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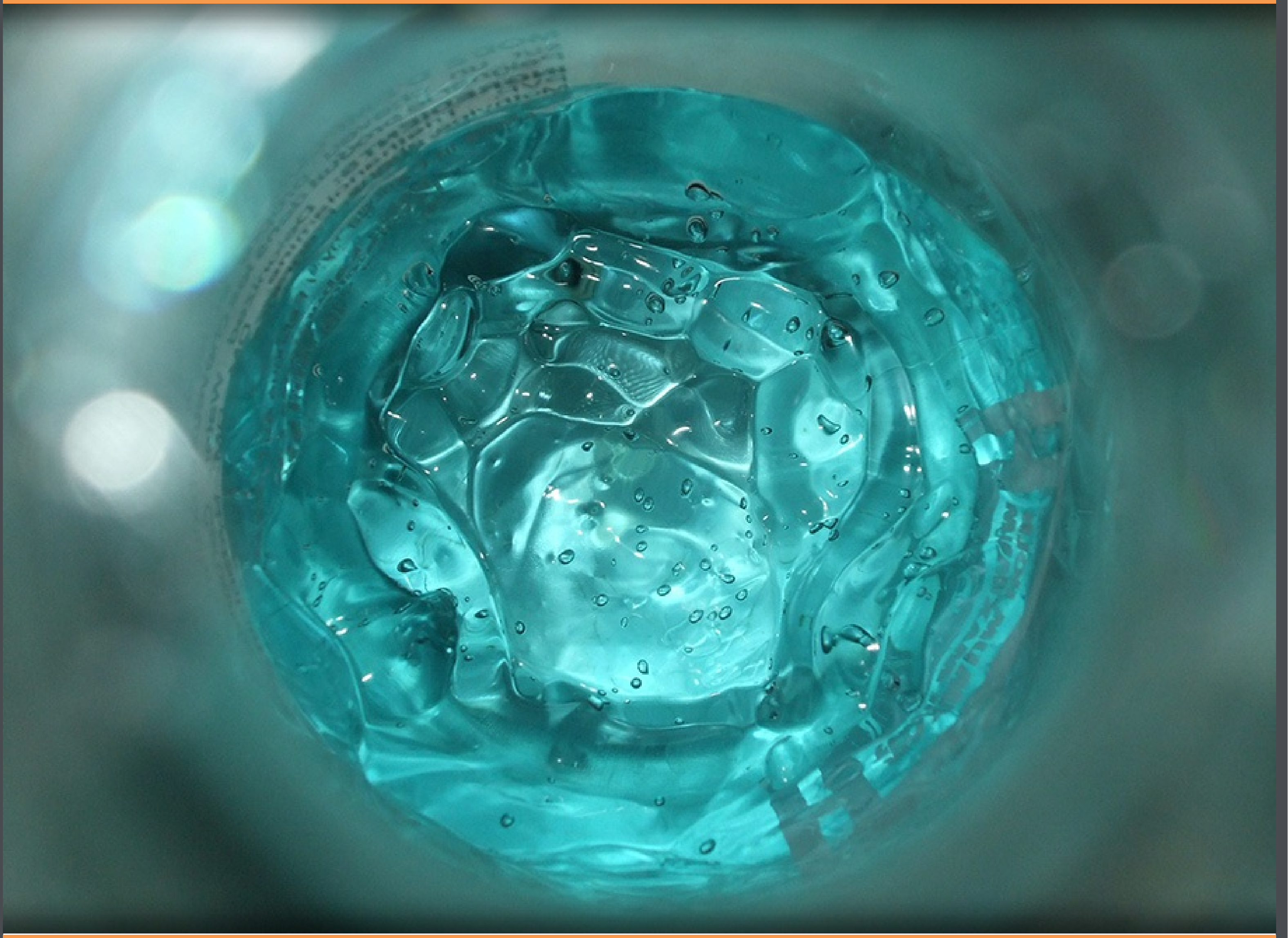
Advanced Granulation Theory at Particle Level

Peter Dybdahl Hede



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Contents

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The present text concerns the micro-level (particle-level) perspective on the different stages of the granulation process. A range of the newest and advanced quantitative models is presented hereby introducing recent advances in wetting and nucleation modelling, and theory describing granule growth behaviour. The different bonding mechanisms and the strength of liquid bonded particles are emphasised and recent advances in simulation of wet granule breakage is reviewed. Further, some of the more advanced coalescence models are introduced with primary focus on class I models accounting for coalescence of non-deformable as well as deformable granules.

The text is aimed at undergraduate university or engineering-school students working in the field chemical and biochemical engineering as well as particle technology. Newly graduated as well as experienced engineers may also find relevant new information as emphasis is put on the newest scientific discoveries and proposals presented in the last few years of scientific publications. It is the hope that the present text will provide a complete and up-to-date image of how far modern granulation theory has come, and also further provide the reader with qualitative rules of thumb that may be essential when working with granulation processes. The comprehensive literature list may also hopefully be an inspiration for further reading.

I alone am responsible for any misprints or errors and I will be grateful to receive any critics and/or suggestions for further improvements.

Copenhagen, September 2006
Peter Dybdahl Hede

1 Fluid bed agglomeration at particle level

An understanding of the various processes and mechanisms in the granulation process at micro- or particle-level is essential in any type of modelling approach. If the particle-level mechanisms are not fully understood, an adequate modelling of the entire system at meso- or macro-scale does not have a fair chance of success. The following text focuses is on the particle-level modelling of some of the most important processes that may take place during wet granulation.

1.1 Mechanisms involved in the growth rate of granules

Fluidised bed granulation is sometimes referred to as a one-pot system as the elementary steps of the process occur in the same chamber. Fluidisation and mixing of the solid bulk are provided by an upward hot air flow. Fine droplets of liquid solvent with binder material are distributed by the nozzle. As the droplets come into contact with solid particles, a liquid layer forms at the particle surface. When a wet particle collides with another particle in the fluid bed a liquid bridge appears between the two particles. When subsequent drying occurs, the solvent evaporates and a solid bridge arises due to the solidification of the binder material. The repetition of these steps causes growth of the fluidised bed particles through agglomeration until a point where growth is counteracted by breakage due to insufficient liquid binder material (Turchiuli et al., 2005 and Iveson et al., 2001a). Formally, these different steps can be divided into three principal mechanisms being: wetting and nucleation, agglomeration and growth by layering, and finally, breakage and attrition (Iveson et al., 2001a and Cameron et al., 2005).

In respect to the modelling of the agglomeration and coating process, it is obviously the mechanisms associated with agglomeration that have the primary interest. Hence, the primary focus in the following chapter concerns advanced modelling aspects of wet granule agglomeration and theory describing the mechanical properties of wetted particles. The phenomena associated with wetting and nucleation were extensively covered in Hede (2005 & 2006b) and only some of the latest approaches will be presented in the present document. For more fundamental information on nucleation, Hapgood (2000) and Wauters (2001) should be consulted. Likewise will breakage and attrition of dry granules not be covered as these topics were covered extensively in Hede (2005 & 2006b) besides being reviewed lately by Reynolds et al., (2005).

1.2 Wetting and nucleation

The initial step in the wet agglomeration processes is the process of bringing liquid binder into contact with the particles powder and attempt to distribute this liquid evenly throughout the fluidised particles. This is usually referred to as *wetting*. In batch granulation, *nucleation* refers to the formation of initial aggregates in the beginning of the granulation process and the formed nuclei provide the initial granular stage for further agglomeration (Cameron et al., 2005). Only in the last few years, the effects of nucleation on the final product properties have been recognised and within the last two years more advanced approaches have been introduced. Litster et al. (2001) presented the dimensionless spray flux as a measure of the density of droplets landing on a particle bed surface. The dimensionless spray flux[1] is used as a tool to predict the controlling mechanism of the nucleation process. Hapgood et al. (2004) extended this work using a Monte Carlo[2] model to predict the extent of droplet overlap in the spray zone and therefore the proportion of droplets that produces single nuclei. Work by Hapgood et al. (2003) and Litster (2003) further introduced the nucleation regime map[3] being capable of predicting the controlling nucleation mechanism as a function of the dimensionless spray flux and the liquid droplet penetration time τ_d divided by the particle circulation time[4] τ_c. This nucleation regime map is to some extent capable of describing previously reported data by Tardos et al. (1997) but the original dimensionless spray is not adequate enough to predict and describe any full nuclei size distribution, which nevertheless is a prerequisite if the nucleation regime map should have any practical importance. This is due to the fact that the original dimensionless spray flux does not take into account that a single nucleus formed from a single droplet is larger than the original droplet due to the extra volume of the solids. Therefore the fraction particle bed coverage of nuclei will be higher than the fraction particle bed coverage of the droplets from which they are made (Wildeboer et al., 2005).

Schaafsma et al. (1998 & 2000a) defined in accordance with Hapgood et al. (2004) the nucleation ratio[5] J as the ratio of the volume (or mass) of a nucleus granule formed to the volume (or mass) of the droplet. However, in the case such a nucleation ratio should have any relevance for practical nucleation or agglomeration purposes it is the projected area of the granules that have the primary interest. In recent work by Wildeboer et al. (2005) they introduced another similar parameter being the nucleation area ratio according to:

$$K_a = \frac{a_n}{a_d} \tag{1.1}$$

where a_n is the projected area of the nuclei granules and a_d is the projected area of the binder droplets. Although not very likely the case, Wildeboer et al. (2005) assumed for simplicity that the nucleation area ratio is droplet-size independent and thereby constant. The probability of a single droplet forming a single nucleus will then relate to $K_a\psi_a$ rather than to ψ_a as in the original approach by Litster (2003) and Hapgood et al. (2003). As an extension of the original dimensionless spray flux expression, Wildeboer et al. (2005) suggested a dimensionless spray number according to:

$$\Psi_n = K_a \cdot \Psi_a = \frac{3 \cdot \dot{V} \cdot K_a}{2 \cdot \dot{A} \cdot d_d} \tag{1.2}$$

where $\dot{A}$ is the powder flux through the spray zone, $\dot{V}$ the volumetric spray rate of spherical droplets produced by the nozzle and d_d is the liquid droplet diameter.

