flux as a function of position within the spraying zone. Nozzle used: TP650017, nozzle height as denoted in the legend, pressure: 3.5 bar.

dimensionless spray flux in the spray zone as well as a lower maximum, it is expected that the nozzle height in the drum will have a significant effect.
3.3. RESULTS AND DISCUSSION

Figure 3.8: Dimensionless spray flux as a function of position within the spraying zone. Nozzle used: TP650017, nozzle height as denoted in the legend, pressure: 5 bar.

3.3.2 Pre-mix experiments

Method of sampling

In Figure 3.9 the particle size distributions of some of the samples are plotted. It can be seen that the first sample slightly underrepresents the largest fraction and slightly overrepresents the middle fractions. There was no trend visible in the other samples. The differences in the other samples can be attributed to experimental error. Since the changes in particle size during the growth stages were very large, it was concluded that the first sample was representative for the entire particle size distribution in the drum and therefore, the sampling technique was considered adequate for this study. In addition, segregation was not visually observed either.

Growth behaviour

In Figure 3.10 the results of some experiments are plotted. If one studies the course of the mean diameter of the experiment with a binder amount of 38.40 %, it is clear that there is a period of very little growth, i.e. the induction stage. After this stage, very rapid growth occurs. Apparently, chalcopyrite exhibits induction type behaviour. One of the main characteristics of induction type behaviour is that the granules are consolidated during the induction stage until liquid is squeezed onto the granule surface. In other words, the granules become surface wet. This was in accordance with visual observations, as is shown in Figure 3.11. Iveson et al. have determined the deformability of the chalcopyrite and
Figure 3.9: Particle size distributions of four of the nine samples taken. For the sake of clarity, not all distributions are shown.

water formulation to include it in their updated regime map [33], see also Section 2.3.5 and Figure 2.13. According to their measurements, this system of chalcopyrite and water, when it is granulated in a rotating drum, is in the induction regime.

From Figure 3.10 a number of observations can be made. First of all, chalcopyrite exhibits three growth types, being nucleation only, when the binder level is less than approximately 37%, induction type behaviour, when the binder level is between 37% and 43.39% and rapid growth for binder levels starting from 43.39%. The "nucleation only" growth type means that the induction time is infinite, i.e. no rapid growth stage occurs. Although it is not shown in Figure 3.10, the experiment was terminated after 3000 revolutions, i.e. 90 minutes, and no rapid growth stage had occurred at that time. This also shows the effect of increasing the binder content on the induction time, which is in accordance with the theory [26] and other experimental observations [29]. In Table 3.3, the induction times of all the experiments are depicted, including their binder content.

Since some of the binder evaporated during an experiment, the amount of binder present in the sample was not the same at the beginning of the experiment as at the beginning of the growth stage. Binder loss rates during an experiment varied slightly, but typically they were around 0.4 vol.% per 100 revolutions (i.e. binder levels went from, for example, 40.4 vol.% to 40 vol.% in 100 revolutions). The binder amounts as depicted in the legend are the binder amounts at the beginning of the rapid growth stage, rather than at the beginning of the experiment. This is because it may well be possible that
3.3. RESULTS AND DISCUSSION

![Graph showing the evolution of mass mean diameter in time for different amounts of binder.](image)

**Figure 3.10:** Evolution of mass mean diameter in time for different amounts of binder.

the amount of binder at the beginning of an experiment is above the minimum required level for reaching the rapid growth stage. However, if the binder level drops below that minimum level due to evaporation during the induction stage of an experiment, the rapid growth stage does not occur. This may lead one to think that the starting binder level is insufficient for rapid growth to occur, which is not the case if the experiment were to be repeated in a climate controlled laboratory, where no evaporation occurs. For the experiment with no rapid growth, the binder amount was approximately 37 vol.% at the start of the experiment. Obviously, the rapid growth stage was not reached. Since the binder level decreased during the experiment it is difficult to say what the critical binder level is for rapid growth to occur, but it must be around or below 37 vol.%.

When the induction times of all the experiments that exhibited a rapid growth stage are plotted versus their binder amount at the start of the rapid growth stage, Figure 3.12 is obtained. An empirical model to describe these results is given by:

$$
\tau_{\text{ind}} = \frac{C_1}{(m - m^*)}
$$

(3.5)

In this equation, $\tau_{\text{ind}}$ is the induction time, $m$ the amount of binder ($m^3$ of binder/$m^3$ of solid), $C_1$ a constant and $m^*$ is the critical binder amount. It can be seen that at the critical binder amount, the induction time is infinite, in other words, the rapid growth stage does not occur. Naturally, for binder levels below the critical binder amount, Equation 3.5
Figure 3.11: Samples taken during an experiment with 38.4% binder (see also Figure 3.10). Samples #3 through #6 are shiny due to the fact that these granules are surface wet. This marks the start of the rapid growth stage. The samples were taken at the following number of revolutions: #1: 0 revs, #2: 107 revs, #3: 203 revs, #4: 257 revs, #5: 385 revs, #6: 646 revs.

should not be used. Fitting Equation 3.5 to the experimental results yields: \( C_1 = 7.9 \pm 2.1 \) (revs) and \( m^* = 0.350 \pm 0.009 \) (m³ of binder/m³ of solid).

Compacting behaviour

A fundamental way to study induction times is by looking at the granule porosity and the pore saturation. As stated before, in granulating systems that exhibit induction type behaviour, rapid growth starts when the binder liquid is squeezed onto the surface of the granules. This implies that the binder liquid, which is in the interior of the granule is gradually being squeezed out. This is due to a decrease in porosity and therefore an increase in pore saturation. Pore saturation is defined as the volume of binder liquid divided by the volume of the pores in a granule, therefore:

\[
S = \frac{m(1 - \epsilon)}{\epsilon}
\]  

(3.6)

Here \( S \) is the granule pore saturation. The porosity of the granules was monitored in six experiments. A typical result of the change of the porosity during one experiment is depicted in Figure 3.13. It can be seen that the data is in good agreement with the
Table 3.3: List of the “pre-mix” experiments (see items 1. and 2 in Section 3.1).

<table>
<thead>
<tr>
<th>Binder content (vol %)*</th>
<th>Induction time (Revs)</th>
<th>Porosity determined?</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 37 % **</td>
<td>∞ **</td>
<td>no</td>
</tr>
<tr>
<td>&lt; 37 % **</td>
<td>∞ **</td>
<td>no</td>
</tr>
<tr>
<td>37.0 %</td>
<td>345</td>
<td>yes</td>
</tr>
<tr>
<td>38.1 %</td>
<td>116</td>
<td>yes</td>
</tr>
<tr>
<td>38.4 %</td>
<td>324</td>
<td>no</td>
</tr>
<tr>
<td>38.8 %</td>
<td>249</td>
<td>no</td>
</tr>
<tr>
<td>39.4 %</td>
<td>118</td>
<td>yes</td>
</tr>
<tr>
<td>40.1 %</td>
<td>130</td>
<td>no</td>
</tr>
<tr>
<td>40.4 %</td>
<td>82.8</td>
<td>yes</td>
</tr>
<tr>
<td>40.5 %</td>
<td>179</td>
<td>no</td>
</tr>
<tr>
<td>41.9 %</td>
<td>68.4</td>
<td>yes</td>
</tr>
<tr>
<td>42.0 %</td>
<td>150</td>
<td>no</td>
</tr>
<tr>
<td>42.9 %</td>
<td>47</td>
<td>yes</td>
</tr>
<tr>
<td>43.4 %</td>
<td>40.8</td>
<td>no</td>
</tr>
</tbody>
</table>

*Due to evaporation, the actual binder content differed from the added amount of binder. In order to be able to compare the experiments, the moisture content that was determined at the end of the induction stage is stated here.

**In these experiments, the rapid growth stage did not occur. Therefore, the binder content is said to be below the critical amount below which the rapid growth stage does not occur.

first order model as given by Equation 3.2. The results of the fitting are summarised in Table 3.4. In one case, the fit produced a negative minimum porosity and the results of this experiment were not used for further analysis. In contrast with Iveson et al. [48, 49], who found that with more amount of binder, the final porosity of the granules was lower, no effect of the amount of binder on the extent and rate of compaction can be observed. However, it is very well possible that the amount of scatter obscured the effect of the amount of binder on \( \epsilon_{\text{min}} \) and \( k \).

Table 3.4: Results of fitting the porosity data

<table>
<thead>
<tr>
<th>Binder amount</th>
<th>( \epsilon_0 ) (-)</th>
<th>( \epsilon_{\text{min}} ) (-)</th>
<th>( k ) (revs(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>36.98 %</td>
<td>0.317 ± 0.006</td>
<td>0.309 ± 0.003</td>
<td>0.05 ± 0.011</td>
</tr>
<tr>
<td>38.07 %</td>
<td>0.328 ± 0.006</td>
<td>0.311 ± 0.004</td>
<td>0.043 ± 0.04</td>
</tr>
<tr>
<td>39.36 %</td>
<td>0.320 ± 0.002</td>
<td>0.25 ** ± 0.16</td>
<td>0.0021 ± 0.0006</td>
</tr>
<tr>
<td>40.44 %</td>
<td>0.393 ± 0.003</td>
<td>0.335 ± 0.002</td>
<td>0.25 ** ± 0.12</td>
</tr>
<tr>
<td>42.93 %</td>
<td>0.331 ± 0.015</td>
<td>0.25 ** ± 15</td>
<td>0.0019 ± 0.007</td>
</tr>
</tbody>
</table>

** These values were arbitrarily set, as fitting yielded values which were physically not possible.

The pore saturation is calculated using Equation 3.6. An example of this is plotted
Figure 3.12: Induction time as a function of binder amount at the beginning of the rapid growth stage.

Figure 3.13: Porosity versus number of revolutions for a single experiment. Binder amount: 38.07 vol.%. The points indicated by crosses were not used for fitting Equation 3.2 since these samples were drawn during the rapid growth stage.

in Figure 3.14. The fitted line was obtained by using the porosity fit and the measured
and interpolated values for the amount of binder. In Figure 3.14 the course of the mass mean diameter is also plotted. At the end of the induction stage, the granules reached a critical pore saturation and they became surface wet. In this case, the critical pore saturation was 0.897 (-). The fact that the granules were surface wet although the critical pore saturation was less than unity can be explained by the fact that air pockets were trapped inside the granules [17]. In Figure 3.15 the pore saturations of all the experiments are plotted. The pore saturation at the the point where the induction stage ended is also indicated in this figure. It can be seen that the pore saturation is around 0.85 when the rapid growth stage starts. In three cases, the pore saturation reached a maximum and then decreased before the induction stage ended. However, one would expect the pore saturation to increase steadily during the induction stage and, after reaching a critical value, one would expect the rapid growth stage to start. What caused this phenomenon is not clear. Due the fact that only a limited number of the porosity measurements could be used for fitting Equation 3.2, there was some scatter in the porosity fits. In addition, the amount of binder was another source of error in the calculation of the pore saturation. It may be possible that due to these errors, it may appear that the pore saturation first reached a maximum and then decreased before the rapid growth stage started. However, this hypothesis could not be tested.

![Figure 3.14: Pore saturation and mass mean diameter as a function of the number of revolutions for a single experiments. The bar indicates the end of the induction stage. Binder amount: 39.36 vol.%](image)

### 3.3.3 Spray-on experiments

**Growth behaviour**

In Figure 3.16 two typical results of the spray-on experiments are shown. This figure does not reveal an influence of the pressure of the nozzle in the range that was used. Figure
3.17 shows the induction times for all experiments that were conducted with a nozzle height of 10 cm. No clear trend can be observed that would support the notion that the pressure of the nozzle has an influence.

On the other hand, nozzle height seems to have an influence on the growth kinetics. Figure 3.18 shows that the induction time is slightly shorter at a nozzle height of 17 cm. The trendlines were obtained by fitting Equation 3.5. These serve as an indication, since the number of data points was small and only data from a narrow range of binder contents was available. However, the data suggest that when the distance from the nozzle is larger, the induction time is shorter. The data of Figure 3.12 is also plotted in Figure 3.18 in order to allow a comparison of the spray-on and pre-mix data.

**Binder distribution in axial direction**

As described in Section 3.2.3, the drum was divided into three imaginary sections, Front, Centre and Back (see Figure 3.3). Samples were drawn from each of these sections and the binder content and the particle size distribution of the samples was determined. In Figure 3.19 the binder content of the samples is plotted. The binder content of a sample is plotted as the deviation from the average binder content of all samples of that experiment. This facilitates comparison of the different experiments, since not all experiments had the same amount of binder, probably due to different rates of evaporation. The results of
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![Graph showing mean diameter as a function of the number of revolutions with different pressures and binder contents.]

**Figure 3.16:** Mean diameter as a function of the number of revolutions. The nozzle height was 10 cm.

![Graph showing induction time as a function of binder content with different pressures.]

**Figure 3.17:** Induction time as a function of binder content. The nozzle height was 10 cm, the operating pressures of the nozzle were 2, 3.5 and 5 bar (see legend).

the experiments with a nozzle height of 10 cm and the results of the experiments with a nozzle height of 17 cm are plotted in a different figures.

A number of observations can be made from Figure 3.19. First of all, shortly after spraying the binder liquid, the granules in the centre section of the granulator contain
Figure 3.18: Induction time as a function of binder content for all experiments.

(a) Nozzle height: 10 cm  
(b) Nozzle height: 17 cm

Figure 3.19: Liquid distribution in axial direction in the drum for two nozzle heights. The binder content is plotted as the difference between the measured binder content and the average binder content of an experiment.

more binder than the granules in the other two sections. This result was to be expected since the results from the characterization of the spray revealed that more binder liquid was delivered to the centre of the spray zone. Another striking observation is that the distribution of binder liquid in the drum is not entirely symmetrical. In some cases, granules in the front section of the drum contain more binder liquid than the granules
in the back section and vice versa. However, the most important observation is that the binder liquid distribution in the axial direction is more homogeneous when a nozzle height of 17 cm was used. In addition to this finding, it can be seen that the binder liquid is distributed evenly throughout the drum after a shorter period of time.