What is also of importance regarding the nucleation formation is the distribution of the liquid binder mass underneath the spray zone. Experiments in rotating drum granulator by Wauters et al. (2002) indicated that the density of liquid binder mass is highest in the center underneath the spray and decreases further away from the center. This means that the assumption of uniform droplet distribution across the width of the spray zone is problematic. In a new approach by Wildeboer et al. (2005) the spray zone is represented by a one-dimensional flat fan spray where the binder liquid distribution along the direction of particle movement (x direction) is projected onto the center line of the spray[6] instead of being assumed uniformly distributed. With this approach, any type of nozzle with its own typical two-dimensional binder liquid distribution can be represented. Based on the data by Wauters et al. (2002), a normal distribution was fitted for which it was seen that such a distribution describes the liquid binder distribution well. One problem in representing the spray distribution with a normal distribution is that there will be loss of binder mass outside the finite width of the spray zone. To account for this, Wildeboer et al. (2005) defined a dimensionless nuclei distribution function along the width of the spray zone (y direction) given by a truncated normal distribution according to:

$$\Psi_n(y) = \begin{cases} \dfrac{N(y, \mu_{mean}, \sigma_{width})}{P(-0.5 \cdot W < y < 0.5 \cdot W)} \cdot W \cdot K_a \cdot \Psi & \text{for - } 0.5 \cdot W < y < 0.5 \cdot W \\ 0 & \text{elsewhere} \end{cases} \tag{1.3}$$

in which to $\psi_n(y)$ is the local dimensionless nucleation function and relates directly to the local probability of nuclei overlap at position y in the spray zone. P(-0.5W < y < 0.5W) is the probability of a droplet from distribution $N(y, \mu_{mean}, \sigma_{width})$ falling within the defined spray zone of width W. Wildeboer et al. (2005) chose W so that P > 0.95. $N(y, \mu_{mean}, \sigma_{width})$ is a simple Gaussian distribution according to:

$$N(y, \mu_{mean}, \sigma_{width}) = \frac{1}{\sigma_{width}\sqrt{2\pi}} \exp(-½ \cdot ((y - \mu_{mean})^2 / \sigma_{width})^2) \tag{1.4}$$

where μ_{mean} is the mean in the Gaussian distribution and σ_{width} is the standard deviation of liquid binder spread along the width of the spray zone.

Based on the developed model in equation 1.3 Wildeboer et al. (2005) performed a number of Monte Carlo simulations thereby simulating a real spray of liquid binder droplets and the formation of nuclei accounting for droplet overlap. It was observed that the effects of the liquid binder flow rate and the velocity of particles perpendicular to the width of the spray zone are the same, as both parameters affect only the density of droplets on the particle bed without changing the individual droplet properties. Changes in droplet diameter d_d obviously changed the number and volume of the droplets but as the variation in d_d does not change the total volume of the nuclei produced, the effect on particle size distribution was observed to be quite small. The parameter K_a on the other hand does change the total volume of the nuclei produced and hence K_a was observed to have a large effect on the particle size distribution. Simulations clearly indicate its importance regarding the control of the produced particle size distribution.

Although the wetting and nucleation step may be seen as a minor part of the granulation process it is nevertheless a vital part of the process, and spray rate conditions and particle flux in the spray zone has primary importance for the entire process and the resulting granule properties. The current work by Wildeboer et al. (2005) and Wauters et al. (2002) makes it possible to simulate the nuclei size distribution based on relevant process parameters with adequate precision. The model by Wildeboer et al. (2005) may be used to model the spray zone where partially wetted particles are presented to the spray. This further makes the model somewhat suitable for replacing the traditional nucleation term in one-dimensional population balance models which will be introduced in chapter three. Implementation of fundamental knowledge of nuclei formation and wetting conditions may lead to predictions of nuclei size, porosity- and moisture distributions which are all vital properties in respect to the quality of the final granules.

1.3 Granule growth behaviour and kinetics

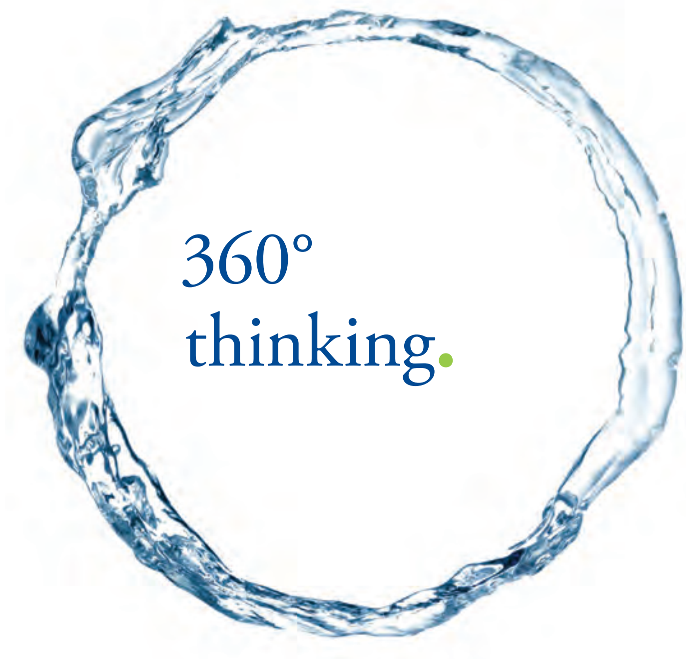
Granule growth occurs whenever the wetted particles in the fluid bed collides and sticks permanently together. For two large granules this process is traditionally referred to as *coalescence* or simply *agglomeration*. The sticking of fine material onto the surface of large pre-existing granules is sometimes referred to in old articles as *layering* but (e.g. Kapur & Fuerstenau, 1969) but as the distinction between layering and coalescence depends on the chosen cut-off size used to demarcate fines from granulates, *agglomeration* or *coalescence* are often the only terms used. Nowadays *layering* is used as a synonym for coating being growth due to droplet impact only (Iveson et al., 2001a).

Whether or not a collision between two granules results in permanent coalescence depends on a wide range of factors including the mechanical properties of the granules and the availability of liquid binder at or near the surfaces of the granules. Being a complex phenomenon, agglomeration has traditionally been treated qualitatively and quite a lot of articles exist in which the influence of different factors on agglomeration tendency has been treated qualitatively as it has been reviewed by Hede (2006b).

In the process towards a full quantitative description of the agglomeration process the agglomeration situation must necessarily be somewhat simplified. The majority of models treating agglomeration at particle level analyses the situation by viewing the granulation situation between two particles. This allows detailed studies of mechanical properties as well as collision studies far from the chaotic situation inside fluid beds. This naturally limits the applicability regarding the description of the entire agglomerating system in real fluid beds, but as it will be emphasised in later chapters much vital information for the use in macro-scale models can in fact be achieved from simplified particle-level studies.

1.3.1 Mechanical properties of liquid-bound granules

An agglomerate can exist in a number of different spatial structures depending on the binder liquid saturation. It is the amount of liquid binder as well as the humidity conditions in the bed that determines the degree of saturation, which again determines the spatial structure of the final granule (Jain, 2002). Such wet liquid bridges are obviously only temporary structures and more permanent bonding within the granule is created by solid bridges formed as solvent evaporates from the bridges during further fluidisation. Solid bridges between particles may take basically three forms: crystalline bridges, liquid binder bridges and solid binder bridges. If the material of the particles is soluble in the binder liquid, crystalline bridges may be formed when the liquid evaporates.



The process of evaporation reduces the proportion of liquid in the granules again producing high strength pendular bridges before crystals form. Alternatively, the dissolved binder takes effect upon evaporation of the solvent. In some cases a finely ground solid binder material may be dispersed in the binder liquid thereby producing a cement-like solid binding bridge upon evaporation of the solvent (Rhodes, 1998). In any of the three cases, the initial forming of the liquid bridge is of primary importance regarding the properties and spatial structure of the final agglomerate, and it is almost always the case that the solid bridge will have the form of the liquid bridge (Summers & Aulton, 2001).

The particles are held together by liquid bridges at their contact points in the pendular state. This situation requires that the saturation is low enough to let discrete binary bridges exist between the solid surfaces. Such a lens-shaped ring of liquid cause adhesion due to the surface tension forces of the liquid/air interface and the hydrostatic suction pressure in the liquid bridge (Summers & Aulton, 2001). The capillary structure occurs when a granule is saturated. All the voids between the particles are filled with binder liquid and the surface liquid of the agglomerates is drawn back from the surface into the interior of the agglomerate. The particles are held together in this configuration due to capillary suction at the liquid/air interface, which is now only at the agglomerate surface. The funicular structure is a transition between the pendular and the capillary state where the voids between the particles are not fully saturated. The droplet structure occurs when the particles are held within or at the surface of a liquid binder droplet (Jain, 2002 and Iveson et al., 2002). This situation almost never happens in fluid beds (Kunii & Levenspiel, 1991 and Litster & Ennis, 2004). A sketch of the different formal spatial agglomerate structures can be seen in figure 1.

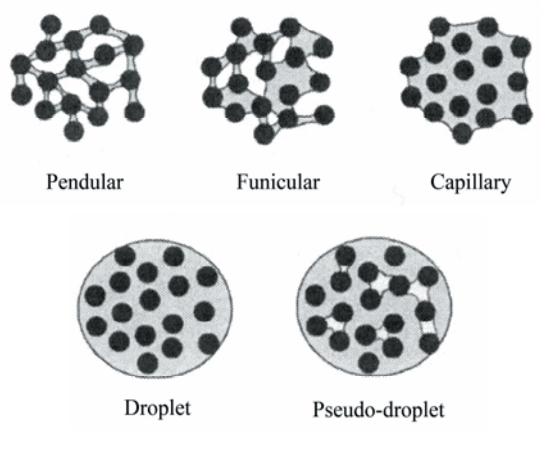


Figure 1: Spatial agglomeration structures.
The different formal spatial structures of liquid-bound agglomerates depending of liquid saturation (Iveson et al., 2001a).