Segregation

In Section 3.3.2 it was concluded that there was no appreciable segregation (see also Figure 3.9). However, in this case where the binder liquid and the powder were pre-mixed. The results in the previous paragraph show that when the binder liquid is sprayed onto the powder, the centre section of the drum receives more binder liquid than other sections of the drum. It would therefore seem logical that the granules formed in the centre are larger since they contain more binder liquid. An additional experiment was conducted with a nozzle height of 8 cm. Since the nozzle height is even smaller in this case, the effect of inhomogeneous binder liquid distribution is expected to be more pronounced. In Figure 3.20, a number of photographs taken during this experiment are shown. One can observe that directly after the binder liquid has been delivered, large granules are in the centre section of the drum and small granules are in the outer sections. Subsequently, these large granules migrate to the sides of the drum and remain in these sections. It is obvious that segregation occurs in the drum granulator, but it is not observed when the particle size distribution is relatively narrow. However, when the binder liquid is not distributed homogeneously, the particle size distribution will be wider and this can then lead to segregation.

Binder distribution among the particle sizes

One experiment was conducted with a nozzle height of 10 cm, a nozzle pressure of 5 bar and a binder content of 37.8 vol.%. Samples were taken which were immediately frozen using liquid nitrogen. The granules were then sieved while they were still frozen. It was found that when the granules were sieved while wet, the sieves became clogged. Hence the results of only one experiment (see Table 3.1) were useful. In Figure 3.21 these results are given.

After the samples were sieved, several size classes were combined in order to produce one size class that contained approximately 40 grams of granules. This was done in order to reduce the statistical error in the determination of the moisture. Therefore, each graph in Figure 3.21 contains only four size classes. One can also note that the boundaries of these size classes shift because the granules grew larger during the course of an experiment.

From Figure 3.21 a number of observations can be made. Firstly, after 105.7 revolutions, which is shortly after the spraying stage, which lasted 42.3 revolutions, the binder is not distributed homogeneously among the particle size classes. The binder content of the largest granules is markedly higher than that of the smaller granules. Butenski and Hyman also found that the larger granules contained more binder liquid than the finer fractions [53]. This situation persist until the end of the induction stage. In this experiment, the induction stage ended after approximately 550 revolutions. Therefore, the last
(a) Photograph taken directly after spraying (50.3 revolutions). Large, overwet, granules in the centre of the drum and small, dry, granules in front and back.

(b) Photograph taken after 113.5 revolutions. Large granules have segregated to the front and back of the drum. Smaller granules can be seen in the centre.

(c) Photograph taken after 208.5 revolutions. The larger granules remain segregated. The granules have become surface-wet.

**Figure 3.20:** Series of photographs taken during an experiment demonstrating segregation. Nozzle height: 8 cm, nozzle pressure: 3.5 bar, 37.8 vol.% binder.

sample (676.3 revolutions) was well within the rapid growth stage. This is also indicated by the boundaries of the size classes (recall that the size classes were chosen in such a way that each size class contained a sufficient mass of granules). From studying the liquid distribution in the last sample, it becomes clear that once the induction stage is ended, the binder liquid is distributed evenly among the particle size classes. This is consistent with the findings of Knight et al. [28]. They granulated a fine powder in a high shear mixer and added the binder liquid by simply pouring it onto the dry powder after which they switched on the impellers. In their case rapid growth started when the binder liquid
3.3. RESULTS AND DISCUSSION

Figure 3.21: Binder content as a function of granule size class for one experiment. Samples were taken at various times. Each chart represents one sample. Nozzle height: 10 cm, nozzle pressure: 5 bar, 37.8 vol.% binder.

was distributed homogeneously.

Effect of smaller granules

When the evolution of the particle size distribution rather than the mean diameter is studied, Figure 3.22 is obtained. This figure indicates that after the induction stage a dramatic change occurs. During this particular experiment, the induction stage ended after approximately 450 revolutions. It can be seen that the particle size distribution during the induction stage is narrow and does not change appreciably. The particle size distribution after 441 revolutions, i.e. at the end of the induction stage, is much wider. During the rapid growth stage, the particle size distribution widens considerably and shifts to the right along the particle size axis.

In Figure 3.23, the course of the mean diameter of the same experiment is plotted as well as the fraction of small granules (defined as granules smaller than 500 μm). It is clear
that the induction stage ends when the small granules have disappeared. The results of the three experiments with different binder contents support this finding.

The results shown above seem to indicate that the amount of small granules controls the duration of the induction stage. In order to test this hypothesis, a total of seven experiments were conducted (see Table 3.1) in which the amount of small granules was manipulated. During three of these experiments, the contents of the drum were removed after approximately 200 revolutions and riffle split into two equal parts. One part was then placed back into the drum and the other part was hand sieved over a 710 μm sieve. All these actions took approximately ten minutes. A sieve with a slightly larger aperture size than 500 μm was chosen in order to prevent clogging since the granules were wet and also because it was assumed that with hand sieving in a relatively short period of time, a complete separation of particles smaller and larger than 500 μm could not be achieved with a 500 μm sieve. However, two of these experiments yielded no appreciable growth, even after several thousand revolutions. Apparently, too much binder had evaporated during the riffle splitting and the subsequent sieving. When the granules were placed back in the drum, the binder content was below the critical binder content. For the third experiment it was decided to increase the binder content by increasing the spraying time. However, this resulted in overwet granules since it was later found that the particular nozzle used for that experiment had a higher flowrate than initially assumed. In two other experiments it was decided to remove the drum contents and hand sieve the particles over a 710 μm sieve after approximately 200 revolutions. One experiment was conducted in an identical manner but the hand sieving was performed after 100 revolutions.
Figure 3.23: Mass mean diameter as a function of number of revolutions for three different binder contents (see legend). The fraction of small granules (<500 μm is also plotted. The arrows indicate the termination of the induction stage.

The results of the aforementioned experiments can be compared to the results of experiments conducted under identical conditions (most notably identical binder contents) but where the sieving action was omitted. Figure 3.24 shows the results of three experiments, two of which show identical results. During these two experiments, the fines were removed. Figure 3.24 shows that the results of these two experiments were reproducible. In addition it can be seen that the induction time is shortened by approximately 200 revolutions. The binder content of the three experiments is also shown in Figure 3.24.
This shows that the binder content of the experiment in which the fines were not removed was slightly higher. Normally one would expect the induction time of that experiment to be slightly shorter, but this is not the case.

![Graph showing mean diameter and binder content versus number of revolutions](image)

**Figure 3.24:** Mass mean diameter and binder content versus number of revolutions. The smaller granules were removed after 200 revolutions during experiments 1 and 2. During experiment 3 the smaller granules were not removed.

From the results presented above it can be concluded that the fraction of smaller granules has a profound effect on the growth behaviour, most notably on the duration of the induction stage. This effect has not been noted before and it has led to a description of the mechanism of induction type behaviour which is presented in the following section.

### 3.3.4 The mechanism of induction type behaviour

In previous publications, the mechanism of induction type behaviour has been described as follows (e.g. [8, 26, 29, 30, 54]): after the liquid addition stage, relatively strong granules with partially filled pores are formed. These granules slowly compact during the induction stage. While they are compacting, they cannot coalesce successfully until they are surface wet. As soon as they become surface wet, the granules start growing rapidly. All the publications mentioned also indicate that the duration of the induction stage is shortened when more binder liquid is added. The results in the Section 3.3.2 indicate that compaction of the granules indeed occurs. However from the results presented in the previous section it can be concluded that the start of the rapid growth stage coincides
with the disappearance of the smaller granules. It has also been shown that these smaller granules contain less binder liquid than the larger granules. The fact that when the smaller granules are removed, the induction stage is shortened supports the finding that the content of these smaller granules dictates the duration of the induction stage.

The proposed mechanism for induction type growth is as follows: during the liquid addition stage nuclei are formed. Due to the fact that the liquid is not added homogeneously, some regions receive more binder liquid than others. Inevitably, this leads to the formation of large and relatively wet nuclei and smaller and drier nuclei. After the liquid addition stage, an induction stage is entered. During this induction stage, the granules are compacted. The large and wet granules continuously become surface wet, but as soon as patches of liquid appear at their surface, small and dry granules stick to the liquid at the surface. This results in a lower binder content of the large granules. Therefore, the granules do not appear to be surface wet. When no more smaller granules are present, further compaction of the large granules produces large, surface wet, granules that remain surface wet since they cannot pick up small and dry granules. At this stage, the large and surface wet granules coalesce with each other resulting in a sharp increase in the growth rate. This transition is the rapid growth stage. The binder liquid is then homogeneously distributed among the granules. This illustrates that the induction stage can also be regarded as a stage of liquid redistribution.

All the results presented in Section 3.3.3 support this proposed mechanism:

- The effect of the fraction of small granules and, more notably, the effect of the removal of small granules: Figure 3.23 shows that the end of the induction stage coincides with the disappearance of the smaller granules and Figure 3.24 shows that the induction time can be shortened considerably when the smaller granules are removed.

- The effect of a more homogeneous liquid distribution: The results in Section 3.3.1 indicate that when the distance from the nozzle to the powder is increased, the liquid distribution is more homogeneous. When the distribution of the dimensionless spray flux is studied, the effect of an increased nozzle height is more pronounced than the effect of a change in nozzle pressure, i.e. increasing the nozzle height is more effective than either increasing or decreasing the nozzle pressure for obtaining a homogeneous liquid distribution. This explains the results shown in Figure 3.18. Apparently, increasing the distance from the nozzle to the powder improves the binder distribution, which in turn shortens the induction time. The induction time of the pre-mix experiments is shorter for two reasons: first of all, the binder liquid is distributed more homogeneously and secondly, the granules were less porous since they were pushed through a 2 mm sieve.

- The moisture distribution among the particles size classes: Figure 3.21 shows that after the liquid addition stage, the larger granules contain considerably more binder liquid than the smaller granules. This situation persist until the end of the induction stage. At this stage the moisture is distributed evenly among the particle sizes.
3.4 Conclusions

In this chapter the growth and compaction behaviour of a chalcopryrite and water formulation in a rotating drum was studied. It was demonstrated that this material exhibited induction type behaviour. Induction type growth is characterised by an induction stage during which little or no growth occurs, followed by a rapid growth stage. The duration of the induction stage depends on the amount of binder liquid. When more binder is added, the induction time is shorter. Both the experimental data from the experiments where the powder and binder liquid were pre-mixed as well as the experiments where the binder liquid was sprayed onto the powder confirmed this. The data from the pre-mix experiments was fitted to an empirical equation and it was found that the data fitted the equation well.

Granules that exhibit induction type behaviour are surface dry during the induction stage. At some point, they become surface wet (and therefore shiny) and the presence of a liquid layer at their surface allows them to stick to other particles and thus grow rapidly, marking the start of the rapid growth stage. It is generally thought that the granules are gradually being compacted during the induction stage until their pores are saturated. This has been observed visually. In order to demonstrate the mechanism of induction type behaviour, the compaction behaviour of the granules was studied. A volume displacement method was used in order to measure the granule porosity. One limitation of this technique was revealed as it was discovered that the measurements could only be reliable during the compaction stage when the granules were not surface wet. After the granules had become wet, a further reduction of the pore volume would lead to an expulsion of binder liquid onto the granule surface but this would not change the displaced volume and therefore the observed porosity did not change. Due to this limitation, some of the measurements became unsuitable for fitting. Therefore, it would be advisable to compare a mercury intrusion technique with the volume displacement method in future studies. The porosity as determined by the mercury intrusion technique would be expected to continue to decrease after the induction stage and the porosity as determined by the volume displacement method would be expected to remain constant.

It was expected that during the induction stage, the porosity would decrease to a minimum value and that the pore saturation would increase and, after exceeding a certain critical value equal to or slightly below unity, the granules would become surface wet and the rapid growth stage would start. A trend of decreasing porosity was observed as expected. However, in some cases, the pore saturation reached a maximum and then decreased before the rapid growth stage started. This deviation from the expected behaviour can be attributed to the scatter in the porosity measurements and the fact that only a limited amount of data point could be used for the porosity fits. In addition, the moisture measurements were another source of error in the determination of the pore saturation. Another possibility is that perhaps a different mechanism is responsible for the observed behaviour. It was demonstrated that the rapid growth stage occurred when the pore saturation was around 0.85.

The results of the "spray-on" experiments led to the postulation of a modified mech-
anism for induction type behaviour, which is described extensively in Section 3.3.4. It was shown that the method of binder delivery is a crucial parameter for controlling the growth behaviour. The nozzles that were used had a binder flux distribution with a maximum in the centre. By applying the concept of the dimensionless spray flux, the effect of increasing the pressure of the nozzle (and thus the flow rate) as well as the effect of the distance from the nozzle to the powder was determined. It was found that increasing both the nozzle height as well as the pressure increased the width of the spray and thus the area covered by the spray. However, increasing the nozzle height had a more profound effect on the granulation behaviour: as can be seen in Figure 3.18, a higher nozzle height resulted in a shorter induction time and in addition to this, placing the nozzle too near the powder surface can result in a wide distribution of nuclei sizes which can result in segregation (see Figure 3.20). These phenomena can be explained by the fact that the distribution of binder is more homogeneous when the nozzle height is increased. It can be concluded that the distance of the nozzle to the powder bed is a key parameter in controlling the binder distribution. In addition, the binder distribution affects the growth behaviour. This can be explained by the fact that the duration of the induction stage is determined by the amount of smaller granules, which contain less binder liquid. As soon as all the smaller granules have been picked up by the larger granules, the induction stage is ended and the granules appear to be surface wet and the rapid growth stage starts. Thus, the binder liquid is redistributed during the induction stage. This leads to the conclusion that granulation can be viewed as a mixing process.

**List of symbols**

\[ \hat{A} \] powder flux through the spray zone \((m^2 \text{ s}^{-1})\)
\[ \hat{A}_i \] powder flux in column \(i\) \((m^2 \text{ s}^{-1})\)
\[ C_i \] constant in Equation 3.5 \((\# \text{ revs})\)
\[ d_d \] droplet diameter (m)
\[ k \] compaction rate constant \((\# \text{ revs}^{-1})\)
\[ m \] binder content \((m^3 \text{ of binder} / m^3 \text{ of solid})\)
\[ m^* \] critical binder amount \((m^3 \text{ of binder} / m^3 \text{ of solid})\)
\[ N \] number of drum revolutions \((\# \text{ revs})\)
\[ S \] granule pore saturation (-)
\[ \dot{V} \] volumetric spray rate \((m^3 \text{ s}^{-1})\)
\[ \dot{V}_i \] volumetric spray rate in column \(i\) \((m^3 \text{ s}^{-1})\)

**Greek symbols**
\[ \epsilon \] granule porosity (-)
\[ \epsilon_0 \] initial granules porosity (-)
\[ \epsilon_{\text{min}} \] minimum granule porosity (-)
\[ \rho_g \] apparent granule density \((\text{kg m}^{-3})\)
\[ \rho_l \] liquid density \((\text{kg m}^{-3})\)
\[ \rho_s \] solid density (kg m\(^{-3}\))

\[ \tau_{\text{ind}} \] induction time (\# revs)

\[ \Psi_a \] dimensionless spray flux (-)

\[ \Psi_{a,i} \] dimensionless spray flux in column \(i\) (-)
Chapter 4

One-dimensional population balances

This chapter explains the fundamentals of population balances. The basic equation is derived and the different forms of the coalescence kernel are introduced. A large part of this chapter is reserved for an example of a one-dimensional population balance that describes granulation in a high shear mixer. Finally, some of the shortcomings of this method of modelling are discussed.

4.1 Introduction

Population balances are mathematical models that describe changes in populations in which each member of the population has one or more different, characteristic, properties. In particle technology, the most obvious property is particle size and population balances have often been applied to model changes in the size distribution during processes in which size changes occur such as grinding, crystallization and granulation. Since particle size is one of the major parameters that determine the behaviour of particles, the need for these models is clear. Population balances have been applied to the aforementioned processes for quite a long time. They have been used for grinding since the late 40’s and early 50’s [55]. In the 60’s, the use of population balances for crystallization [56] as well as granulation [50] started. With the advent of the micro-computer and ever-increasing computing power, as well as developments in numerical methods, the practical applications of population balances have increased dramatically over the past two decades.

4.2 Derivation of the general population balance

4.2.1 Number density function

When mathematically describing processes in which particle properties are changing, it is convenient to use a number density function, as opposed to a mass density function. The number density can be a function of so-called internal and external co-ordinates [57].
External co-ordinates refer to the location of the particle in physical space and internal co-ordinates refer to particle properties such as size, but numerous others are possible. Since this chapter deals with one-dimensional population balance modelling, only size will be considered as an internal co-ordinate and the volume of interest is considered to be well-mixed. Thus, external co-ordinates need not be considered. The number function is now defined as follows:

\[ N = \int_{L}^{L+\Delta L} n(L) \, dL \]  

(4.1)

Here \( N \) equals the number of particles in the size interval \( L \) to \( L + \Delta L \). Throughout this chapter, \( N \) will refer to a number of particles and \( n \) to a number density.

### 4.2.2 Size changing mechanisms

In analogy with crystallization, Sastry and Fuerstenau [54] proposed a number of mechanisms of size changes which occur during granulation. They also divided the material in the granulator into a continuous phase, consisting of the primary, feed, particles and a discrete, particulate, phase, consisting of well-defined granules. This division is also in parallel with crystallization.

The basic size changing mechanisms are (see Figure 4.1):

- **Nucleation**: several feed particles form one single granule
- **Shatter**: one single granule breaks and forms a number of primary feed particles
- **Coalescence**: two granules collide and stick together, thus forming one larger granule
- **Breakage**: one granule splits into two (or more) fragments
- **Layering**: one granule picks up smaller feed particles, thus growing in size
- **Attrition**: small feed particles are abraded from the surface of one granule
- **Abrasion transfer**: part of one granule is transferred to another granule

Nucleation, coalescence, breakage and layering will be discussed in more detail in the following paragraphs and their mathematical forms will be given.

### Nucleation

The term nucleation stems from crystallization. It is used to denote the formation of one single particle, or nucleus, from the continuous phase, which is the super-saturated solution in crystallization. It is usually assumed that only nuclei of a certain size are formed. In Equation 4.2 the mathematical form of nucleation is given for a batch crystallizer or granulator, etc.

\[
\frac{\partial n}{\partial t} = B \delta(l - l_0)
\]

(4.2)
In Equation 4.2 $B^0$ represents the nucleation rate, $\delta$ the Delta-Dirac function, $l$ the size of the particles and $l_0$ the size of the nuclei. The nucleation rate in crystallization depends on the super-saturation and can follow a simple power law [57]. For granulation, the nucleation rate will depend on factors such as the powder flux through the zone where the nozzle is situated and the flow of binder liquid. The size of the nucleus is determined by either the size of the binder drops or the shearing forces inside the granulator (see Section 2.3.3). However, the basic form of Equation 4.2 is the same for granulation as well as crystallization.
Coalescence

Coalescence occurs when two particles collide and stick together and form one larger particle. Normally it is assumed that volume is conserved, so the resulting particle has a volume equal to the added volumes of the two colliding particles. When dealing with systems that exhibit coalescence, it is more convenient to use particle volume rather than particle size, since volume is conserved:

$$\frac{\partial n(u)}{\partial t} = B(u) - D(u)$$ (4.3)

Here $B(u)$ is the birth rate of particles of size $u$, i.e. the rate at which particles of size $u$ are formed and $D(u)$ is the death rate, i.e. the rate at which particles of size $u$ disappear. Every time two particles collide and stick together, two particles die and one particle is born. The birth rate of particles of size $u$ is given by the following equation:

$$B(u) = \frac{1}{2} \int_0^u \beta(v, u - v) n(v) n(u - v) \, dv$$ (4.4)

Here $\beta$ is the coalescence kernel, which is a measure for the rate of coalescence and will be explained in more detail in Section 4.2.3. Similar to Equation 4.4 the death rate is described by:

$$D(u) = n(u) \int_0^\infty \beta(v, u) n(v) \, dv$$ (4.5)

Breakage

Breakage is mathematically described in two parts: the selection function and the breakage function. The former dictates the rate at which particles of a certain size break, the latter describes the sizes of the fragments formed when a particle of a certain size breaks. Therefore particles disappear through breakage, but they are also formed. Hence:

$$\frac{\partial n(u)}{\partial t} = B(u) - D(u)$$ (4.6)

The death rate is determined by the selection function as follows:

$$D(u) = S_{br}(u) n(u)$$ (4.7)

In Equation 4.7, $S_{br}(u)$ is the selection function. The breakage function $b(v, u)$ is a two dimensional function that describes how many particles of size $u$ are formed when a particle of size $v$ breaks. Using the breakage function, the birth rate through breakage can be calculated:

$$B(u) = \int_u^\infty b(v, u) D(v) \, dv = \int_u^\infty b(v, u) S_{br}(v) n(v) \, dv$$ (4.8)
4.2. DERIVATION OF THE GENERAL POPULATION BALANCE

Combining Equations 4.6 through 4.8 yields:

\[
\frac{\partial n(u)}{\partial t} = \int_{u}^{\infty} b(v, u) S_{br}(v) n(v) \, dv - S_{br}(u) n(u)
\]

(4.9)

Layering

Layering is described analogous to growth in crystallization, i.e. material from the continuous phase is deposited onto the surface of particles, which results in a continuous increase of the size of the particle. It is more convenient to use particle size as the internal co-ordinate when describing layering or growth. Thus:

\[
\frac{\partial n}{\partial t} = - \frac{\partial G n}{\partial l}
\]

(4.10)

Here \( l \) is the particle size and \( G \) is the growth rate.

When the primary feed particles are considered to be particulate matter rather than a continuous phase, layering can be seen as a special case of coalescence and then Equation 4.3 can be applied.

4.2.3 The coalescence kernel

The most crucial parameter describing coalescence is the growth kernel, \( \beta \). Equations 4.4 and 4.5 show that \( \beta(v, u - v) \) is a measure for how successful a binary collision of particles of volumes \( v \) and \( u - v \) is. The degree of success of a collision of two particles depends on process parameters, such as the rotational speed of the drum or mixing tools, the fluidization intensity, the geometry of the granulator, etc., but also on the formulation parameters, such as the initial particle size distribution, the amount of binder, the binder viscosity and surface tension, the contact angle and so on. In addition, the sizes of the colliding granules also determine the degree of success of a binary collision. At present, no kernel for agglomeration has been derived from first principles. As a consequence, one has to resort to all kinds of empirical and semi-empirical forms [58]. Kapur [59] recognized the fact that the size of the colliding particles affected their chance of coalescence and Sastry [60] derived a general form for the coalescence form which is still being used. Sastry suggested that the kernel be separated into two different parts, one depending on the size of the colliding granules and the other part depending on all other process and material properties:

\[
\beta(v, u - v) = \beta_0 \beta^*(v, u - v)
\]

(4.11)

Here \( \beta_0 \) is the size independent part of the kernel and \( \beta^* \) is the size dependent part. Usually, all process and material properties are lumped into \( \beta_0 \). Sometimes this can be a constant, sometimes it is assumed to be time dependent. Kapur proposed the following form for the size dependent part of the kernel:

\[
\beta^*(v, u - v) = \frac{((v) + (u - v))^a}{((v)(u - v))^b}
\]

(4.12)
Here $a$ and $b$ are empirical constants. In principle, an infinite number of different forms of the kernel exist, but only a limited number of these are used. Adetayo [61] and Ilievski et al. [62] list a number of them, which can be found in Table 4.1.

**Table 4.1:** Different types of coalescence kernels, from Adetayo [61] and Ilievski et al. [62]

<table>
<thead>
<tr>
<th>Kernel</th>
<th>Size dependent part ($\beta^*(u,v)$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant (Random)</td>
<td>1</td>
</tr>
<tr>
<td>Sum (Golovin)</td>
<td>$(u + v)$</td>
</tr>
<tr>
<td>Sastry [60]</td>
<td>$(u^{2/3} + v^{2/3})(1/u + 1/v)$</td>
</tr>
<tr>
<td>Brownian motion (Smoluchowski)</td>
<td>$(u^{1/3} + v^{1/3})(u^{-1/3} + v^{-1/3})$</td>
</tr>
<tr>
<td>Laminar, Shear (Smoluchowski)</td>
<td>$(u^{1/3} + v^{1/3})^3$</td>
</tr>
<tr>
<td>Berry</td>
<td>$(u^{1/3} + v^{1/3})^2</td>
</tr>
<tr>
<td>Thompson</td>
<td>$(u - v)^2/(u + v)$</td>
</tr>
<tr>
<td>Drake</td>
<td>$(u^{1/3} + v^{1/3})^2</td>
</tr>
<tr>
<td>Empirical # 1, Adetayo [61]</td>
<td>$uv/(u + v)$</td>
</tr>
<tr>
<td>Product</td>
<td>$(uv)$</td>
</tr>
<tr>
<td>Empirical # 2, Ilievski et al. [62]</td>
<td>$(u^{1/3} + v^{1/3})\gamma$</td>
</tr>
<tr>
<td>Empirical # 3, Ilievski et al. [62]</td>
<td>$(u^{1/3} + v^{1/3})\gamma(u^{-1/3} + v^{-1/3})\lambda$ **</td>
</tr>
</tbody>
</table>

$\gamma$ and $\lambda$ are parameters to be fitted.

In order to derive a kernel based on the physical mechanism of granulation, Adetayo and Ennis developed a new kernel [58]. Their approach was based on the Stokes regime analysis, as proposed by Ennis et al. [15]. From the model of Ennis et al., it followed that there exists a critical size, $W^*$. Granules larger than this size cannot coalesce upon collision. Based on this, Adetayo and Ennis proposed the following kernel:

$$\beta = \begin{cases} 
\beta_0 & W \leq W^* \\
0 & W > W^* 
\end{cases}$$  \hspace{1cm} (4.13)

Here $W$ is the effective volume of two colliding particles, which is defined as follows:

$$W = \frac{(uv)^a}{(u + v)^b}$$  \hspace{1cm} (4.14)

Here $a$ and $b$ are empirical constants. In order to be dimensionally correct, $2a - b$ has to be unity.

Adetayo and Ennis have used this kernel successfully in their studies and they were able to simulate seemingly different types of growth behaviour with one kernel, showing its potential. More recently, Liu et al. [63] have derived a physically based kernel. They used the regime analysis of Liu et al. [17] which divides coalescence into two types: in the case of the first type, the liquid binder layer is responsible for dissipating the kinetic energy of two colliding granules (similar to Ennis et al.'s approach [15]) and in the case
of the second type, both the binder liquid layer and the granule deformation are responsible for dissipating the kinetic energy. They incorporated granule parameters such as deformability, liquid layer thickness and size into the kernel and validated it with existing granulation data. Their results were in good agreement with the experimental data, demonstrating its suitability.

4.2.4 Free in space vs. restricted in space

Equations 4.4 and 4.5 use a product of the form \( n(x)n(y) \). Coalescence can only occur when two particles collide\(^1\). The product \( n(x)n(y) \) is the total number of possible collisions between particles of size \( x \) and size \( y \). Sastry and Fuerstenau [64] divided agglomeration processes into two classes: free-in-space and restricted-in-space (see Figure 4.2). Free-in-space systems are very dilute systems such as an aerosol and restricted-in-space systems have relatively high concentrations of particulate matter.

![Diagram](image)

**Figure 4.2**: Two classes of agglomeration systems. a: free-in-space, b&c: restricted-in-space. From Sastry and Fuerstenau [64]

In a free-in-space system any given particle can collide with all other particles as the paths to the other particles are not blocked. Therefore, the number of possible binary collisions between particles of size \( x \) and size \( y \) equals \( n(x)n(y) \) as mentioned before. In a restricted-in-space system this is not the case as any given particle can only collide with the particles in its immediate vicinity. The number of possible binary collisions between particles of size \( x \) and size \( y \) therefore is significantly less than \( n(x)n(y) \). Sastry and Fuerstenau introduced a means to correct for this error and they stated that the number of possible binary collisions between particles of size \( x \) and size \( y \) equals \( n(x)n(y)/N_{\text{tot}} \). Here \( N_{\text{tot}} \) equals the total number of particles. This division over the total number of particles will be used throughout this chapter.

\(^1\)Collisions of three or more particles can also occur but these are far less likely to occur and can therefore be safely neglected.
4.2.5 Solving the population balance

A population balance describing coalescence, as depicted in Equations 4.3 through 4.5 is a partial-integro-differential equation. Analytical solutions only exist for a very limited number of idealized cases, with special initial distributions and volume independent growth kernels [65, 66]. In the vast majority of cases, one has to resort to numerical methods. Ramkrishna [65] and Adetayo [61] give an overview of the numerical methods available. In the early days of numerically solving population balance workers in the field resorted to relatively crude methods such as the method of moments and self-preserving distributions, but as computing power increased over the years more accurate methods were developed. A very popular method is the sectional method, sometimes called the method of discretization. In this method, the particle size domain is divided into discrete sections and then an ordinary differential equation is derived for each section. Thus, the partial-integro-differential equation is transformed into a set of ordinary differential equations. Solving these equations is straight-forward. A widely used method was developed by Batterham et al. [67]. They used particle volume rather than particle size and they built a grid where every upper boundary of section $i$ is twice the volume of the upper boundary of section $i - 1$, such that $\frac{V_i}{V_{i-1}} = 2$. This method has a number of advantages [66], such as allowing to simulate a wide size distribution with a high level of accuracy in the smaller size while keeping the number of sections low at the same time. Another advantage is that when two particles in section $i$ coalesce, they always form a particle in section $i + 1$. With this method of discretization, the population balance equation can be written as follows:

$$\frac{dN_i}{dt} = \frac{1}{N_{tot}} \left( N_{i-1} \sum_{j=1}^{i-2} 2^{j-i+1} \beta_{i-1,j} N_j + \frac{1}{2} \beta_{i-1,i-1} N_{i-1}^2 - N_i \sum_{j=1}^{i-1} 2^{j-1} \beta_{i,j} N_j - N_i \sum_{j=1}^{\infty} \beta_{i,j} N_j \right)$$  \hspace{1cm} (4.15)

Here $N_i$ is the number of particles in section $i$. This method has been adopted by Hounslow et al. [66] for modelling crystallization and they showed that this technique was very useful. Adetayo et al. have applied the technique for simulating fertilizer granulation circuits successfully [68].