During granulation, it is possible for the saturation state of the agglomerates to change from e.g. the pendular state to the droplet state either due to the continuous addition of liquid binder or the saturation of the pores of each particle. The pendular structure is however the most common in fluid bed granulation due to the usual processed particle sizes versus the droplet sizes (Kunii & Levenspiel, 1991 and Litster & Ennis, 2004). Typical examples of agglomerates being bound by solidified pendular liquid bridges can be seen in figure 2 in which Na_2SO_4 cores agglomerated during coating with a Na_2SO_4/Dextrin solution. Hence, regarding the agglomeration process in fluid beds, the primary attention should be given to the modelling of the pendular liquid bridge.

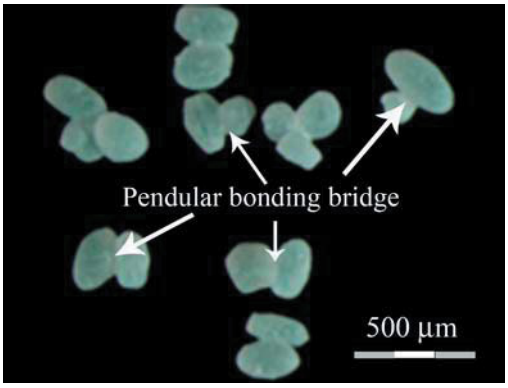


Figure 2: Pendular bonding bridges.
Examples of agglomerates being bound by pendular bonding bridges (Hede, 2005).

Liquid-bound granule strength is dominated by three types of forces being interparticle forces, static strength forces and dynamic strength forces (Iveson et al., 2001a). The first two are interrelated as the tensile force of the liquid bridge acts to pull particles together and this normal force at particle contacts activates friction. Static strength forces as surface tension and capillary forces are conservative forces in the sense that they always act to pull particles together in wetted systems. Frictional and viscous forces are dissipative as they always act against interparticle motion. The complex interaction of these different forces means that it is often impossible in industrial situations to predict a-priori the effect of changing any particular granule property, unless the precise magnitude of each of these three types of forces is well-known (Iveson et al., 2002). Hence the following sub sections will introduce the available theory regarding each of the three types of forces, primarily in respect to the most important agglomerate structure being the pendular liquid bridge.

1.3.1.1 Interparticle forces

The normal force generated by liquid bridges at inter-particle contacts activates inter-particle friction forces. There are a whole range of different types of interparticle forces including van der Waal´s forces, forces due to absorbed liquid layers, electrostatic forces and friction forces (Yates, 1983). According to Rumpf (1962) and Rhodes (1998) the friction forces and the forces associated with the liquid/solid bridges (static and dynamic forces) are nevertheless the only forces of significance in wet systems with particle sizes above roughly 10 µm. This can be visualised from figure 3 illustrating the relative magnitude of the different interparticle forces as function of particle size.

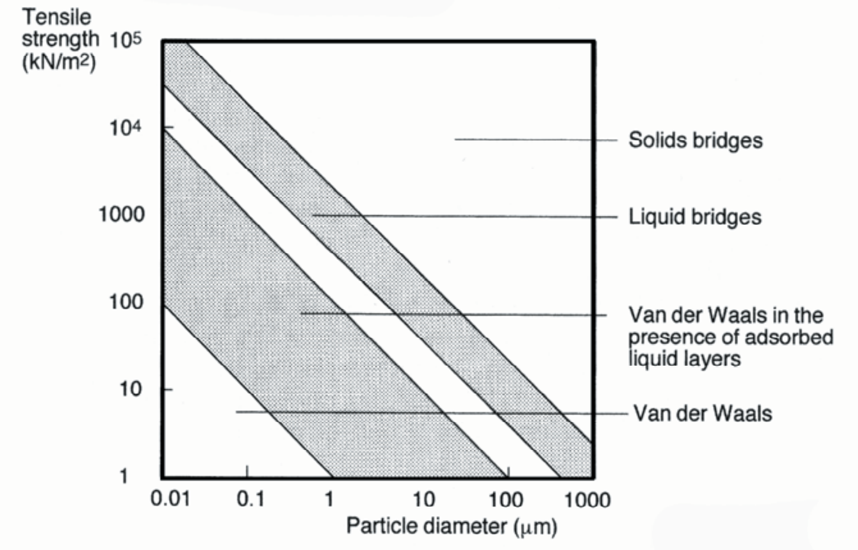


Figure 3: Agglomeration strength overview.
Theoretical tensile strength of agglomerates with different bonding mechanisms
(based on Rumpf, 1962 and Rhodes, 1998).

Internal friction forces inside agglomerates are often described in terms of a Columbic relationship according to (Nedderman, 1992):

$$\sigma_f = \mu_f \sigma_n + c \qquad (1.5)f$$

in which σ_f is the macroscopic shear stress at failure, μ_f the coefficient of internal friction, σ_n the macroscopic normal stress and c the cohesivity being in other words the shear strength at zero normal load. This simple model represents the cumulative effect of several contributing mechanisms. In an ensemble of particles in an agglomerate, resistance to shear deformation arises from true tribological interaction between touching particles and particle interlocking of which the last is a macroscopic locking mechanism depending on size and shape of the particles constituting the agglomerate (Iveson et al., 2002). Generally, the amount of reported work regarding internal friction forces in the presence of a viscous binder is very limited. Some advances has been made in the understanding of the fundamental nature of the tribological component of the friction force and these results indicate that the presence of a lubricating film binding the particles together lowers the friction at particle as well as at the macroscopic level (Cain et al., 2000). Iveson et al. (2002) present a short review of the latest advances in the field of friction forces. Important trends to note from this review are that internal friction forces inside an agglomerate are dissipative and not strongly strain-rate dependant at strain rates commonly experienced in fluid bed granulation processes (Iveson et al., 2002).

1.3.1.2 Static strength – capillary and surface tension forces

The static strength of a pendular liquid bridge consists of two components. There is a suction pressure caused by the curvature of the liquid interface and a force due the interfacial surface tension acting around the perimeter of the bridge cross-section[7]. In the absence of gravitational effects[8] arising from bridge distortion and buoyancy, the total force F acting between two spherical particles both of radius R_p is given by the sum of two components being the axial component of the surface tension acting on the three-phase contact line and the hydrostatic pressure acting on the axially projected area of the liquid contact on either particle. This leads to the following expression commonly known as the *boundary method* (Lian et al., 1993):

$$F_{\text{pendular,boundary}} = \pi \cdot \Delta P \cdot R_p^{\;2} \cdot \sin^2(\varphi) + 2\pi \cdot \gamma_{lv} \cdot R_p \cdot \sin(\varphi) \cdot \sin(\varphi + \Theta) \tag{1.6}$$

in which φ is the half-filling angle, θ the contact angle and γ_{lv} the liquid surface tension. The situation may be seen formalised according to figure 4:

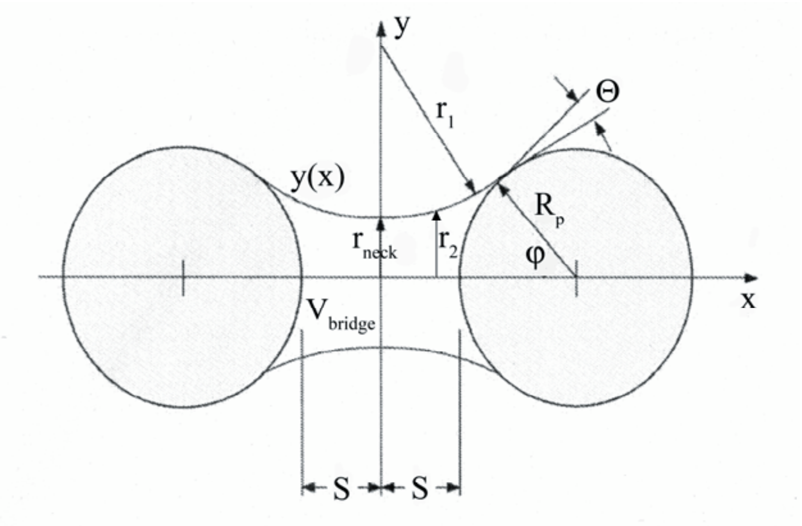


Figure 4: Formal bonding schematic of an agglomerate.

Schematic representation of a liquid bridge of volume V_{bridge} between two spheres both of radius R_p separated by a distance 2S with a neck radius of r_{neck}, a liquid-solid contact angle θ and a half filling angle of φ (Based on Iveson et al., 2002 and Willet et al., 2000).

ΔP is the pressure difference across the curvature of the air-liquid interface[9] and assuming that the liquid surface has constant mean curvature, ΔP is given by the Laplace-Young equation (Goodwin, 2004 and Fairbrother & Simons, 1998):

$$\Delta P = \gamma_{lv}\left[\frac{1}{r_1} - \frac{1}{r_2}\right] \tag{1.7}$$

in which r_1 is and r_2 are local principal radii of normal curvature in orthogonal directions at points along the meridional bridge profile as shown in figure 4 (Iveson et al., 2001a). Conventionally, r_2 is evaluated in a direction orthogonal to the meridional profile such that its center of curvature is located along the surface normal on the bridge axis of symmetry. Hence, the center of curvature of r_2 is always within the bridge, or one of the spheres, and r_2 itself is positive and equals r_{neck} when calculated at the neck point. r_1 is evaluated in a direction containing the meriodional bridge profile and can be positive or negative depending on whether or not its center of curvature lies inside or outside the liquid bridge. A positive value of the parentheses in equation 1.7 leads to a positive pressure difference ΔP and thereby an attractive contribution to the pendular force in equation 1.6 (Willet et al., 2000). The values of r_1 and r_2 can be evaluated at any point along the bridge profile r(x) as it can be shown that the Laplace-Young equation can be rewritten according to (Willet et al., 2000 and Iveson et al., 2001a):

$$\Delta P = \gamma_{lv}\left(\frac{\frac{d^2r}{dx}}{\left(1+\left(\frac{dr}{dx}\right)^2\right)^{3/2}} - \frac{1}{\left[r\cdot\left(1+\left(\frac{dr}{dx}\right)^2\right)\right]^{½}}\right) \tag{1.8}$$

The determination of the exact surface profiles requires complex numerical procedures even for the simple case of equally sized spheres and equation 2.8 cannot be solved analytically. This has led to the use of approximate geometries such as circular (torodial) and hyperbolic arcs, which have been shown to result in errors in bridge areas and volumes of the order of 1 % (Simons et al., 1994). This has further led to a debate as to whether the surface tension and capillary pressure should be evaluated at the mid-point of the liquid bridge where $r_2 = r_{neck}$ instead of being evaluated at the surface of the particles as it is the case with the boundary method. The prior principle is often referred to as the *gorge method* and according to Lian et al., (1993), this approach will give an expression for the pendular force according to:

$$F_{pendular,\,gorge} = \pi\cdot\Delta P\cdot r_{neck}{}^2 + 2\cdot\pi\cdot r_{neck}\cdot\gamma_{lv} \tag{1.9}$$

in which r_{neck} is the pendular bridge neck radius according to figure 5.