Recently, Nicmanis and Hounslow demonstrated the advantages of adopting a finite-element method rather than a sectional method [69]. They showed that their method, though mathematically considerably less straight-forward, was both more accurate as well as faster than the sectional method. Obviously Nicmanis’ and Hounslow’s method has great potential. At this moment, however, the method has not been applied by others.
4.3 A three stage population balance model for high shear granulation

In this section, an example of an application of a one dimensional population balance is given. Experimental results from Hoornaert et al. [29] were analyzed and simulated.

4.3.1 Experimental

The details of the experiments have been described extensively by Hoornaert et al. [29]. All of the experiments were carried out in a Lödige high shear mixer, type FM 50, which had a total volume of 50 l and was equipped with three ploughshare shovels attached to a rotating horizontal shaft and a side-mounted spinning chopper, see Figure 4.3. The operation was batch. The rotational speed of the ploughshares was set at 200 rpm for all of the experiments and the chopper speed was fixed at 3000 rpm. The Lödige mixer was equipped with a cooling jacket in order to prevent excessive heating of the granulating mass.

![Schematic drawing of the Lödige mixer](image)

Figure 4.3: Schematic drawing of the Lödige mixer

A complex mixture of solids, as detailed in Table 4.2, was used as the test solid and an aqueous solution of PVP K-30 was used as the binder. Despite the comment of Knight et al. [28], there was no hydration, as shown by thermogravimetry [29]. The reason for using this mixture was to mimic a formulation used in an actual production process. Various amounts of binder liquid were used, all with the same viscosity of 3.9 mPas. Table 4.3 lists the various conditions of the experiments. The liquid was added by pouring it through a reservoir with a large number of 5 mm holes in the bottom which then distributed the liquid fairly evenly over the top of the powder bed. The procedure took approximately 20 seconds to achieve. This rapid addition of the liquid was chosen to be short compared to
the batch processing time [25]. During the experiment samples were periodically removed, dried in an oven at 80 °C and were analyzed using sieves.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Purpose</th>
<th>Mass (kg)</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$SO$_4$ · 0aq</td>
<td>filler</td>
<td>10.575</td>
<td>70.5</td>
</tr>
<tr>
<td>CaSO$_4$ · ½ aq</td>
<td>filler</td>
<td>0.450</td>
<td>3.0</td>
</tr>
<tr>
<td>Potato protein</td>
<td>dummy enzyme</td>
<td>0.750</td>
<td>5.0</td>
</tr>
<tr>
<td>Micro-crystalline cellulose</td>
<td>anti-lumping agent, filler</td>
<td>3.000</td>
<td>20.0</td>
</tr>
<tr>
<td>PVP K-30 (polyvinylpyrrolidone)</td>
<td>binder (added as aqueous solution)</td>
<td>0.225</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>15.000</strong></td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.3: Overview of the experiments**

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Binder content (%)</th>
<th>y (-)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.8</td>
<td>0.801</td>
</tr>
<tr>
<td>2</td>
<td>17.8</td>
<td>0.801</td>
</tr>
<tr>
<td>3</td>
<td>18.4</td>
<td>0.834</td>
</tr>
<tr>
<td>4</td>
<td>19.1</td>
<td>0.880</td>
</tr>
<tr>
<td>5</td>
<td>19.1</td>
<td>0.880</td>
</tr>
<tr>
<td>6</td>
<td>19.1</td>
<td>0.880</td>
</tr>
<tr>
<td>7</td>
<td>19.1</td>
<td>0.880</td>
</tr>
<tr>
<td>8</td>
<td>19.8</td>
<td>0.926</td>
</tr>
<tr>
<td>9</td>
<td>20.4</td>
<td>0.964</td>
</tr>
<tr>
<td>10</td>
<td>20.4</td>
<td>0.964</td>
</tr>
</tbody>
</table>

**The solution phase ratio, $y$, is a measure for the ratio between the liquid and solid phase, taking dissolution into account.

4.3.2 Results and discussion

In Figure 4.4, the development with time of the mass mean diameter is plotted for several experiments. In this graph three separate stages can be observed. First, a short stage of fast growth occurs during the first minute. This is the nucleation stage and is marked as “A” in the figure. The nucleation stage is followed by a period during which no growth occurs. This is the induction stage and is marked as “B” in Figure 4.4. With the exception of the experiment using 17.8% of binder, all of the experiments exhibit a third stage in which growth occurs by coalescence. This is marked as “C” in Figure 4.4. The experiment
using 20.4% of binder liquid exhibits a fourth stage where the mean diameter is reduced. Breakage was obviously the main mechanism in this stage. In the following paragraphs the nucleation, induction and coalescence growth stages will be discussed in more detail.

![Graph showing mass mean diameter over time for different binder liquid contents.](image)

**Figure 4.4:** Mean diameter in time for a number of experiments with different binder liquid contents. “A” marks the nucleation stage, “B” the induction stage and “C” the coalescence growth stage.

Nucleation stage

As stated in Section 2.3.3, nuclei are formed when droplets of the binder liquid come into contact with the dry powder. A number of parameters influence the way in which the nuclei are formed as well as the size of those nuclei [36]. Among these are the size of the droplets, the flow rate of liquid binder and the rate at which powder that has not yet been wetted appears at the surface. Litster et al. combined these parameters to define a
dimensionless spray flux $[41]$: 

$$\Psi_a = \frac{3 \dot{V}}{2 \dot{A} d}$$  \hspace{1cm} (2.8)

Here $\Psi_a$ is the dimensionless spray flux, $\dot{V}$ is the volumetric spray rate, $\dot{A}$ is the powder flux through the spray zone and $d$ is the size of the droplets of binder. In addition to these parameters, other powder and binder properties such as contact angle, surface tension and viscosity also play a role. These parameters dictate how the binder will disperse and at what rate. The drop penetration time is a derived quantity and results from a combination of powder and binder properties $[38]$. Hapgood et al. $[42]$ combined the process characteristics, represented by the dimensionless spray flux, and the powder and binder characteristics, represented by the ratio of the drop penetration time and the powder circulation time, to develop a nucleation regime map (see also Section 2.3.3). This is shown in Figure 2.10. Here the nucleation mechanisms are divided into two regimes, the drop controlled regime and the mechanical dispersion regime. When the dimensionless spray flux is small (< 0.1) and the penetration time is short, each droplet of binder liquid forms one individual nucleus. This is the drop controlled regime. When either the penetration time is long or the dimensionless spray flux is large, mechanical forces are mainly responsible for the eventual size distribution of the nuclei. This is the mechanical dispersion regime.

An estimate of the dimensionless spray flux can be made for these experiments:

- 3.8 liters of binder is added in approximately 20 seconds, which yields $\dot{V} = 1.9 \times 10^{-4}$ (m$^3$ s$^{-1}$)
- The spray zone covers a circular area of approximately 20 cm which is refreshed 100 times per minute. This yields $\dot{A} = 5.24 \times 10^{-2}$ (m$^2$ s$^{-1}$)
- The size of the droplets is proportional to the size of the holes in the liquid container, which had a diameter of 5 mm

With these values, the dimensionless spray flux has a value of 1.08. It is therefore safe to assume that the penetration time played no role and that the nucleation occurred in the mechanical dispersion regime. Figure 4.5 shows a graphical representation of the probable mechanism of nuclei formation: large droplets come into contact with the dry surface of the powder. If such a droplet hits the bed of particles, a granule is formed within the droplet. This nuclei will not have much strength $[5, 51]$ and will almost immediately be broken up by the ploughshares and the chopper into a number of smaller nuclei which are strong enough to withstand the shearing forces. This mechanism is similar to the destructive nucleation mechanism proposed by Vonk et al. $[40]$.

**Induction stage**

The second stage, the induction stage, has sometimes been referred to as the "compaction stage" by Hoornaert et al. $[29]$ and as the "nuclei region" by Kapur $[30]$). It is characterized
by a constant particle size. During this stage, the granules are gradually compacted until they reach a certain critical pore saturation when the surface of the granules becomes wet. This transition can be observed visually [27] (see also Figure 3.11). In those experiments copper concentrate was granulated and it was observed that the surface of the granules became shiny at the end of the induction stage. This finding was also confirmed through measurements of the pore saturation. Similar measurements have been made by other workers [5, 7, 26, 30]. After the granules have become surface wet, they can continue to grow by coalescence.

There exist critical minimum and critical maximum limits to the amount of binder. Below the minimum value, the second growth stage does not occur and the induction stage persists indefinitely. Above the maximum value, the induction stage is missed and the second growth stage immediately follows the nucleation stage [26]. Between these two critical values, the induction stage is shorter when more liquid binder is present. This fact has been mentioned in the literature by various authors [26, 27, 28, 29, 30]. The experimental results reported here all support these findings. From Figure 4.4 it can be seen that, in this case, the critical minimum binder value lies between 17.8% and 18.4% and that the maximum value is around 20.4%. Between these two values the
induction time decreases with an increasing amount of binder. In Figure 4.6 the induction
time is plotted as a function of the solution phase ratio. The solution phase ratio is a
concept derived by Sherington [43] that expresses the ratio of the volume of liquid to solid,
taking into account the effect of dissolution. Figure 4.6 implies that the induction time
is linearly dependent upon the initial binder content. It also implies, therefore, that the
rate of compaction of the granules is linear with time.

Coalescence growth stage

Figure 4.4 demonstrates the effect of the amount of binder. At a higher binder content the
growth rate is higher, which is in accordance with the literature [5, 7, 21, 24, 25]. When
considering the particle size distribution rather than simply the mean size, an intriguing
phenomena is revealed. Although it appears from Figure 4.4 that the size of the granules
is gradually increasing, not all of the particles seem to be growing. In Figure 4.7 the
particle size distributions of four samples are shown. The particle size distribution after
one minute, which is the distribution after nucleation, is a monomodal distribution with a
modal size of about 150 μm. The particle size distributions of the other three samples are
all bimodal with one modal size of about 150 μm and another mode whose size gradually
increases. This indicates that some of the nuclei that are formed are not growing during
the coalescence growth stage. It is thought that this phenomenon, which was observed
in all of the experiments, was caused by liquid maldistribution, although it could also be
due to dead zones within the granulator.
4.3.3 The population balance model

Based on these observations, a population balance of granulation is now derived from the experimental results, in which each stage is modelled separately.

Nucleation stage

Since the nucleation was controlled by the shear mechanism, process conditions such as the intensity of the agitation mainly controlled the particle size distribution of the granules during the nucleation stage. This mechanism of nucleus formation is complex and interpretation requires knowledge of the motion within the granulator. Furthermore, process conditions such as the rotational speed of the ploughshares as well as of the chopper were kept constant in all of these experiments. Consequently, the particle size distribution was assumed to be constant after the nucleation stage and thus the average distribution at the end of the nucleation stage was used for the model. To assess this average, the results of both of the experiments conducted with 20.4% binder were not used since in those cases it was thought probable that growth already had started after one minute.

Induction stage

During the induction stage, no growth was observed. It is therefore reasonable to assume that the kernel $\beta$ in Equation 4.15 is equal to zero. At the end of the induction stage, the granules are surface wet and growth then starts. The kernel $\beta$ will then be positive.
Figure 4.7: Size distributions of samples taken after the nucleation stage (1 min) and during the coalescence growth stage (56 min, 86 min and 106 min). Experiment #5, 19.1 % binder liquid amount.

Iveson et al. [48] proposed a first order model for granule consolidation:

$$
\epsilon = \epsilon_{\text{min}} + (\epsilon_0 - \epsilon_{\text{min}})e^{-kt}
$$

(3.2)

Here \(\epsilon\) is the porosity of the granule, \(\epsilon_{\text{min}}\) is the minimum possible porosity of the granule, \(t\) is the time, \(k\) is the rate constant and \(\epsilon_0\) the initial porosity. Iveson et al. found that this model was in good agreement with the experimental data. This model has been successfully applied [27] (see also Section 3.3.2). Iveson et al. observed that with low viscosity binders, the minimum porosity decreased with increasing binder liquid content. In addition, he observed that the rate of consolidation did not depend upon the content of binder liquid. If these two observations are combined with the assumption that the porosity at the beginning of the compaction stage was the same in all of the experiments, then the change in porosity can be calculated for all of the five values of binder liquid used. These calculations are plotted in Figure 4.8.

The saturation of the granules is a simple function of granule porosity and binder liquid content and can be calculated using the following equation:

$$
S = \frac{y \cdot (1 - \epsilon)}{\epsilon}
$$

(4.16)
4.3. A THREE STAGE POPULATION BALANCE MODEL

Figure 4.8: Porosity, $\epsilon$, and pore saturation, $S$, as a function of time for the five different amounts of binder liquid used, expressed as solution phase ratio, $y$.

In this equation $S$ is the granule pore saturation and $y$ is the solution phase ratio. In Figure 4.8 the granule pore saturation is plotted as a function of time. It is interesting to see that the time it takes to reach full saturation, that is $S$ is unity, is almost exactly equal to the induction time. For instance, the average compaction time for a solution phase ratio of 0.880 was 32 minutes. The time calculated with the model equals 28 minutes. Additionally, the granule pore saturation for a solution phase ratio of 0.801 never reaches unity, which is in accordance with the experimental observations. The experiments carried out with this solution phase ratio never entered the coalescence stage. It must be stressed however, that precise porosity data was not available. The values for the porosities, $\epsilon$, $\epsilon_0$, $\epsilon_{\text{min}}$, and $k$ were estimated using data from Kristensen et al. [12], who did measure the porosity of granules produced in a high shear mixer.