Whereas results by Hotta et al. (1974) supports the use of a slightly modified boundary method, other results by Lian et al. (1993) indicates that the gorge method is the most precise and versatile. Attempts of approximation of the total pendular force instead of relying on an analytical bridge profile solution have been reported by Willet et al. (2000), and one example for a small pendular bridge volume between two spheres is:

$$F_{pendular,\ equally\ sized\ spheres} = \frac{2\pi\cdot R_p\cdot\gamma_{lv}\cdot\cos\Theta}{1.0+2.1\left(\frac{S^2R_p}{V_{bridge}}\right)^{½}+10.0\left(\frac{S^2R_p}{V_{bridge}}\right)} \tag{1.10}$$

in which R_p is the radius of the equally sized spheres according to figure 5.

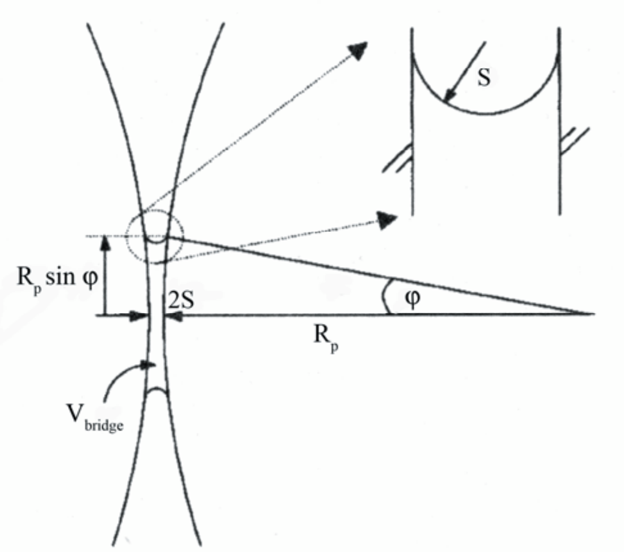


Figure 5: Liquid bridge bonding two primary particles.
A schematic representation of a small liquid bridge between two equally sized spheres where the radius of curvature of the bridge surface is approximately given by the half-separation distance S (Willet et al., 2000).

Interestingly, it can be seen from equation 1.10 that the pendular bridge force is directly proportional to the liquid adhesion tension ($\gamma_{lv} \cdot \cos \theta$). This is in accordance with the wetting thermodynamic studies reviewed by Hede (2005).

Other expressions for equally sized spheres can be found in Israelachvili (1992). Rabinovich et al. (2005) have suggested one of the newest expressions according to:

$$F_{\text{pendular, equally sized spheres}} = -\frac{2\pi \cdot R_p \cdot \gamma_{lv} \cdot \cos\Theta}{1 + (S/d_{sp/sp})} - 2\pi \cdot R_p \cdot \gamma_{lv} \cdot \sin\varphi \cdot \sin(\Theta + \varphi) \tag{1.11}$$

in which:

$$d_{sp/sp} = S \cdot \left(-1 + \sqrt{1 + V_{bridge}/(2\pi \cdot R_p \cdot S^2)}\right) \tag{1.12}$$

There is a general lack of reliable theoretical formulas for the calculation of the pendular force between two unequal spheres although as an approximation, the radius term R_p in the previously presented equations may be replaced by an effective particle radius R_{eff} according to the following equation (Rabinovich et al., 2005):

$$R_{eff} = \frac{2R_1R_2}{R_1 + R_2} \tag{1.13}$$

Granule static strength decreases as binder surface tension is lowered in respect to the surface tension of the solid particle material. This is because the capillary suction pressure ΔP as well as the surface tension forces are both proportional to the liquid surface tension γ_{lv} (Rumpf, 1962 and Iveson, 2001). Likewise is it also expected that granule strength will decrease as the contact angle increases due to the decreased wetting as emphasised in Hede (2005 & 2006b).

Static strength of liquid-bound granules is commonly measured and described in terms of tensile static strength. Pioneer work by Rumpf (1962) in the sixties has lead to a generally accepted form for the pendular bridge according to (Pierrat & Caram, 1997 and Ennis & Sunshine, 1993):

$$\sigma_{t,p} = k_{cn} \frac{(1-\varepsilon)}{\varepsilon} \frac{F_{pendular,\ boundary}}{d_p^{\ 2}} \tag{1.14}$$

in which k_{cn} is the coordination number being a function of the particle packing density[10], ε is the particle void fraction, d_p the particle diameter and $F_{pendular,\ boundary}$ is given by equation 1.6. The model is based on the assumption that all of the powder particles are monosized spheres distributed uniformly in the agglomerate on an average. Secondly, it is assumed that the pendular bonds are, on an average, uniformly distributed over the surface and over the directions in space. Finally, the effective pendular bonding forces are assumed to be distributed around a mean value, which can be used in the calculations. These assumptions are generally accepted and several empirical correlations based on the original Rumpf form exist. Schubert (1973 & 1975) reviews a few suggestions being globally of the same form as equation 1.14. Pierrat & Caram (1997) have fitted data from a range of different articles by different workers into a more general although empirical relation:

$$\sigma_{t,p} = 7.80 \cdot (1-\varepsilon)^{3.03} \cdot \frac{1}{d_p} \cdot \gamma_{lv} \cdot \cos\Theta \tag{1.15}$$

In the case of capillary liquid bridges where all the pores are completely filled with liquid, the interfacial forces exist only at the surface of the agglomerate and a negative capillary pressure develops in the interior, holding the particles together. In that case, the static tensile strength is given as (Schubert, 1975 and Pierrat & Caram, 1997):

$$\sigma_{t,c} = S_{sat} \cdot a' \cdot \frac{1-\varepsilon}{\varepsilon} \cdot \frac{\gamma_{lv} \cdot \cos\Theta}{d_p} \tag{1.16}$$

in which a′ is a material constant taking a value of 6 for uniform spheres and a value between 6 and 8 otherwise, depending on sphericity, and S_{sat} is the saturation amount defined as the ratio of the void volume occupied by the liquid to the total void volume (Pierrat & Caram, 1997).

The static tensile strength of a funicular liquid bridge can be related to $\sigma_{t,c}$ and $\sigma_{t,p}$ according to (Pierrat & Caram, 1997) as:

$$\sigma_{t,f} = \sigma_{t,p} \cdot \frac{S_c - S_{sat}}{S_c - S_f} + \sigma_{t,c} \cdot \frac{S_{sat} - S_f}{S_c - S_f} \tag{1.17}$$

in which S_c and S_f are the upper saturation limits for the funicular/capillary transition and pendular/funicular transition states respectively. Considerations by Flemmer (1991) indicate that for randomly packed monosized particles, S_f is equal to 0.34 and S_{sat} is usually ranging between 0.25 and 0.50. S_c is usually above 0.90 (Pierrat & Caram, 1997).

The original Rumpf model as well as the models in equation 1.16 and in equation 1.17 predict that granule tensile strength is proportional to the liquid surface tension and saturation, and that $\sigma_{t,c}$ further increases with decreasing porosity and is inversely proportional to the particle diameter. All of these trends have been validated by experimental data, but quantitatively the models tend to over-predict the granule strength due to fact that these models fail to account for the presence of extensive pore networks in the particles forming the agglomerate. As it has been showed by Beekman (2000), failure often occurs by crack growth along such pore structures and not by sudden failure across the whole liquid bridge plane. Some of the newer tensile strength models try to account for this problem but as still most of the work on tensile strength of liquid bound granules is performed at slow and invariant strain rates, the applicability of the above presented equations is still not accurate enough for quantitative granulation purposes. This is due to the fact that it is the amount of impact deformation and breakage that is critical in determining agglomerate growth and breakage behaviour in fluid bed granulation equipment (Beekman, 2000 and Hede, 2005). That means that dynamic forces may become significant in the fluid bed granulation process, especially when viscous binders are involved. Hence, the following sections focus on the dynamic strength of liquid bridges.

1.3.1.3 Dynamic strength – viscous forces

The dynamic strength of a liquid bound granule can be approximated using lubrication theory as a viscous force F_{vis}, which according to Lian et al. (1998) and Iveson et al. (2001a) may be expressed as:

$$F_{vis} = 6\pi \cdot \eta_{liq} \cdot r_{harm} \cdot u_0 \cdot \lambda \tag{1.18}$$

in which u_0 is the relative initial velocity of the two particles, η_{liq} the liquid viscosity and λ is a parameter being a function of the harmonic mean radius[11] of the two particles r_{harm} and the separation distance between the two spheres H. For small separation distances between two spheres in an infinite fluid, λ may be found as (Weinbaum & Caro, 1976):

$$\lambda = 1 + \frac{2r_{harm}}{H} \tag{1.19}$$

A more general expression has been derived by Adams & Perchard (1984) using classical lubrication theory for flow between two spheres according to:

$$\lambda = \frac{r_{harm}}{2H} \tag{1.20}$$

None of the two mentioned expressions for λ are appropriate to calculate precisely the viscous forces as the underlying assumption that the particles move in an infinite fluid does not hold. Instead, Jen and Tsao (1980) have found another expression for λ based on the half-filling angle φ according to:

$$\lambda = ½ - ½ \cdot \cos\varphi \tag{1.21}$$

The expression for λ is thereby independent of the separation distance H which is in contrast to experimental results reported by other authors (Ennis et al., 1990 and Iveson et al., 2001a). Acknowledging that liquid bridges also have a viscous resistance to shear strain besides the previously solely assumed axial strain, Goldman et al. (1987) derived another relationship based on lubrication theory for small separation distances according to[12]:

$$F_{vis} = 6\pi \cdot \eta_{liq} \cdot r_{harm} \cdot u_0 \left(\frac{8}{15} \ln\left(\frac{r_{harm}}{H} \right) + 0.9588 \right) \tag{1.22}$$

Results by Mazzone et al. (1987) indicated that dynamic liquid bridges are much stronger than geometrically identical static liquid bridges in which the attraction forces is due to surface tension only, as presented in the previous section. It was seen that the force required to separate two moving particles is often significantly higher than that required in static situations because the viscosity of the liquid resists the motion in the dynamic case. These observations help to explain why even small amounts of liquid can drastically change the properties and fluidisation behaviour during e.g. fluid bed coating.

1.3.1.4 Breakage and attrition of wet granules

The granule breakage phenomena may in principle be divided into the breakage of wet and breakage of dry granules. Whereas dry granule breakage is often treated as a separate discipline often without much attention to the process conditions, wet granule breakage is closely related to the previously introduced theory. Although much of the basic theory and parameters regarding the mechanical strength and breakage mechanisms are similar, there are a number of differences between the breakage of a liquid bridge and the breakage of a solid amorphous or crystalline bond or layer. The mechanical properties and breakage phenomena of dried granules and coating layers were extensively covered in Hede (2005 & 2006b) and more introductionary information can be found in Beekman (2000) as well as in a comprehensive recent review by Reynolds et al. (2005). The topics on breakage and attrition of wet granules were however only slightly covered and more on this topic will be presented below.

In the last step of the granulation process, the agglomerates grow too large to resist the agitative motions in the bed. Coalescence will be counteracted by either an attrition of debris of the granule surface either partly or totally, or by fracture of the agglomerate bonding. This is due to insufficient binder distribution or simply due to the static stress in the drying liquid bridges (Iveson et al., 2001a). A total fracture of wet or dry granules is seldom a problem in fluid bed granulation however. The low shear properties in the bed rarely give sufficient kinetic energy to fracture the granules completely (Waldie, 1991 and Schaafsma, 2000b). Simulations as well as experiments performed by Khan & Tardos (1997) indicate that agglomerates are often broken upon deformation by stretching when being sheared. They further showed that the stability of wet agglomerates is closely related to the Stokes deformation number St_{def} and that two regimes exist involving high and low deformation characteristics based on the St_{def} number. Khan & Tardos (1997) defined the Stokes deformation number according to:

$$St_{def} = \frac{m_{aggl} \cdot u_0^2}{2 \cdot V_{aggl} \cdot \sigma(\dot{\gamma})} \qquad (1.23)$$

in which m_{aggl} is the mass of the agglomerate, V_{aggl} the volume of the agglomerate and $\sigma(\dot{\gamma})$ is some characteristic stress in the agglomerate. In the most general case, this stress can be taken according to the Herschel-Bulkley fluid model[13] being:

$$\sigma(\dot{\gamma}) = \sigma_y + \eta_{app} \cdot \dot{\gamma}^{n_{fl}} \qquad (1.24)$$

where σ_y is the yield strength, η_{app} is an apparent viscosity, n_{fi} the flow index and $\dot{\gamma}$ the shear rate (Tardos et al., 1997 and Fu et al., 2004). The Stokes deformation number defined in equation 1.23 increases with increasing particle size and reaches at some point during granulation a critical value of St_{def}^* above which the agglomerates start to deform and eventually break. The critical Stokes deformation number is not as well-defined as the critical viscous Stokes number introduced in Hede (2005 & 2006b). This is due to the fact that, from a rheological point of view, the system consisting of particles bound by viscous liquid bridges is a complex system that exhibits both yield strength as well as non-Newtonian behaviour. Assuming that the agglomerate is a very concentrated slurry of the binder material and the original particles, a first assumption is that the apparent viscosity η_{app} is negligible compared with the yield strength meaning that $\sigma(\dot{\gamma}) \approx \sigma_y$. It is further assumed that in fluid beds, the collision velocity u_0 can be approximated according to[14]:

$$u_0 \approx r_{aggl} \cdot \dot{\gamma} \tag{1.25}$$

These approximations all in all lead to a rough estimate of a theoretical expression for the critical Stokes deformation number according to:

$$St_{def}^* = \frac{m_{aggl} \cdot (r_{def}^* \cdot \dot{\gamma})^2}{2 \cdot V_{aggl} \cdot \sigma_y} \tag{1.26}$$

in which r_{def}^* is the critical radius of the agglomerate after which deformation and breakage occurs. Equation 1.26 thereby predicts an inverse linear relationship between the critical agglomerate radius and the shear rate, which in fact has been observed in simulations as well as experiments by Tardos et al. (1997) and Khan & Tardos (1997).

There is generally very limited experimental work on fracture and attrition of wet granules in fluid beds as most work focuses on higher intensity mixer and hybrid granulators as drum and high shear mixing (e.g. Fu et al., 2004). In fact the works of Tardos et al. (1997) and Khan & Tardos (1997) are the only works so far specialised on fluid bed granulation. This is most likely due to the fact that the high intensity granulation makes it much easier to estimate the average shear forces and the collision velocity based on equipment parameters. Some of the newest experimental studies by Fu et al. (2005) indicate conveniently that the failure patterns of wet granules in high shear mixing equipment have a number of common features that have been observed for dry granules including the formation of debris with conical geometry. Most of the basic theory regarding mechanical strength and breakage mechanisms cannot however be applied readily for wet granules.

Fu et al. (2005) observed that at small impact velocities, the agglomerates displayed homogenous elastic, elastoplastic and plastic deformation. At some critical strain, stable meridian cracks propagate from the impact zone in accordance with the theory emphasised in Hede (2005 & 2006b). At larger strains, chips were formed and the formation of larger fragments increased with increasing impact velocity for the wet granules. It was seen additionally, that the critical impact velocity for the formation of observable cracks increased with decreasing granule size and increasing binder viscosity. Further it was concluded that agglomerates made with relative coarse primary particles were generally more friable than agglomerates made with very fine primary particles, and thus it was observed for the wet coarse particle agglomerates, that the critical impact velocity decreased monotonically with increasing binder because of the reduction in the fracture strength (Fu et al., 2005).

1.3.1.5 Wet granule strength summary

As emphasised in previous sections, the strength of agglomerates in the size range of roughly 10–1200 μm is controlled by three main types of forces being static (capillary), frictional and viscous (dynamic) forces. These forces are interrelated in a complex way and their relative importance varies greatly with process and formulation conditions. This makes systematic experimental investigations of wet granule strength a difficult subject although studies of wet granular strength are somewhat more important than dry granular strength in respect to granulation (Fu et al., 2005).

As it has been reviewed in earlier sections, traditional models do not include all three types of forces, and e.g. the often quoted model by Rumpf (1962) consider only capillary forces. Such simplified models may be sufficient for coarse particle systems held together by non-viscous binders but must be considered invalid for agglomerates composed of fine particles bound by viscous binders (Iveson et al., 2001a). That means that if any model should be quantitatively applicable to industrial granulation processes, this model must include all three types of forces. Developing models capable of predicting the complex interactions of capillary, viscous and frictional forces that occur during wet granule impacts will be a challenging task. Some of the latest results by Fu et al. (2005) indicate however that that impact failure mechanisms of wet granules have a number of common features observed for breakage of dry granules including the formation of debris with certain geometries etc. This is fortunate as the breakage of dry granule traditionally has been more widely studied than the breakage of wet granules.

One of the modern approaches has been to try to simulate breakage of wet granules using primarily discrete element method (DEM). The use of DEM in simulations seems to make some progress in this field. E.g. have Lian et al. (1998) performed discrete element modelling simulations of dynamic granule impacts. They simulated the collision of agglomerates in the pendular states under conditions found in common fluid bed granulators. Results indicated that granule strength is controlled by viscous and interparticle frictional energy dissipation with static surface energies playing only a minor role. The use of DEM to simulate the breakage of wet agglomerates is nevertheless a relative new scientific field and it still remains to be seen whether this technique can be used to predict the complex effects of binder content, wetting behaviour and other variables such as the influence of particle morphology on wet granule strength (Reynolds et al., 2005 and Iveson et al., 2001a).

1.3.2 Granule growth modelling – Class I and Class II models

There are a large number of theoretical models available in the literature for predicting whether or not the collision of two wetted particles will either result in permanent coalescence or just in rebound. All models are associated with a number of assumptions and simplifications regarding the mechanical properties of the particles as well as the system in which the particles collide. Some of the first models were developed for predicting the sintering of fluidised beds used in the mining industry, but later models have adapted to specifically describe the granulation process (Iveson et al., 2001a). Although being very different in nature Iveson et al. (2001a) have divided the granulation models into two classes of which the distinction principles can be sketched according to figure 6.