Coalescence growth stage

Analysis of the experimental results has indicated that some of the nuclei do not grow further after their formation. It was decided therefore to divide the particle size distribution into two portions. One portion grows, the other remains unaltered. In Figure 4.9, an example is given of how a bimodal distribution is decomposed into two parts. The size distribution of the non-growing fraction of particles was estimated from the particle size distribution of samples taken at longer granulation times since then the two modes are almost completely separated. Figure 4.10 shows how the mass fraction of the granules that are not growing decreases with increasing amount of binder. This also supports the notion that the bimodal distribution is caused by maldistribution of the liquid.

Previous simulations revealed that the value for $\beta_0$ decayed exponentially with time [70]. The random and sum kernel $\beta_0$, were therefore chosen to be time-dependent:

$$\beta_0 = Ae^{-Bt} \quad (4.17)$$
Figure 4.9: Decomposition of a bimodal particle size distribution into two distributions. Sample taken after 30 minutes, Experiment #8, binder content 19.8%.

In this equation two extra parameters are introduced: $A$, which is the so-called kernel proportionality constant, and $B$ which is the kernel time constant.

In order to find the optimum values for these constants as well as to find the most suitable kernel, an optimization criterion was required. Adetayo used the following criterion [61]:

$$SSE = \sum_s \sum_i (cum_{s,i,exp} - cum_{s,i,sim})^2$$  \hspace{1cm} (4.18)

Here $SSE$ is the sum of squared errors, $cum_{s,i}$ is the cumulative mass of granules smaller than sieve size $i$ of sample number $s$. The subscripts $exp$ and $sim$ refer to experimental values and values from the simulations, respectively. Adetayo’s rationale behind using this criterion was that he observed considerable scatter in the experimentally determined mass density distribution which made it unsuitable for parameter estimation. More accuracy is obtained by using the cumulative distribution since this is directly determined using the sieving technique. Thus, a sieve separates particles into one portion with particles larger than the aperture size and a portion with particles smaller than the aperture size which is the cumulative undersize. Unfortunately, in this case the boundaries of the size classes of the model did not coincide with the sieve sizes and $cum_{s,i,sim}$ was therefore calculated by linear interpolation between the boundaries of the size classes of the model.

In Figure 4.11 the results of simulations with each of the three kernels for one experiment are shown. The results were obtained using Equation 4.18. Obviously, the sum kernel leads to a very wide particle size distribution and therefore produced poor results.
Both the random kernel and the Adctayo and Ennis kernel looked better. However, the random kernel was chosen to be the best since it gave a smaller sum of squared errors. Figure 4.12 shows a complete simulation of the same experiment using the random kernel and shows three time stages. It can be seen that the simulations follow the experimental results extremely well. Similar results were achieved for all of the simulations and it seems that the random kernel fits the experimental data best. Ilievski et al. also found that the random kernel was the best kernel for simulating their experimental results from crystallization [62]. This result implies that the growth by coalescence is dominated by the surface wetness and is not dependent upon the size of the colliding granules.

In Table 4.4, the results of the simulations can be seen. It is clear that the parameters $A$ and $B$ are not independent. This is shown in Figure 4.13 and can be explained by the fact that a larger value of $B$ will lead to a more rapid decline of $\beta_0$ which can be compensated by a larger value of $A$. The time-averaged value of $\beta_0$ is then similar. Furthermore, Table 4.4 does not reveal how the kinetic parameters $A$ and $B$ depend on the amount of binder. For this purpose a more meaningful parameter is $A/B$. This parameter is plotted versus the solution phase ratio in Figure 4.14. As expected, this kinetic constant is larger for larger values of the solution phase ratio.
The three staged model

In the previous sections each of the stages was modelled separately. However, it is desired to derive a more general model that incorporates the influence of the amount of binder. The particle size distribution of the granules after the nucleation stage has to be determined experimentally. Once this is known, a general model can be constructed that describes the two following stages, using Equation 4.15. The coalescence kernel then becomes:

$$\beta = \begin{cases} 
0 & S < 1 \\
A e^{-Bt} & S \geq 1 
\end{cases}$$

(4.19)

Here $S$ is the pore saturation, which can be calculated using Equations 3.2 and 4.16. It is assumed that $B$ does not depend on the amount of binder and the average value can be used. $A$ then shows a clear dependency of the binder amount:

$$A = 7.81y - 5.09 \quad \text{and} \quad B = 0.13$$

(4.20)

Using Equations 4.19 and 4.20, the granulation behaviour during the induction stage and the coalescence growth stage can be modelled.
4.3.4 Conclusions regarding the three staged population balance

The results showed that it is possible to simulate the results obtained from the experiments accurately. However, the model was rather empirical. Models such as proposed by Ennis et al. [15] or the model proposed by Liu et al. [17], which is an extension of Ennis' et al. model, are based on first principles. Ideally, one would want to use a kernel based on these models. This would allow the population balance model to be used for predicting the granulation process. Unfortunately, this requires knowledge of a large number of granule and process properties, which is often difficult or even impossible to obtain.

Granule porosity proved to be a critical property since it controlled the duration of the induction stage. It is therefore suggested that this parameter is included in the population balance. Anapragada and Neilly have suggested this before [71]. In addition, liquid distribution also had a pronounced effect on the granulation behaviour. Apart from granule porosity, granule moisture content should also be included in the population balance model for further simulation attempts. Iveson has acknowledged the need to extend the population balance to multiple dimensions before [72]. Although apparently the need for multi-dimensional population balances exists, they have yet to be developed.
Table 4.4: Results of the simulations

<table>
<thead>
<tr>
<th>y (\text{-})</th>
<th>A (\text{min}^{-1})</th>
<th>B (\text{min}^{-1})</th>
<th>A/B (\text{-})</th>
<th>SS_{res}</th>
<th>SS_{res}/# samples \text{**}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.834</td>
<td>0.880</td>
<td>0.0792</td>
<td>11.1</td>
<td>2.89 \times 10^{-2}</td>
<td>9.62 \times 10^{-3}</td>
</tr>
<tr>
<td>0.88</td>
<td>1.49</td>
<td>0.0990</td>
<td>15.0</td>
<td>1.78 \times 10^{-1}</td>
<td>3.55 \times 10^{-2}</td>
</tr>
<tr>
<td>0.88</td>
<td>0.805</td>
<td>0.0519</td>
<td>15.5</td>
<td>5.30 \times 10^{-2}</td>
<td>1.06 \times 10^{-2}</td>
</tr>
<tr>
<td>0.88</td>
<td>1.25</td>
<td>0.0867</td>
<td>14.4</td>
<td>2.10 \times 10^{-1}</td>
<td>4.21 \times 10^{-2}</td>
</tr>
<tr>
<td>0.88</td>
<td>1.40</td>
<td>0.102</td>
<td>13.8</td>
<td>2.75 \times 10^{-1}</td>
<td>5.49 \times 10^{-2}</td>
</tr>
<tr>
<td>0.926</td>
<td>3.39</td>
<td>0.239</td>
<td>14.2</td>
<td>1.81 \times 10^{-1}</td>
<td>4.52 \times 10^{-2}</td>
</tr>
<tr>
<td>0.964</td>
<td>4.66</td>
<td>0.287</td>
<td>16.2</td>
<td>3.09 \times 10^{-2}</td>
<td>1.03 \times 10^{-2}</td>
</tr>
<tr>
<td>0.964</td>
<td>1.45</td>
<td>0.0601</td>
<td>24.2</td>
<td>4.71 \times 10^{-1}</td>
<td>1.18 \times 10^{-1}</td>
</tr>
</tbody>
</table>

\text{**}In some experiments a different number of samples was taken. In order to make a comparison of the simulation of each experiment, it was therefore necessary to divide the total sum of squared errors (See Equation 4.18).

Figure 4.13: Contourplot of the sum of squared errors as a function of the model parameters A and B. Contourlines were only drawn near the minimum. Experiment #5, binder content 19.1\%.
Figure 4.14: Kinetic parameters of the model as function of solution phase ratio.

for granulation processes. The reason for this is that considerable computing power is required. Apart from that, measuring a particle size distribution as well as the moisture and porosity distribution present a challenge for the experimenter and it has not been done before.

List of symbols

- $a, b$: empirical constants in Equations 4.12 and 4.14 ($\cdot$)
- $A$: kernel proportionality constant ($s^{-1}$)
- $\dot{A}$: powder flux through the spray zone ($m^2 s^{-1}$)
- $b$: breakage function ($m^3$)
- $B$: kernel time constant ($s^{-1}$)
- $B(u)$: birth rate of particles of volume $u$ ($m^{-3} s^{-1}$)
- $B^0$: nucleation rate ($m^{-2} s^{-1}$)
- $cum_{s,i}$: cumulative mass fraction of granules smaller than sieve size $i$
of sample number \( s \) (-)

\( D(u) \) death rate of particles of volume \( u \) (m\(^{-3}\) s\(^{-1}\))

\( d_d \) size of the binder droplets (m)

\( G \) rate of growth by layering (m s\(^{-1}\))

\( k \) consolidation rate constant (s\(^{-1}\))

\( L, l \) particle size (m)

\( l_0 \) nucleus size (m)

\( n \) number density (m\(^{-3}\))

\( N \) number of particles (#)

\( N_i \) number of particles in size class \( i \) (#)

\( N_{\text{tot}} \) total number of particles (#)

\( S \) granule pore saturation (-)

\( S_{\text{br}} \) selection function for breakage (s\(^{-1}\))

\( SSE \) sum of squared errors (-)

\( t \) time (s)

\( u, v \) particle volume (m\(^3\))

\( \dot{V} \) volumetric spray rate (m\(^3\) s\(^{-1}\))

\( W \) effective volume of collision (m\(^3\))

\( W^* \) critical effective volume of collision (m\(^3\))

\( y \) the solution phase ratio (-)

\textit{Greek symbols}

\( \alpha, \nu \) particle volume (m\(^3\))

\( \beta \) coalescence kernel (s\(^{-1}\))

\( \beta_0 \) size-independent part of coalescence kernel (s\(^{-1}\))

\( \beta^* \) the size dependent part of coalescence kernel (-)

\( \gamma, \lambda \) empirical constants from Table 4.1 (-)

\( \epsilon \) granule porosity (-)

\( \epsilon_0 \) initial granule porosity (-)

\( \epsilon_{\text{min}} \) the minimum granule porosity (-)

\( \Psi_a \) dimensionless spray flux (-)
Chapter 5

Multi-dimensional population balance modelling

In this chapter the multi-dimensional population balance is introduced. The model presented in the previous chapter is rewritten in order to include the volume of solid, liquid and air in the granules. Thus, it allows us to incorporate more fundamental knowledge of the mechanisms. In addition, this chapter also presents a solution to the multi-dimensional population balance and the results of a simulation are compared to experimental results.

5.1 Introduction

In recent years, researchers have realized that particle size is not the only granule property that determines its behaviour. Many applications of population balances reveal a time dependency of the kernel. For example, Randolph and Larson used particle age as a so-called internal co-ordinate [57] and Pearson et al. investigated the time dependency of the agglomeration kernel [73]. Although it is true that agglomeration behaviour changes with time, this effect is not caused by the age of the granules, but by some other granule property which changes in time. This is obvious in systems that exhibit induction type growth. Granule porosity is an essential parameter that has a profound effect on the growth behaviour. Below a certain critical porosity, the pore saturation is such that the binder liquid is inside the granules and the granules remain surface dry. Above that critical porosity, the pores are almost completely filled with liquid and liquid is squeezed onto the surface \(^1\). When this occurs, the granules start growing rapidly, as has been shown before (see for example Chapter 3, Sections 3.3.2 and 3.3.3). Therefore, especially in the case of induction type growth systems, porosity, which is directly coupled with pore saturation, is a crucial parameter. One can imagine that granule porosity also has an effect on deformability and strength and therefore it can have a marked effect on

\(^1\)The critical pore saturation need not be unity for the granules to be surface wet, but can be lower due to entrapped air. Indeed, this has been observed experimentally [7, 27]
growth and breakage rates. Anapragada and Reilly [71] mentioned that porosity is an essential granule parameter which should be incorporated into the population balance. They base their conclusion on the fact that, according to their observations, during the liquid addition phase, porous, and consequently weak, granules are formed, which break quickly after they are formed. These fragments then coalesce and form denser, stronger granules. Consequently, the rate of breakage decreases and aggregation becomes the dominant mechanism.

In addition to the porosity, the moisture content of a granule also plays a role. The vast majority of papers written on granulation experiments deal with the effects of moisture content. It is well known that the amount of binder added to a granulating system has a profound effect. Virtually all papers conclude that the more binder is added, the higher the rates increase [5, 6, 7, 21, 24, 25] or the induction time decreases [26, 27, 28, 29, 30]. Consequently, when the binder liquid is not distributed evenly, one can imagine that the granules which have more liquid can grow quicker. Unlike in experiments in which the binder and the powder are premixed [5, 6, 7, 24, 27, 48], usually the binder is added by a spray or nozzle and consequently the binder is not distributed homogeneously. Knight et al. [28] have reported this and they have reported the effect of inhomogeneous liquid distribution. Therefore, the binder content of each individual granule should be incorporated rather than the average binder content, since inhomogeneous binder distribution is not uncommon, especially in industrial applications, and this inhomogeneity has a profound effect. Indeed, Iveson [72] proposed that the population balance be extended to four dimensions, with granule porosity and binder content as added dimensions.

It is interesting to see that the importance of incorporating more granule properties into the population balance has been recognized before. This has led to publications on the application of a multi-dimensional population balance to a granulation process, but so far, no publications exist that show a solution of the multi-dimensional population balance. This is perhaps due to the sheer mathematical complexity or the lack of multi-dimensional data, i.e. experimental data consisting of the size, porosity and binder content of granules.

Multi-dimensional population balances, i.e. population balances with more than one internal co-ordinate, have been applied in aerosol science by Xiong and Pratsinis [74] and Vemury et al. [75]. Xiong and Pratsinis derived a population balance that describes the changes in particle size as well as morphology that occur during powder production by gas phase processes where coagulation and sintering occur simultaneously. At high temperatures, sintering is instantaneous with particle collisions, yielding spherical particles. However at low temperatures, the rate of sintering is lower and irregularly shaped particles are formed. Therefore, Xiong and Pratsinis derived a population balance with particle volume and particle surface area as the particle properties. From these two parameters, the surface fractal dimension can be calculated, which is a measure for the morphology of the particle. This population balance was solved by dividing both the volume as well as the surface area domain in sections. Vemury et al. modelled the coagulation of charged aerosol particles [75]. They extended Hounslow et al.'s sectional method [66]. Particle charge was used as an internal co-ordinate in addition to particle volume. Vemury et
al. incorporated the effect of repulsion of particles with the same polarity and the effect of attraction of particles with an opposite polarity. They simulated size and charge changes of particle distributions having both a symmetric and an asymmetric bipolar charge. It was found that when the particles had a symmetric bipolar charge, the number concentration decreased mainly due to coagulation and therefore the size of the particles increased. On the other hand, when the particles had a asymmetric bipolar, the number concentration decreased due to electrostatic dispersion and as a consequence the increase in particle size was markedly lower. Both these findings were in accordance with published experimental results.

5.2 Derivation of the multi-dimensional population balance

5.2.1 Particle size distributions

The previous section has demonstrated the necessity of incorporating particle properties such as moisture content and porosity into the population balance, in addition to the particle size. In this section, the multi-dimensional population balance equation will be derived. The dimensions (or independent variables) of this equation are the volume of solid in a particle, $s$, the volume of liquid in a particle, $l$, the volume of air in a particle, $a$, and time, $t$. When two particles coalesce the volumes of their three different phases can simply be added, which cannot be done when size, moisture content and porosity are used as the dimensions [72]. It is tacitly assumed that coalescence is an instantaneous event and that no compaction occurs during the coalescence of two granules.

The first step is to re-define the particle density function, $n$. Historically, the particle density is defined as follows: the number (or mass or volume, etc.) of particles, $N$, in the size interval $L$ to $L + \Delta L$ equals:

$$ N = \int_{L}^{L+\Delta L} n(L) dL $$  \hspace{1cm} (5.1)

However, in this particular case, the particle density is a function of three particle properties ($s$, $l$, $a$) instead of one. Therefore, the particle density function is re-defined analogously as follows: the number (or mass or volume, etc.) of particles, $dN$, in the solids volume interval $s$ to $s + \Delta s$ and the liquid volume interval $l$ to $sl + \Delta l$ and the air volume interval $a$ to $a + \Delta a$ equals

$$ N = \int_{s}^{s+\Delta s} \int_{l}^{l+\Delta l} \int_{a}^{a+\Delta a} n'(s, l, a, t) \, ds \, dl \, da $$  \hspace{1cm} (5.2)

It is obvious from this equation that the units of both particle density functions, $n$ and $n'$ are different. The units are respectively ($\#$/m) and ($\#$/m$^9$). Although $n'$ is a number
distribution, it is of course very well possible to calculate the mass distribution from \( n' \):

\[
q_m = n' (s \rho_s + l \rho_l)
\]  

(5.3)

Here \( q_m \) is the mass distribution. The mass of the air volume is neglected here.

### 5.2.2 Size changing mechanisms

The size changing mechanisms in granulation are:

- **Coalescence**, where two particles stick together and form one particle.
- **Compaction**, where the porosity of a particle decreases.
- **Breakage**, where one particle is broken up into more than one particle, the latter being smaller than the first.
- **Nucleation**, where a cluster of primary particles comes into contact with a liquid drop and forms a granule.

Other size changing mechanisms like layering or attrition and shatter can be viewed as coalescence of larger and small particles and breakage where small particles are formed. In the following paragraphs coalescence and compaction will be dealt with in more detail.

#### Coalescence

When two particles stick together and form a larger particle, the two particles disappear and a larger particle appears. The former is called death, the latter birth. The birth and death rates are derived below.

- \( V_s = \kappa \)
- \( V_l = \lambda \)
- \( V_n = \mu \)

![Diagram of coalescence](image)

**Figure 5.1**: Coalescence: two granules collide and form a larger particle

Particles possessing a solid volume \( x \), a liquid volume \( y \) and an air volume \( z \) can be formed by two particles, one having solid volume \( \kappa \), liquid volume \( \lambda \) and air volume \( \mu \), the other having solid volume \( x - \kappa \), liquid volume \( y - \lambda \) and air volume \( z - \mu \) (see Figure 5.1). The birth rate is given by the following equation:

\[
B = \frac{1}{2} \int_0^z \int_0^y \int_0^z \Omega n'(\kappa, \lambda, \mu, t) n'(x - \kappa, y - \lambda, z - \mu, t) \, d\kappa \, d\lambda \, d\mu
\]  

(5.4)
5.3. SOLVING THE MULTI-DIMENSIONAL PBM

Here \( B \) is the birth rate and \( \Omega \) is a six-dimensional kernel since the rate of coalescence depends on the particle properties of both particles. The death rate, \( D \), is derived similarly:

\[
D = n'(x, y, z, t) \int_0^\infty \int_0^\infty \int_0^\infty \omega n'(\kappa, \lambda, \mu, t) \, d\kappa \, d\lambda \, d\mu
\]  (5.5)

Compaction

Granule compaction, i.e. porosity reduction, has been modelled before by Iveson et al. [48] and Wauters et al. [27]. In both papers a first order model is used:

\[
\frac{d\epsilon}{dt} = -k(\epsilon - \epsilon_{\text{min}})  \tag{3.1}
\]

Here \( \epsilon \) is the porosity of the granule, \( \epsilon_{\text{min}} \) is the minimum porosity of the granule, \( t \) the number of drum revolutions and \( k \) is the rate constant. Porosity can be written in terms of \( s, l \) and \( a \):

\[
\epsilon = \frac{l + a}{s + l + a}  \tag{5.6}
\]

Compaction occurs through a reduction of the volume of air in a granule. Therefore, Equation 3.1 must be rewritten in terms of \( s, l \) and \( a \). Assuming \( s \) and \( l \) remain constant (i.e. there is no evaporation):

\[
\frac{d\epsilon}{dt} = \frac{\partial a}{\partial t} \frac{s}{(s + l + a)^2}  \tag{5.7}
\]

Combining Equations 3.1 and 5.7 yields:

\[
\frac{\partial a}{\partial t} = -k \left( \frac{(l + a)}{s} \left( \frac{(s + l + a)}{s} - \frac{\epsilon_{\text{min}}(s + l + a)^2}{s} \right) \right) = C'(s, l, a, t)  \tag{5.8}
\]

Here \( C'(s, l, a, t) \) is the compaction rate, which depends on all three particle properties.

The multi-dimensional population balance can also be extended to cover other processes that occur during granulation, such as evaporation. Examples of multi-dimensional population balances that include evaporation are given by Iveson [72] and Verkoeijen et al. [76].

5.3 Solving the multi-dimensional population balance

From Equations 5.4 to 5.8 it is evident that solving the multi-dimensional population balance is quite a challenge. When \( \Omega \) is a function of \( s, l \) and \( a \) rather than a constant, an analytical solution cannot be obtained [77]. Since the purpose of the multi-dimensional population balance is to describe the size changes in the granulation process, with the knowledge that multiple properties of the granules affect its behaviour, \( \Omega \) must be a function of \( s, l \) and \( a \). Therefore an analytical solution cannot be obtained and numerical
methods must be adopted. One could in fact extend the sectional method which is explained in Section 4.2.5 and applied in Section 4.3. However, this poses some problems. The first is related to the computing power required. If we were to discretize each internal co-ordinate (i.e. \(s, l\) and \(a\)) in 30 sections, which is the same number as used in Section 4.3, then that would yield \(30^3 = 27000\) ordinary differential equations, which are all coupled. It is obvious that such a vast set of equations will put an enormous demand on the computational time. Another problem involved with adopting the aforementioned sectional method is the low resolution. This can be explained as follows: say we take one section, with a lower boundary for the volume of solid of \(v_i\) and an upper boundary of \(v_{i+1} = 2v_i\). The lower boundary for the volume of liquid equals, say, \(v_j\) and the upper boundary equals \(v_{j+1} = 2v_j\). Then the particle with the lowest binder content in this section have a binder content of \(v_j/2v_i\) and the particles with the highest binder content \(2v_j/v_i\) (all binder contents are expressed as volume of liquid per volume of solid, the same manner as in Chapter 3). In other words, the "wettest" granules contain four times more binder than the "driest" granules in the same section. Given the results presented in Chapter 3, which showed that granulation occurs within a narrow margin of binder liquid contents, this level of resolution is clearly unsatisfactory. If a different sectional method with a higher resolution were to be adopted, two additional problems are encountered. Firstly the number of equations to be solved will increase and secondly, there will be a problem related to the conservation of mass. An intrinsic problem of discretization is that the total volume (or mass) of particles is not conserved [78]. Hounslow et al. have shown that with the \(\sqrt{2}\) sectional method this was not the case [66]. One approach that does not pose the aforementioned difficulties is using Monte Carlo simulations. In fact, Monte Carlo simulations are perfectly suitable for discrete processes, such as agglomeration, as the next section will demonstrate.

5.4 Monte Carlo simulations of a multi-dimensional population balance

A Monte Carlo simulation is "a mathematical experiment in which the behaviour of a system is simulated and which incorporates stochastic behaviour modelled using a randomness generator to vary the behaviour of the system [79]." They have been applied to several particulate processes. For example, Kaye has used Monte Carlo simulations to model powder mixing [79]. Van Peborgh Gooch and Hounslow have applied Monte Carlo simulations for modelling aggregation, growth and nucleation in crystallization [80]. Yang and Matsoukas [81], Smith and Matsoukas [82] and Lee and Matsoukas [83] have applied Monte Carlo simulations for solving population balance equations describing processes in which aggregation, fragmentation or simultaneous aggregation and fragmentation occurs. Smith and Matsoukas distinguish between a number of different Monte Carlo methods [82]:

- Time-driven Monte Carlo simulations, in which a time interval, \(\Delta t\) is chosen. Which and how many events (i.e. particles coalescing or breaking) are realized is decided.
stochastically.

- Event-driven Monte Carlo simulations. In this case, an event is selected to occur and the time is increased with a certain value, based on the rates of the processes. The event-driven Monte Carlo simulation can be further subdivided into:
  
  - Constant volume methods in which the total volume of particles is conserved. Therefore, the number of particles in the simulation decreases when agglomeration is simulated and increases when breakage is simulated.
  
  - Constant number methods in which the number of particles in the simulation remains constant. The advantage of this method when simulating agglomeration is that the population remains large enough in order for the Monte Carlo method to be accurate. In addition, the particles can grow indefinitely whereas a constant volume method is limited by the total volume of particles present in the simulation. In principle the simulation can only proceed until one particle, which has the summed volume of all the initial particles in the simulation, remains. When modelling breakage processes with the constant volume method, the number of particles can become very large, which puts a high demand on the computing power. Yang and Matsoukas have shown that the constant number method is highly suitable for modelling both agglomeration and grinding processes [81].

Smith and Matsoukas used the constant number method for simulating an agglomeration process and compared their solution with an analytical solution [82]. The results from their simulation were in agreement with the analytical solution. However, they only compared the moments of the distribution. In Appendix C the results of a constant number Monte Carlo simulation are compared with an analytical solution. In this case, the whole particle size distribution was used for the comparison of the numerical and analytical solution. As can be seen in Appendix C, the results of the simulation are in excellent agreement with those of the analytical solution, demonstrating its suitability.

Because of its advantages and suitability, a constant number method was adopted to model the multi-dimensional population balance. The principle of the constant number method is briefly outlined in Figure 5.2. For every event, a pair of granules is randomly chosen from the array of particles and the probability of the event, i.e. the two granules sticking together, is determined. If this probability is larger than a random number, then coalescence of the two granules occurs. If this is not the case, a new pair is chosen until an event occurs. After that, the matrix is updated. This consists of two steps. First, the newly formed granules takes the place in the array of one of the granules that have coalesced. The place in the array of the other granule is replaced by a copy of a randomly chosen particle from the array. When the number of particles in the array is sufficiently large this will introduce a negligible error, as has been shown in the literature [81, 82, 83] and in Appendix C. Finally, the time step is calculated (which will be explained in Section 5.5) and the procedure is repeated. In our case, after the time step was calculated, the volume of air of all particles in the array was adjusted according to the extent of
compaction that had occurred during the duration of the time step. Equation 3.1 was used for this purpose.

![Diagram of particle coalescence](image)

**Figure 5.2**: Concept of the constant number Monte Carlo method: a pair of particles from an array is chosen randomly. If the pair coalesces, the newly formed particle takes the place in the array of one of the parent particles while the place in the array of the other parent particle is filled with a copy of a randomly chosen particle from the whole array.

### 5.5 Calculation of the time step

Smith and Matsoukas calculated the time step after an event as follows: the change in the particle concentration in the system that is being simulated after one successful event equals:

$$
\Delta C_\kappa = -\Delta t_\kappa \sum_l R_l
$$

(5.9)

Thus:

$$
\Delta t_\kappa = -\frac{\Delta C_\kappa}{\sum_l R_l}
$$

(5.10)

Here $\Delta C_\kappa$ is the change in number concentration after $\kappa$ events, $\Delta t_\kappa$ is the time step and $R_l$ is the rate of event $l$, i.e. the coalescence of particles A and B. The minus sign appears in both Equations 5.9 and 5.10 because the number concentration decreases when two particles coalesce. For the calculation of $R_l$, $\Omega$ has to be known. $\Omega$ is, in analogy with the one-dimensional coalescence kernel, split into two parts: a constant and a coalescence probability which is a function of six variables, being $s$, $l$ and $a$ of both particles:

$$
\Omega(s_A, l_A, a_A, s_B, l_B, a_B) = \Omega_0 f_{A,B}(s_A, l_A, a_A, s_B, l_B, a_B)
$$

(5.11)

According to the mechanism described in Section 3.3.4 an estimation for $f_{A,B}$ can be made. As stated in Section 3.3.4, small granules are picked up by wet spots on the large granules.
These wets spots are formed due to the expulsion of binder liquid onto the surface of the large granules due to compaction. As soon as the small granules have disappeared, the large granules become surface wet and this marks the start of the rapid growth stage during which large granules can coalesce with each other. From these observations $f_{A,B}$ can be constructed, but first a definition for “small”, “large”, “wet” and “dry” has to be given. In Figure 3.23 the fraction of particles smaller than 500 $\mu m$ is plotted. This value therefore seems a logical choice as cut-off size for “small” and “large” particles. As for the criterion whether a particle is “wet” or “dry”, a certain value of the pore saturation seems appropriate. In Section 3.3.2 it was concluded that granules had a pore saturation of approximately 0.85 (-) when the rapid growth stage starts. Therefore this value was chosen. The aforementioned can be summarized in equations:

$$\sqrt[3]{6(s + l + a)} \frac{l}{\pi} < 500\mu m \quad \text{"small"}$$

$$\sqrt[3]{6(s + l + a)} \frac{l}{\pi} > 500\mu m \quad \text{"large"}$$

$$\frac{l}{l + a} < 0.85 \quad \text{"dry"}$$

$$\frac{l}{l + a} > 0.85 \quad \text{"wet"}$$

As a first approximation, it is assumed that a pair of particles either always or never coalesce, in other words, the probability is either zero or one. The probabilities of all the possible combinations of properties of granules A and B are summarized in Table 5.1.