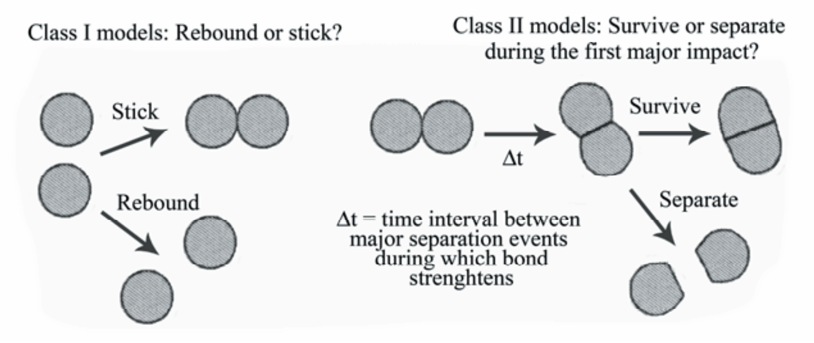


Figure 6: Principles behind different classes of agglomeration models.
Schematic diagram of the two general classes of coalescence models:
Class I models: Stick or rebound, Class II models: Survival or separation (based on Iveson, 2001).

Class I models assume that the granules are free to move and that elastic properties of the particle bodies are important. These models assume that initial coalescence occurs only if the kinetic energy of collision is entirely dissipated and that otherwise the granules will rebound and move apart. Various combinations of energy dissipation has been considered by different authors including elastic losses, plastic deformation, viscous and capillary forces in the liquid binder and adhesion energies of the contact surfaces. In class I models it is implicitly assumed that if the initial impact results in permanent coalescence, then none of the subsequent impacts will be able to break the two granules again. This means in other words that coalescence is assumed to occur whenever the two particles do not possess sufficient kinetic energy to rebound (Iveson et al., 2001a). It further implies that all collisions at near-zero velocities will result in permanent coalescence (Iveson, 2001).

Class II models on the other hand assume that elastic effects are negligible during the initial collision usually because it is assumed that the granules are plastic in nature and/or physically constrained by surrounding granules. This leads to the simplification that all colliding granules are in contact for a finite time Δt during which a liquid bridge develops between them. Permanent coalescence thereby only occurs if this liquid bridge is strong enough to resist being broken apart by subsequent collisions or shear forces. The strength of the binding bridge is assumed to be dependent on factors such as the initial amount of plastic deformation and the length of time that the two particles were in contact, which in other words means that it is assumed that the bonding bridge will increase in strength as the liquid bridge turns into a solid bridge upon evaporation of the binder solvent.

Due to the simplicity of both model classes, a lot of relevant critics are associated with both views on modelling the agglomeration part of the granulation process. The coalescence criteria in Class I models are typically criticised for being unreasonable for most fluid bed granulation applications because this class of models neglects the effect of subsequent collisions. Two granules which stick initially together may in reality be so weakly held together that they would quickly break apart again. It is also unreasonable to assume that coalescence is controlled solely by the initial collision energy, when in many applications the granules are constrained in contact with one another for significant lengths of time as it occurs in the quiescent zones of a fluid bed. In these cases there is no single and uniform single collision event. Instead the granules are constantly in contact with several others (Iveson, 2001). This means in other words that although non-rebound is a necessary condition for permanent coalescence, it is not always a sufficient condition. Not only do the particles need to stick when they first collide but they must also form a bond strong enough to resist being broken by subsequent impacts in the fluid bed. This is not accounted for in Class I models thereby being an obvious limitation.

In all existing Class II models, only the first major separation event is considered and the magnitude of separation is usually approximated by some global average value. If the particle-particle bonding bridge survives this single event then it is considered to be a permanent agglomeration bond. However, in many granulators the separation events may have a wide range of magnitudes and may further be distributed randomly in time. Therefore some criticisers state that it is inappropriate to model coalescence by assuming a mean separation force which occurs at regular intervals and that the probability of the survival of a bonding bridge rather will depend on the history of impacts and the rate at which the binding bridges strengthens as they are kneaded together by a number of low-level impacts (Iveson, 2001).

Class II models have generally been developed and optimised for high collision granulation equipment such as high shear mixing or drum granulation. It is necessary to account for deformability of the granules during collision as well as the rupture forces in such high agitative equipment and a number of different class II coalescence models have been presented by e.g. Ouchiyama & Tanaka (1975) for drum granulation. In fluid bed equipment, the agitative forces and thereby the collisions are quite small which also implies that deformation of the particles upon collision may often be neglected with good approximation. This means that assumptions associated with Class I models have proven to be more accurate than those associated with Class II models, and the latter type is almost never applied with fluid bed systems. Hence, only Class I models will be presented here. For most industrial fluid bed purposes it is often adequate to model the situation in which non-deformable particles collide and coalesce and only in rare cases is it necessary to study coalescence of deformable particles, although it may be necessary in some granulating fluid bed systems depending on the bed material. Both types of class I models will be introduced in the following section.

1.3.2.1 Class I models: Coalescence of non-deformable granules

The gentle agitative forces in fluid beds mean that little permanent deformation usually occurs. Under such low-agitative conditions granules coalesce by viscous dissipation in the surface liquid before the granule core surfaces contact (Liu et al., 2000). As the two particles approach each other, first contact is made by the outer liquid binder layer. The liquid will subsequently be squeezed out from the space between the particles to the point where the two solid surfaces will touch. A solid rebound will occur based on the elasticity of the surface characterized by a coefficient of restitution[15] *e*. The particles will start to move apart and liquid binder will be sucked into the interparticle gap up to the point where a liquid bridge will form. This bridge will either break due to further movement in the bed or solidify leading to permanent coalescence (Tardos et al., 1997). In the described principle, granule coalescence will occur only if there is a liquid layer present at the surface of the colliding particles. This growth principle continues until insufficient binder liquid is available at the surface to bind new particles (Schaafsma et al., 1998). The relative amount of binder liquid present at that stage is called the wetting saturation S_w and it depends on the contact angle of binder liquid and the pore structure of the granule (Tardos et al., 1997). The wetting saturation reflects the wettability of the particle and it is often approximated by the binder droplet volume divided by the pore volume of a particle, under the assumption that no drying occurs (Schaafsma et al., 2000a). Schaafsma et al. (2000a) have showed that S_w is inversely proportional to the nucleation ratio J and the mean granule porosity $\bar{\varepsilon}_g$.

Ennis et al. (1991) have modelled the situation of coalescence in a fluid bed by considering the impact of two solid non-deformable spheres each of which is surrounded by a thin viscous binder layer. The simplified situation can be seen in figure 7.

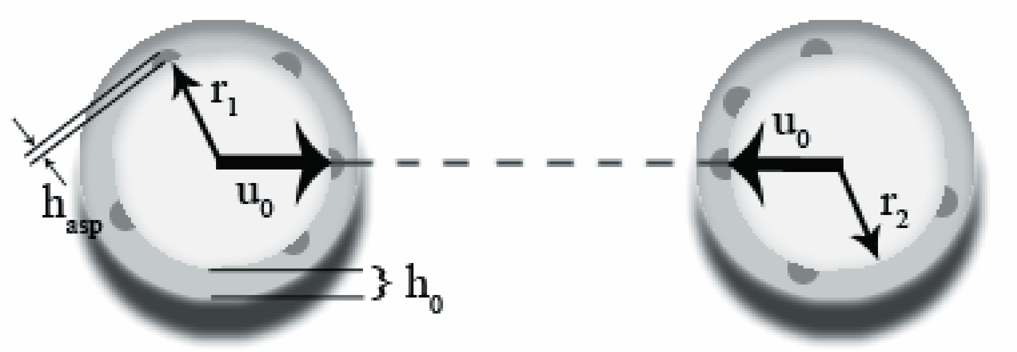


Figure 7: Principles of the original Ennis et al. agglomeration model.
Schematic of two colliding granules each of which is covered by a viscous binder layer of thickness h_0
(Based on Ennis et al., 1991).

The principles of the model by Ennis et al. (1991) was introduced in Hede (2005 & 2006b) but will be further emphasised in the present section. Being a typical Class I model it assumes successful coalescence to occur if the kinetic energy of impact is entirely dissipated by viscous dissipation in the binder liquid layer and only elastic losses in the solid phase. The model predicts that collisions will result in coalescence when the viscous Stokes number (St_v) is less than a critical viscous Stokes number (St_v^*). The two numbers are given as (Ennis et al., 1991)[16]:

$$St_v = \frac{8 \cdot \rho_g \cdot r_{harm} \cdot u_0}{9 \cdot \eta_{liq}} \tag{1.27}$$

and

$$St_v^* = \left(1 + \frac{1}{e}\right) \cdot \ln\left(\frac{h_0}{h_{asp}}\right) \tag{1.28}$$

where η_{liq} is the liquid binder viscosity, e is the coefficient of restitution, ρ_g is the granule density, h_0 is the thickness of the liquid surface, h_{asp} is the characteristic height of the surface asperities and r_{harm} is the harmonic mean granule radius of the two spheres given as (Iveson et al., 2001a):

$$r_{harm} = \frac{2 r_1 r_2}{r_1 + r_2} \tag{1.29}$$

u_0 is the initial collision velocity which is not easily obtainable due to the various phenomena influencing the granule motion in fluid beds. A rough estimate based on the bubble rise velocity U_{br} has been presented by Ennis et al. (1991):

$$u_0 \approx \frac{12 U_{br} r_{harm}}{d_b \delta^2} \tag{1.30}$$

where d_b is the gas bubble diameter and δ the dimensionless bubble space defined as the axial fluid bed bubble spacing divided by the fluid bed gas bubble radius. Whereas the gas bubble diameter and spacing can be estimated by the dimensions of the air distributor plate or found by experiments, the bubble rise velocity is somewhat more difficult to determine. Davidson & Harrison (1963) have however proposed the following empirical relation for a fluid bed based on the bubble diameter d_b, gravity g, the minimum fluidisation velocity U_{mf} and the superficial velocity U_s measured on empty vessel basis:

$$U_{br} = U_s - U_{mf} + 0.711 \cdot (g \cdot d_b)^{1/2} \qquad (1.31)$$

The Stokes viscous number St_v can be seen as the ratio of kinetic energy to the viscous dissipation. During fluid bed batch granulation St_v increases as the granules grow in size. This leads to three possible situations. The first so-called "non-inertial regime" occurs when $St_v << St_v^*$. All collisions result in successful coalescence regardless of the size of the colliding granules, granule kinetic energy or binder viscosity. As the granules grow larger the "inertial regime" occurs when $St_v \approx St_v^*$. The likelihood of coalescence now depends of the size of the colliding granules, and granule kinetic energy and binder viscosity begin to play a role (Iveson et al., 2001a and Abbott, 2002). It can be seen from equation 1.29 and 1.27 that the collision between two small or one small and one large granule is more likely to succeed in permanent coalescence than the collision between two large granules due to the size of r_{harm} and thereby the size of St_v versus St_v^*. This is a convenient way to understand why small particles agglomerate into larger ones (Tardos et al., 1997). Eventually the system enters the "coating regime" when $St_v >> St_v^*$. Here all collisions between granules are unsuccessful and any further increase in the St_v will maintain the size of the granules (Iveson et al., 2001a and Tardos et al., 1997). The existence of the three regimes has been proved experimentally in different types of granulators (Ennis et al., 1991).