**Table 5.1:** $f_{A,B}$, probability of coalescence as a function of the properties of granules A and B

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>Big &amp; Wet</th>
<th>Big &amp; Dry</th>
<th>Small &amp; Wet</th>
<th>Small &amp; Dry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Big &amp; Wet</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Big &amp; Dry</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Small &amp; Wet</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Small &amp; Dry</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Consequently, $\sum R_l$ is calculated as follows [82]:

$$\sum R_l = \frac{C}{\Omega_0 C_0} \frac{< f_{A,B}>}{2\tau_c} \left( \frac{C}{C_0} \right)^2$$

(5.12)

Here $C$ is the number concentration and $C_0$ is the initial number concentration and $\tau_c$ is the characteristic coalescence time defined as:

$$\tau_c = \frac{1}{\Omega_0 C_0}$$

(5.13)
In Equation 5.12 \(< f_{A,B} >\) represents the average value of \( f_{A,B} \) which is calculated as follows:

\[
\langle f_{A,B} \rangle = \frac{1}{C^2} \int_0^\infty \int_0^\infty \int_0^\infty \int_0^\infty f_{A,B} c_A(s_A, l_A, a_A) c_B(s_B, l_B, a_B) ds_A dl_A da_A ds_B dl_B da_B
\]  
(5.14)

Here \( c_A \) and \( c_B \) are the concentrations of particles A and B, respectively. Equation 5.14 calculates \(< f_{A,B} >\) for a continuous particle distribution. However, for the Monte Carlo simulations, the particle distribution is discrete and \(< f_{A,B} >\) is then calculated by Equation 5.15:

\[
\langle f_{A,B} \rangle = \frac{\sum_{A}^{N} \sum_{B \neq A}^{N} f_{A,B}}{N(N - 1)}
\]  
(5.15)

Combining Equations 5.10 to 5.15 yields:

\[
\Delta t_\kappa = -\frac{2\tau_C}{\langle f_{A,B} \rangle} \left( \frac{C_0}{C_\kappa} \right)^2 \left( \frac{\Delta C_\kappa}{C_0} \right)
\]  
(5.16)

Mass conservation dictates that:

\[
\frac{C_\kappa}{C_0} = \frac{\overline{M}_0}{\overline{M}_\kappa}
\]  
(5.17)

Here \( \overline{M}_0 \) is the initial average mass and \( \overline{M}_\kappa \) is the average mass after \( \kappa \) events. If the number of particles is sufficiently large, the difference operator may be treated as differential [82]:

\[
-\left( \frac{C_0}{C_\kappa} \right)^2 \left( \frac{\Delta C_\kappa}{C_0} \right) = \Delta \left( \frac{C_0}{C_\kappa} \right) = \frac{\Delta \overline{M}_\kappa}{\overline{M}_0} = \frac{\overline{M}_\kappa - \overline{M}_{\kappa - 1}}{\overline{M}_0}
\]  
(5.18)

In the constant number Monte Carlo method, the difference in the average mass can be calculated in the following manner: at a certain point in time, after \( \kappa \) events, the number of particles in the array is \( N \), representing a concentration of \( C_\kappa \) in the system that is being simulated. A successful event results in the loss of a particle in the simulation which corresponds to a concentration change of \(-C_\kappa/N\). Thus:

\[
C_{\kappa+1} - C_\kappa = -\frac{C_\kappa}{N} \implies \frac{C_\kappa}{C_0} = \left( \frac{N - 1}{N} \right)^\kappa
\]  
(5.19)

Finally, combining Equations 5.16 to 5.19 yields:

\[
\Delta t_\kappa = -\frac{2\tau_C}{\langle f_{A,B} \rangle} \frac{1}{N} \left( \frac{N}{N - 1} \right)^\kappa
\]  
(5.20)

### 5.6 Results of the Monte Carlo simulations

A number of parameters are required for the calculation of the time step, the constants for calculating the compaction and the initial distribution. These parameters are listed
Table 5.2: Constants used in simulation

<table>
<thead>
<tr>
<th>$\Omega_0$ (m$^3$s$^{-1}$)</th>
<th>$\epsilon_0$</th>
<th>$\epsilon_{\text{min}}$</th>
<th>$k$ (rev$^{-1}$)</th>
<th>$C_0$ (m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.37</td>
<td>0.29</td>
<td>0.005</td>
<td>1.899 $10^{11}$</td>
</tr>
</tbody>
</table>

in Table 5.2. The initial distribution from the experiment displayed in Figure 3.21 was used in the simulation.

The estimates for $\epsilon_{\text{min}}$ and $k$ were made using the data as listed in Table 3.4. $\epsilon_0$ was chosen slightly higher, since it can be assumed that the porosity of the nuclei formed by spraying the binder liquid onto the dry powder is higher than that of the nuclei that were produced by pushing them through a 2 mm sieve. $C_0$ was calculated using the initial particle size distribution of the experiment displayed in Figure 3.21, assuming that the porosity of the bed of granules was 0.5. Finally, $\Omega_0$ was the only parameter that needed to be fitted.

![Diagram](image)

Figure 5.3: Result from a Monte Carlo simulation of the multi-dimensional population balance. Both the fraction of granules $< 500$ $\mu$m as well as the mass mean diameter are plotted, similar to Figure 3.23.

In Figure 5.3 the results of one Monte Carlo simulation are shown. The behaviour of the process is in good agreement with the finding as displayed in Figure 3.23. As stated in Section 3.3.3, the mass fraction of granules smaller than 500 $\mu$m decreases while the mean diameter increases slightly. After the smaller granules have been removed, the induction
Figure 5.4: Particle size distribution plotted as the mass fraction in each class as well as the average binder liquid content in each size class.
stage is ended and the rapid growth stage is entered, resulting in a substantial change in particle size. The differences between the experimental results and the results from the simulation are that the decrease of the smaller granules is not linear with time in the simulation and the increase in particle size is not gradual during the induction stage.

Figure 5.4 shows how the particle size distribution changes in time, as well as the liquid content in each size class. It can be observed that similar to the experimental data, at the start of the induction stage, the larger granules have more binder liquid than the smaller granules. During the induction stage, which lasts approximately 200 revolutions, the granules smaller than 500 μm are gradually being depleted. Once the smaller granules have disappeared, rapid growth occurs and the size distribution becomes wider. It must be emphasized that the width of the size classes in Figure 5.4 increases with increasing size.

5.7 Conclusions

In this chapter a multi-dimensional population balance was derived which included three particle properties: the volume of solid, liquid and air in the granule. From these three properties other quantities that govern the behaviour of the granules can be derived such as the granule porosity and the pore saturation. Although the necessity of including other granule properties in addition to granule size has been recognized before, there are only a very limited number of actual applications of a multi-dimensional population balance with a solution. This is most likely due to the complexity of the equations. It was shown that Monte Carlo simulations offer a quick and straightforward way of solving the multi-dimensional population balance.

The results of the Monte Carlo simulation are in agreement with the experimentally observed behaviour of the granulation process. For the simulations a kernel was derived based on the experimental results. Although the kernel is physically based, it is rather simple. One can imagine that the kernel can be modified in several ways. For instance, the boundary between “large” and “small” particles as well as the boundary between “dry” and “wet” particles is sharp. It would be interesting, for example, to create “fuzzy” boundaries.

In summary it can be concluded that the multi-dimensional population balance has great potential for modelling granulation processes. The model is based on the physics of the process and therefore offers possibilities for using the model for process optimization and process design. Monte Carlo methods are very well suited for solving the complex equations. The model can therefore relatively easily be extended to other mechanisms.

List of symbols

\[
\begin{align*}
\alpha & \quad \text{volume of air in particle (m}^3) \\
B & \quad \text{birth rate (m}^{-9} \text{s}^{-1})
\end{align*}
\]
\( C \)
number concentration of particles (# m\(^{-3}\))

\( C_0 \)
initial number concentration of particles (# m\(^{-3}\))

\( C'(s, l, a, t) \)
compaction rate (m\(^3\) s\(^{-1}\))

\( D \)
death rate (m\(^{-9}\) s\(^{-1}\))

\( f_{A,B} \)
coalescence probability of granules A and B (-)

\( k \)
compaction rate constant (# of revs\(^{-1}\))

\( l \)
volume of liquid in particle (m\(^3\))

\( L \)
particle size (m)

\( \bar{M}_0 \)
initial average mass (kg)

\( \bar{M}_\kappa \)
average mass after \( \kappa \) events (kg)

\( n \)
particle number density, one-dimensional (# m\(^{-1}\))

\( n' \)
particle number density, multi-dimensional (# m\(^{-9}\))

\( N \)
particle number (in Equation 5.1) (#)

\( N \)
number of particles used in Monte Carlo simulation (#)

\( q_m \)
mass distribution (kg m\(^{-9}\))

\( R_l \)
the rate of event \( l \) (m\(^{-3}\) s\(^{-1}\))

\( s \)
volume of solid in particle (m\(^3\))

\( t \)
time (s) or number of drum revolutions (# of revs)

**Greek symbols**

\( \Delta t_\kappa \)
time step after \( \kappa \) events (s)

\( \epsilon \)
granule porosity (-)

\( \epsilon_{\text{min}} \)
minimum granule porosity (-)

\( \kappa \)
number of events (#)

\( \rho_l \)
liquid density (kg m\(^{-3}\))

\( \rho_s \)
solid density (kg m\(^{-3}\))

\( \tau_C \)
characteristic coalescence time (s)

\( \Omega \)
multi-dimensional kernel (m\(^3\) s\(^{-1}\))

\( \Omega_0 \)
constant part of kernel (m\(^3\) s\(^{-1}\))
6.1 Conclusions

6.1.1 Mechanisms

In this thesis, the aim was to improve already existing granulation models by incorporating experimentally gained knowledge. First, the mechanism of induction behaviour was studied. It was shown that, in accordance with the literature, the granule porosity decreases during the induction stage and that at the end of the induction stage the granules appear to be surface wet. However, a modified mechanism was proposed, based on the experimental results. It was shown that the liquid distribution and the amount of smaller granules dictate the growth behaviour and in particular the duration of the induction stage. The proposed mechanism for induction behaviour can be summarised as follows:

- During the liquid addition stage, the binder liquid is not added homogeneously to the dry powder. This results in the formation of large and wet granules and smaller granules containing less binder liquid.

- During the induction stage, the larger granules are continuously compacted and as a result, binder liquid is continuously squeezed onto their surface.

- The smaller and drier granules are picked up by the larger granules whenever wet patches appear on the surface of the latter. Therefore, the large granules remain to appear surface dry.

- When all the smaller granules have been removed through selective coalescence with the larger granules a further reduction in the porosity of the large granules will result in the formation of surface wet granules since there are no more small granules left to be picked up.

- Once the large granules are surface wet, they have the possibility to coalesce with other large, surface-wet granules. This results in a fast increase of granule size: the rapid growth stage.
Direct evidence of this proposed mechanism was given by the fact that selective removal of the smaller granules resulted in a shorter induction stage. The implication of this is that if the rapid growth stage is not desirable, fines can be added to the granulator so that layering of small granules onto large granules remains the dominant mechanism of growth, thus controlling the growth rate.

6.1.2 Population balance modelling

Simulations were performed with two types of population balance models: a one-dimensional population balance and a multi-dimensional population balance. The main result from the one-dimensional simulations is that it is possible to simulate existing data with good results using a simple kernel. However, it is not probable that the same simple kernel can be used to model the granulation process outside the range of operation of the model. In other words: the one-dimensional population balance cannot be used to predict the granulation process. Therefore, the application of one-dimensional population balances should be limited to (feed-back) control rather than process design or optimization.

One of the drawbacks of the one-dimensional population balance model, which uses particle size as the granule property of interest, is that it does not reveal much of the physics that govern the various mechanisms. The experimental results indicate that besides particle size, its binder liquid content, its porosity and its pore saturation dictate the behaviour of the granules. Therefore, a multi-dimensional population was derived using volume of solid, liquid and air as the granule properties of interest. A simple coalescence kernel, based on experimental observations, was derived. It was shown that with such a simple kernel, very good results can be obtained. These result are in accordance with the phenomena occurring during the granulation process.

It was shown that Monte Carlo simulations are well suited for solving the multi-dimensional population balance model. Although the model is quite complex, Monte Carlo simulations offer a quick and straightforward manner to solve the equations, whereas other methods are likely to require much more computing power.