Granule growth is promoted by a low value of St_v and a high value of St_v^*. For instance, increasing the binder content will increase the binder layer thickness h_0 which will increase St_v^* and hence increase the likelihood of successful coalescence. The effect of the binder viscosity is not easily predictable in that e.g. increasing the value η_{liq} (lowering St_v) alters the coefficient of restitution *e* decreasing St_v^* as well (Iveson et al., 2001a).

Although the St_v and the St_v^* are important parameters in the prediction of coalescence they are only valid for predicting the maximum size of granules which can coalesce. The parameters state nothing about the rate of granule growth. Different authors have showed however, that fast growth rates are attributed to the non-inertial regime while a slower growth is attributed to values of St_v close to or above St_v^* (Ennis et al. 1991 and Cryer, 1999).

The model by Ennis et al. (1991) was a significant progress in the modelling of particle-level coalescence in fluid beds as it was the first model to consider dynamic affects such as viscous dissipation. Results by e.g. Ennis et al. (1991) and Hede (2005) indeed shows that agglomeration tendency is closely related to the relative sizes of St_v^* versus St_v. The model is nevertheless limited by its many assumptions[17] although is gives a rough number for the indication of the limit between no-agglomeration and successful agglomeration. The model is however only valid for non-deformable surface wet granules where the viscous forces are much larger than capillary forces. These approximations will not always hold for all granulating fluid bed systems and sometimes more advanced models must be used. The next section introduces an extension of the original Ennis et al. (1991) model.

1.3.2.2 Class I models: Coalescence of deformable granules

Despite the gentle nature of fluid bed agitation compared to other granulating systems, some particle materials will deform upon collision in fluid beds. Based on the original model by Ennis et al. (1991), Liu et al. (2000) extended the viscous Stokes theory to include the effect of plastic deformation of the granules upon collision. Granules are assumed to have a strain-rate independent of Young's modulus E and plastic yield stress Y_d. Liu et al (2000) consider two cases being surface wet granules and surface dry granules where liquid is squeezed to the granule surfaces by the impact. In respect to fluid bed granulation and coating, only the first case is relevant and will be presented in the following. Behind the model lies the assumption that coalescence occurs when the kinetic energy of impact is all dissipated through viscous dissipation in the liquid layer as well as through plastic deformation of the granule bulk. It is further assumed that granule surfaces only deform when they come into physical contact, which may hold for fluid bed situations but not in e.g. mixer equipment where the pressure generated by the coating fluid being squeezed between the surfaces will cause some precontact deformation. Of further assumptions should be mentioned that attractive interparticle forces in the contact area are assumed to be negligible and that fluid cavitation does not occur during rebound (Liu et al., 2000).

The model extension by Liu et al. (2000) divides the coalescence phenomenon into two types – type I and type II, which must not to be confounded with the coalescence model of Class I and Class II. Type I coalescence occurs when granules coalesce by viscous dissipation by the surface liquid before the granules are able to touch (Iveson et al., 2001a). That is, the granules are halted and coalesce before their surfaces come into contact. Type II coalescence occurs when granules are slowed to a halt during rebound, after their surfaces have made contact (Liu et al., 2000). In type II coalescence the relative granule velocity is reduced to zero by viscous forces during rebound after their surfaces have made contact. It is important to note that both deformable and non-deformable granules can grow by either mechanism although deformable granules can coalesce by type II over a greater range of St_v values (Liu et al., 2000).

The general simplified coalescence situation for both coalescence types can be illustrated by dividing the particle collision situation into four stages. In figure 8 the collision between two surface wet deformable granules is considered. The first stage is the approach stage. At a separation distance of $2h_0$ the liquid layers touch and merge. This combined liquid layer will then be squeezed by out as the granules approach, dissipating some of the kinetic energy of collision. In the second deformation stage the granules will begin to deform as the separation distance reduces to $2h_{asp}$, which is the height of the surface asperities, and the relative granule velocity is reduced to $2u_1$. The remaining kinetic energy is converted to stored elastic energy and dissipated by plastic deformation. When the relative collision velocity is reduced to zero a contact area of A^* is formed between the granules. In the third separation stage the granules begin to rebound with an initial velocity of u_2 as the stored elastic energy is released. Viscous dissipation in the surface liquid layer will again retard the granule movement. In the fourth last separation stage the liquid layers are assumed to separate and the granule rebound to be complete when the granules are separated to a distance of $2h_0$ leaving the granules with a velocity of u_3.

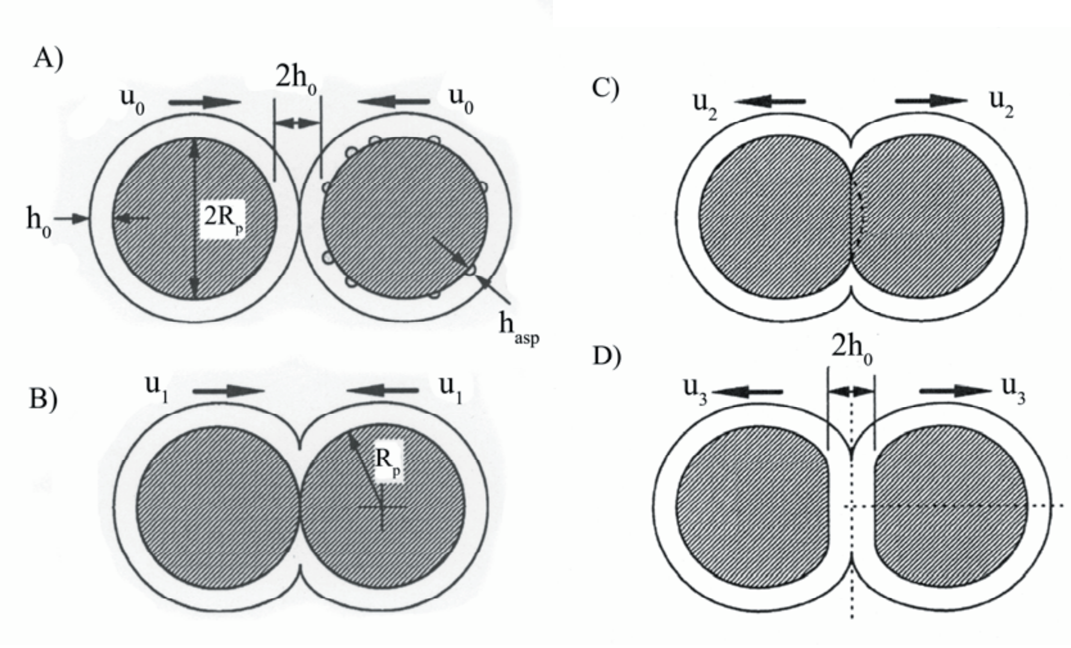


Figure 8: Stages in the agglomeration process of deformable primary particles.
Schematic diagram of the model used to predict coalescence of two surface wet deformable granules. A) Approach stage. B) Deformation stage. C) Initial separation stage. D) Final separation stage (Based on Iveson et al., 2001a and Liu et al., 2000).

Following the terminology of figure 8, type I coalescence occurs if the viscous forces are so high that the granule velocity u_1 is less than zero indicating that coalescence occur before the granule surfaces come into contact. In such a situation, permanent coalescence will occur if the following condition is satisfied:

$$\mathrm{St}_v < \ln\left(\frac{h_0}{h_{asp}}\right) \tag{1.32}$$

in which the viscous Stokes number is defined according to equation 1.27.

For granule collision situations with $u_1 > 0$ at the separation distance of $2h_{asp}$, the granule surfaces come into contact and begin to deform. For granules to permanent coalescence u_3 must obviously be less than zero. The following condition must be satisfied for permanent coalescence to occur (Liu et al., 2000):

$$\begin{aligned}&\left(\frac{Y_d}{E^*}\right)^{1/2}\cdot(St_{def})^{-9/8} < \frac{0.172}{St_v}\left(\frac{2r_{harm}}{h_0}\right)^2\left(1-\frac{1}{St_v}\ln\left(\frac{h_0}{h_{asp}}\right)\right)^{5/4}\cdot\\&\left(\left(\frac{h_0^2}{h_{asp}^2}-1\right)+\frac{2h_0}{\delta_{pdef}}\left(\frac{h_0}{h_{asp}}-1\right)+\frac{2h_0^2}{(\delta_{pdef})^2}\ln\left(\frac{h_0}{h_{asp}}\right)\right)\cdot\\&\left(1-7.36\cdot\left(\frac{Y_d}{E^*}\right)(St_{def})^{-1/4}\right)\cdot\left(\left(1-\frac{1}{St_v}\ln\left(\frac{h_0}{h_{asp}}\right)\right)^{-1/2}\right)^2\end{aligned} \tag{1.33}$$

in which δ_{pdef} is the extent of permanent plastic deformation given by:

$$\begin{aligned}\delta_{pdef} &= \left(\frac{8}{3\pi}\right)^{1/2}\cdot(St_{def})^{1/2}\cdot 2r_{harm}\left(1-\frac{1}{St_v}\ln\left(\frac{h_0}{h_{asp}}\right)\right)\cdot\\&\cdot\left(1-7.36\cdot\left(\frac{Y_d}{E^*}\right)(St_{def})^{-1/4}\right)\cdot\left(1-\frac{1}{St_v}\ln\left(\frac{h_0}{h_{asp}}\right)^{-1/2}\right)\end{aligned} \tag{1.34}$$

and r_{harm} is the harmonic mean radius given by equation 1.29, Y_d is the plastic yield stress and E^* is the granule Young's modulus given by:

$$\frac{1}{E^*} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \tag{1.35}$$

in which E_1 and E_2 are the Young's modulus of the two granules and ν_1 and ν_2 the Poisson ratios[18] respectively. Analogously[19] to the definition of the St_{def} in equation 1.26, the Stokes deformation number is in this case expressed as (Tardos et al., 1997):

$$St_{def} = \frac{m_{harm} \cdot u_0^2}{2 \cdot (2 \cdot r_{harm})^3 \cdot Y_d} \tag{1.36}$$

where m_{harm} is the harmonic mean mass according to:

$$m_{harm} = \frac{2m_1 \cdot m_2}{m_1 + m_2} \tag{1.37}$$

The Stokes deformation number can be seen as the ratio of impact kinetic energy to plastic deformation in the granule core. It gives a measure of the amount of plastic deformation that the granules would have suffered during the collision had there been no viscous liquid layer present.