6.2 Recommendations

Although the compaction and growth mechanisms of granulation are well understood, nucleation and wetting will require more attention. Most industrial processes operate in the shear controlled regime (see Figure 2.10). How the shearing forces operating in the granulator control the size of the granules that are formed is a complex process that is in need of further investigation. One of the true challenges in granulation research in the years to come is to derive a model that describes how the nuclei are formed and consequently if, and how, these nuclei break up to form stable granules. The flow patterns, particularly in high shear granulators, have a profound effect on the shear forces acting upon the granules during collisions with other granules, the granulator walls and the impellers. These patterns need to be investigated, for example through positron emission particle tracking.
The multi-dimensional population balance has proved to be a powerful tool in modelling granulation processes. This introduced the need for ways to measure particle size, liquid content and porosity of each granule independently and accurately. The multi-dimensional kernel used in this thesis was relatively simple. Therefore, other kernels should be tested as well. It is also well conceivable that the multi-dimensional population balance is to be extended to include other granule properties. For example, Iveson [72] included granule composition as an important property since pharmaceutical granulation processes aim to produce granules with a homogeneous composition with respect to the content of the active component. In addition, Scott et al. [84] have shown that the composition of granules is heterogeneous with respect to the size of the constituent particles. Since solving the multi-population balance is no longer an obstacle, the inclusion of other granule properties in the multi-dimensional population balance can, and should, be done.
Appendix A
Characterization of the nozzles

Figure A.1: Contour plots of binder flux distribution. Nozzle: TP500017, nozzle height: 13.2 cm
APPENDIX A. CHARACTERIZATION OF THE NOZZLES

Figure A.2: Contour plots of binder flux distribution. Nozzle: TP650017, nozzle height: 13.5 cm
Figure A.3: Contour plots of binder flux distribution. Nozzle: TP650017, pressure: 3.5 bar

Figure A.4: Contour plots of binder flux distribution. Nozzle: TP650017, pressure: 5.0 bar
Appendix B

Results from one-dimensional population balance modelling

(a) Sample taken after 1 minute, experiment #1
(b) Sample taken after 1 minute, experiment #2

Figure B.1: Results of the simulations for experiments #1 and #2, 17.8% binder.
Figure B.2: Results of the simulations for experiment #3, 18.4% binder.
Figure B.3: Results of the simulations for experiment #4, 19.1% binder.
Figure B.4: Results of the simulations for experiment #5, 19.1% binder.
Figure B.5: Results of the simulations for experiment #6, 19.1% binder.
Figure B.6: Results of the simulations for experiment #7, 19.1% binder.
Figure B.7: Results of the simulations for experiment #8, 19.8% binder.
Figure B.8: Results of the simulations for experiment #9, 20.4% binder.
Figure B.9: Results of the simulations for experiment #10, 20.4% binder.
Figure B.10: Results of the simulations for experiment #5, 19.1% binder. Adegbayo and Ennis kernel used for the simulations.
(a) Sample taken after 41 minutes  
(b) Sample taken after 56 minutes

(c) Sample taken after 66 minutes  
(d) Sample taken after 86 minutes

(e) Sample taken after 106 minutes

**Figure B.11**: Results of the simulations for experiment #5, 19.1% binder. Sum kernel used for the simulations
Appendix C

Testing the Monte Carlo method

C.1 An analytical solution for a population balance with aggregation only

Hounslow et al. stated that there are very few analytical solutions to population balances that contain aggregation [66]. However, they found one special case for which an analytical solution existed. Naturally, this was a rather simple case: it had an idealized initial distribution, being an exponential distribution, and the most simple kernel, i.e. the constant kernel. Thus the population balance is given by Equation C.1 (see also Chapter 4).

$$\frac{\partial n(u)}{\partial t} = B(u) - D(u)$$  \hspace{1cm} (C.1)

In this equation, \(B(u)\) is the birth rate of particles of size \(u\), and \(D(u)\) is the death rate:

$$B(u) = \frac{1}{2} \int_{0}^{u} \beta(v, u - v) n(v) n(u - v) \, dv$$ \hspace{1cm} (C.2)

$$D(u) = n(u) \int_{0}^{\infty} \beta(v, u) n(v) \, dv$$ \hspace{1cm} (C.3)

Here \(\beta\) is the coalescence kernel. In this case, \(\beta = \beta_0\), in other words, the value of \(\beta\) does not depend on the size of the particles colliding.

Hounslow et al. presented the analytical solution to the population balance equation as outlined above, which is [66]:

$$n(v, t) = \frac{4N_0}{v_0(\tau + 2)^2} \exp\left(-\frac{2v/v_0}{\tau + 2}\right)$$ \hspace{1cm} (C.4)

Here \(n(v, t)\) is the number density per unit volume of particles of size \(v\) at time \(t\), \(\tau\) is the dimensionless time, which is defined as \(\tau = N_0\beta_0 t\). Hounslow et al. proceeded to define a dimensionless length:

$$\bar{L}_i = \left(\frac{v_i}{v_0}\right)$$ \hspace{1cm} (C.5)
and a dimensionless number:

\[ \tilde{N}_i = \frac{N_i}{N_0} = \frac{1}{N_0} \int_{v_i}^{2v_i} n dv \]  

(C.6)

Combining Equations C.4-C.6 yields:

\[ \tilde{N}_i = \frac{2}{\tau + 2} \left[ \exp\left(-\frac{2\tilde{L}_i^3}{\tau + 2}\right) - \exp\left(-\frac{4\tilde{L}_i^3}{\tau + 2}\right) \right] \]  

(C.7)

## C.2 Discretizing the initial distribution of the analytical solution

The initial size distribution of the particles is exponential:

\[ n_0 = \frac{N_0}{v_0} \exp\left(\frac{-v}{v_0}\right) \]  

(C.8)

Here \( n_0 \) is the non-normalized number density distribution of the initial particles per unit volume, \( N_0 \) is the total number of initial particles per unit volume, \( v_0 \) is a parameter that dictates the width of the initial particle size distribution and \( v \) is the size (volume) of the particle. Since this is a continuous distribution, it has to be converted to a discrete distribution for use with the Monte Carlo model. Equation C.8 can be integrated from size zero to \( V_1 \), with \( V_1 \) chosen in such a manner that the integration yields one particle (per unit volume):

\[ 1 = \int_0^{V_1} \frac{N_0}{v_0} \exp\left(\frac{-v}{v_0}\right) dv \]  

(C.9)

This yields:

\[ V_1 = -v_0 \ln\left(1 - \frac{1}{N_0}\right) \]  

(C.10)

The interval between \( v = 0 \) and \( v = V_1 \) now contains one particle. In a similar manner \( V_2 \) can be defined in such a manner that the interval between \( v = V_1 \) and \( v = V_2 \) contains one particle. This yields:

\[ V_2 = -v_0 \ln\left(1 - \frac{2}{N_0}\right) \]  

(C.11)

Similarly for \( V_n \), in such a manner that one particle exists in the interval between \( v = V_{n-1} \) and \( v = V_n \):

\[ V_n = -v_0 \ln\left(1 - \frac{n}{N_0}\right) \]  

(C.12)

In principle, the interval in which the last (\( N_0^{th} \)) particle lies cannot be calculated, since this would give \( \ln(1 - N_0/N_0) = \ln(0) \). Therefore the last interval contains 0.9 particle which gives:

\[ V_{last} = -v_0 \ln\left(\frac{0.1}{N_0}\right) \]  

(C.13)
Now the particle size domain is discretized into $N_0$ sections, each containing a single particle. The average of the upper and lower boundary of each section can then be assigned to each particle and thus the initial particle size distribution is discretized.

C.3 Comparing the results of the Monte Carlo simulation to the analytical solution

Using the discretized initial size distribution as presented in the previous section and the Monte Carlo method as outlined in Section 5.4, the change in the particle size distribution can be simulated. Since in this case a volume-independent kernel was used, each randomly chosen pair of particles coagulates. After each event, the array of particles is updated and a time step is calculated as follows:

$$\Delta t_\kappa = \frac{2\tau_C}{<k_{ij}>} \cdot \frac{1}{N} \left( \frac{N}{N-1} \right)^\kappa$$  \hspace{1cm} (C.14)

Here, $\Delta t_\kappa$ is the time increment after $\kappa$ successful events, $\tau_C$ is a dimensionless time:

$$\tau_C = 1/\beta_0 N_0$$  \hspace{1cm} (C.15)

$N$ is the number of particles used in the simulation and $<k_{ij}>$ is equal to unity since a volume-independent kernel was used (see also Section 5.4).

A simulation was performed with $N = N_0 = 10,000$, $\beta_0 = 1.1$ and $v_0 = 5$. The results of the simulation as well as the analytical solution are plotted in Figure C.1. One can conclude that the Monte Carlo simulation is in perfect agreement with the analytical solution.
Figure C.1: A Comparison of the analytical solution and the results from the Monte Carlo simulation. The particle size distributions (see Equation C.7) at four moments in time are shown. The lines represent the analytical solution, the symbols represent the Monte Carlo simulation.
Bibliography


[77] Private communication with Dr. W.T. van Horssen. Dr. Van Horssen is Associate Professor at the Applied Mathematical Analysis Department of the Delft University of Technology. One of his specialties is analytical solutions of partial differential equations. Delft, May 2000.


Samenvatting in het Nederlands

Modelleren en mechanismen van granulatie

Granulatie is de algemene aanduiding voor processen waarbij de grootte van deeltjes toeneemt. De zo gevormde granules hebben verscheidene voordelen ten aanzien van de poeders uit welke zij zijn samengesteld, zoals verbeterde stromings eigenschappen, een verminderd risico op segregatie en een verbeterde homogeniteit van het produkt. Onlangs meer dan vier decennia aan onderzoek, zowel in industrie als aan universiteiten, zijn granulatieprocessen nog steeds moeilijk te modelleren en te regelen. Derhalve zijn hoge recycle ratios en het gedwongen stoppen van een granulatieproces niet ongebruikelijk. De prestaties van het proces zijn sterk afhankelijk van de expertise van de operators. Het is duidelijk dat er een behoefte is aan adequate modellen die kunnen leiden tot verbeterde procesprestaties of een verbeterd granulatorontwerp. In dit proefschrift worden de verkregen experimentele gegevens op twee manieren aangewend: ten eerste worden deze gebruikt voor het verkrijgen van een verbeterd inzicht van het proces in de kwantitatieve zin. Dit inzicht wordt vervolgens gebruikt voor het uitbreiden en verbeteren van bestaande populatiebalans modellen. Op deze manier wordt het inzicht in het proces in de kwantitatieve zin vergroot.

bindervloeistof wordt toegevoegd dan deze kritische hoeveelheid zal de inductieperiode vrijwel oneindig lang duren.

Twee soorten experimenten zijn uitgevoerd: experimenten waarbij de bindervloeistof en het poeder vooraf werden gemengd en door een 2 mm zeef werden gedrukt, waardoor een constante verdeling van de nuclei werd gewaarborgd, en experimenten waarbij de bindervloeistof op het poeder werd gesproeid. De eerstgenoemde experimenten werden uitgevoerd teneinde het groei- en compactiedrag van het materiaal te testen en de laatstgenoemde experimenten werden uitgevoerd teneinde het effect van de manier waarop de bindervloeistof wordt toegevoegd vast te stellen alsmede het effect van de vloeistofverdeling. Het bleek dat tijdens de inductieperiode de porositeit van de granules afnam en dat, aan het begin van de periode van snelle groei, het oppervlak van de granules nat was. Daarnaast is gevonden dat een grote hoeveelheid bindervloeistof resulteerde in een kortere inductieperiode. Deze bevindingen waren in overeenstemming met de literatuur. De resultaten van de experimenten waarbij de bindervloeistof gesproeid werd gaven aanleiding tot het postuleren van een gewijzigd mechanisme van inductiedrag. Het bleek dat de gevormde nuclei bestaan uit grotere granules die relatief meer bindervloeistof bevatten en kleinere granules die relatief minder bindervloeistof bevatten. Dit kan toegewezen worden aan het patroon van de sporeikop die werd gebruikt voor het vernevelen van de bindervloeistof boven het poeder. Aangezien het vloeistofdebat het grootst is in het centrum van de sporeizone, worden hier de grotere en nattere granules gevormd en elders de kleinere en drogere. Het bleek dat tijdens de inductieperiode de fractie van kleinere granules lineair in tijd afnam en dat de periode van snelle groei direct aanving nadat de kleinere granules waren verdwenen. Het selectief verwijderen van de kleinere granules resulteerde in een significante verkorting van de duur van de inductieperiode.

Het mechanisme van inductiedrag wordt op de volgende manier uitgelegd: tijdens het toevoegen van de vloeistof worden nuclei gevormd. Doordat de vloeistof niet homogeen wordt toegevoegd ontvangen sommige zones meer vloeistof dan andere. Het is derhalve onvermijdelijk dat zowel grotere granules, die meer vloeistof bevatten alsmede kleinere, drogere granules worden gevormd. Nadat de vloeistof is toegevoegd begint de inductieperiode. Tijdens deze periode worden de granules gecompatteerd. De grotere granules worden dan continu vochtig aan hun oppervlak, maar de gevormde vochtige plekken aan het oppervlak van de granules nemen direct kleinere en drogere granules op. Hierdoor daalt het relatieve vloeistofgehalte van de grotere granules weer en lijken zij een droog oppervlak te bezitten. Wanneer er echter geen kleinere granules meer zijn leidt verdere compactie tot de vorming van granules met een vochtig oppervlak dat vochtig blijft doordat er geen kleinere, droge, granules meer zijn die aan het vochtige oppervlak kunnen blijven kleven. Vanaf dat moment agglomereren de grote en vochtige granules met elkaar en dat leidt tot een sterke toename van de groeisnelheid. Deze overgang is "snelle groei". De bindervloeistof is dan homogeen verdeeld over de granules. Dit toont aan dat de inductieperiode ook gezien kan worden als een periode van vloeistofverdeling.

Hiernaast is aangetoond dat de afstand van de sporeikop tot het poederbed een significante invloed had op het proces. Een grotere afstand leidt tot een homogenere verdeling van de bindervloeistof. Hierdoor wordt de tijd die nodig is om de bindervloeistof te verde-
len korter en daardoor ook de duur van de inductieperiode. Het variëren van het debiet van de bindervloeistof had geen effect. Derhalve kan geconcludeerd worden dat de hoogte van de sproeikop een cruciale parameter is voor het beheersen van het groeigedrag van een granulatieproces.


Aan de hand van de resultaten van de experimenten met de roterende trommel is een groeikernel voor het multi-dimensionale populatiebalans model afgeleid. Deze groeikernel was gebaseerd op het mechanisme van inductiegedrag. Een Monte Carlo methode werd gebruikt om de multi-dimensionale populatiebalans op te lossen. Monte Carlo methodes werden al eerder toegepast voor het oplossen van één-dimensionale populatiebalansen en het bleek dat deze zeer geschikt zijn voor het modelleren van deeltjesprocessen waarin discrete veranderingen van deeltjesgrootte in plaatsvinden. Het bleek dat de Monte Carlo methode ook goed geschikt was voor simulaties met een multi-dimensionale populatiebalans. Het is zeer de vraag of andere numerieke methoden in staat zijn om dit soort
simulaties uit te voeren met dezelfde snelheid en nauwkeurigheid.

De resultaten van het multi-dimensionale populatiebalans model waren in overeenstemming met de experimentele gegevens. Zowel de verandering in deeltjesgrootte als in vloeistofgehalte van de simulaties volgde die van de experimenten. Het is duidelijk dat de mogelijkheden om met multi-dimensionale populatiebalansen granulatieprocessen te modelleren groot zijn aangezien deze fundamenteler zijn dan één-dimensionale populatiebalansen. De resultaten in dit proefschrift onderstrepen deze bevinding.

P.A.L. Wauters
Acknowledgment

Most acknowledgments start by saying that, although there is only one single name on the cover of the thesis, it could not have been written without the help of other people. After that a (sometimes long) list of people follows all of whom aided in one way or another to the completion of the project. Undoubtedly some of you are hoping for something different. Alas, I'm afraid I must disappoint you... Contemplating the past years I realize that all of this could not have been possible without the help (sometimes unintentional) of a number of people. I would like to take the opportunity to thank them here.

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정말로 사랑합니다

Flip.
Curriculum Vitae

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