Based on the criteria for type I and type II coalescence, a plot of St_v versus St_{def} indicating the boundaries between the two types of coalescence has been suggested by Liu et al. (2000) according to figure 9:

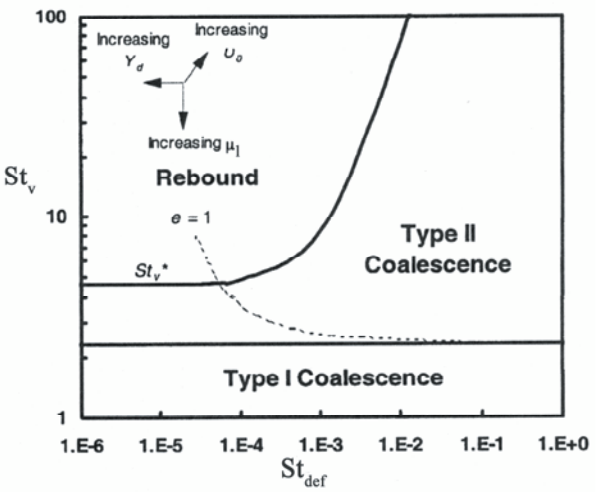


Figure 9: Class I coalescence.
Values of the Stokes viscous number St_v versus the Stokes deformation number St_{def} showing regions of rebound and coalescence for wet deformable granules (Liu et al., 2000).

Figure 9 suggests that three primary regions exists being rebound, type I and type II regions. In accordance with the models in equation 1.27 and equation 1.36, figure 9 suggests that at low St_{def} number the likelihood of coalescence depends only on the critical viscous Stokes number St_v^* as it was suggested by the original model for non-deformable granules by Ennis et al. (1991). In this region all collisions are fully elastic. As St_{def} increases, the coalescence region extends over a wider range of St_v values. This is because permanent granule deformation occurs which improves the likeliness of permanent coalescence in two ways: First of all it dissipates some of the impact energy and secondly, it creates a flat surface of area A^* between the two granules which creates a greater viscous dissipation force during rebound (Iveson et al., 2001a). In comparison to the original model by Ennis et al. (1991), the extension by Liu et al. (2000) results in a model that predicts that when plastic deformation is significant, increasing the impact velocity may actually improve the likelihood of coalescence by shifting a system from rebound back into the coalescence region. This situation is rarely observed in fluid beds however, as the low agitative forces result in coalescence domains in which St_{def} and St_v numbers are both small.

Despite the improvement of the original Ennis et al (1991) model, the model by Liu et al. (2000) still suffers many of the same limitations. E.g. are capillary forces still neglected although these are acknowledged having an importance. Likewise has no account been taken of any possible breakage of chipping during collision. The Liu et al. (2000) model is however most likely currently the best available model to describe coalescence situations at particle level, and validation experiments with glass ballotini cores in drum granulation equipment seems promising (Liu et al., 2000).

1.3.3 Granule growth regimes

With basis in the Stokes deformation number in equation 1.36 Iveson & Litster (1998) proposed that there are basically two broad categories of granule growth behaviour being *steady growth* and *induction growth*. At steady growth the size of the agglomerates increases linearly with time while at the induction growth there is a delay period during which little growth occurs.

Steady growth occurs in systems with weak and deformable granules. Granules in this regime grow by either crushing or deformation, thereby creating a large area during impact which promotes the chance of permanent coalescence. Steady growth is generally exhibited by relatively coarse, narrowly sized particles. Induction growth occurs in systems which are relatively strong. The granules do not deform sufficiently during impact to be able to coalesce without the presence of liquid binder at the particle surfaces. Hence, after the initial nuclei form, there is a delay period during which little growth. If the granules consolidate sufficiently to squeeze binder liquid to the surface, then the granules will begin to grow quickly until a critical size is reached above which the torque experienced by the dumbbell particle pairs becomes too large for further coalescence growth. Induction growth is generally seen in systems with fine widely spread particles and/or viscous binders. Whereas steady growth has been observed in fluid bed granulating systems, induction growth has not yet been reported in fluid beds probably because the impact forces are too low to cause significant consolidation as emphasised in Hede (2005 & 2006b).

Iveson & Litster (1998) suggested that the type of granule growth behaviour is a function of two parameters only being the amount of granule deformation during impact according to equation 1.36 and the maximum pore liquid saturation being a measure of the liquid content according to:

$$s_{max} = \frac{w_{mr} \cdot \rho_p \cdot (1 - \varepsilon_{min})}{\rho_b \cdot \varepsilon_{min}} \tag{1.24}$$

in which w_{mr} is the mass ratio of liquid to solid, ρ_p is the density of the solid particles, ρ_b is the density of the binder liquid and ε_{min} is the minimum porosity the formulation reaches for that particular set of operating conditions. The liquid saturation terms s_{max} must include any extra liquid volume due to solids dissolution but should not include any liquid which is absorbed into the porous carrier particles (Iveson et al., 2001a and 2001b).

Based on values of s_{max} and St_{def}, Iveson & Litster (1998) suggested a granule growth regime map according to figure 10:

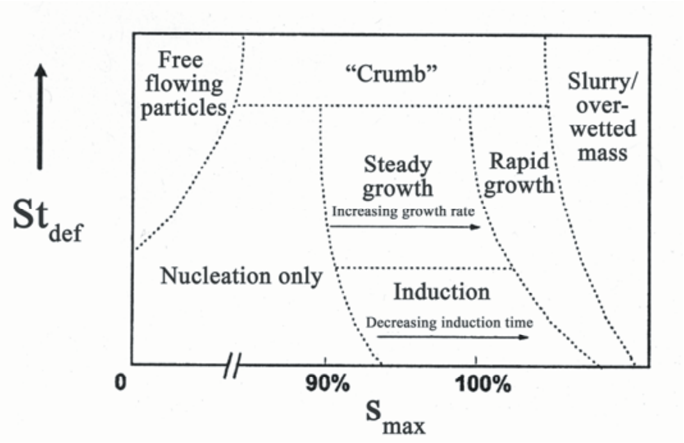


Figure 10: Granule growth regime map (Iveson & Litster, 1998).

In the original regime map by Iveson & Litster (1998) a number of subcategories of steady and induction growth were suggested. Nucleation growth only occurs when granule nuclei form, but on the same time there is insufficient binder to promote further growth. Crumb behaviour occurs when the binder conditions are too weak to form permanent coalesced granules but instead form a loose crumb material which cushions a few larger granules which are constantly breaking and reforming (Iveson et al., 2001a). Overwetting occurs when excess binder has been added and the system forms an oversaturated slush or slurry (Iveson & Litster, 1998). The original regime map does not include any values of the Stokes deformation number for which the regimes change. Work by Iveson et al. (2001b) suggested a modified granule growth regime map in which the location of several of the regime boundaries has been identified quantitatively. Iveson et al. (2001b) suggested that the crumb and slurry regions occur at $St_{def} > 0.1$ with slurries when $s_{max} > 100\%$. The transition from nucleation to induction growth also occurs at $s_{max} = 100\%$. The s_{max} at which steady growth begins is shown to decrease with increasing St_{def}. In accordance with these observations, Iveson et al. (2001b) proposed a modified regime map according to figure 11.

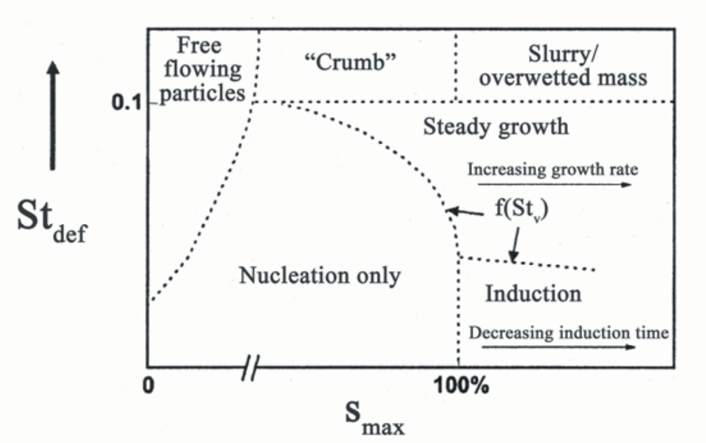


Figure 11: Modified granule growth regime map (Iveson et al., 2001b).

Although being a step towards a quantitative prediction of the agglomeration phenomena, the granule growth regime map is still more of a descriptive tool and not a predictive one. This is due to the fact that the two parameters s_{max} and St_{def} require a-priori knowledge of the maximum extent of consolidation since this affects granule yield stress as well as pore saturation. Another significant shortcoming is the very simplistic rheological model used to describe the mechanical properties of the granules. It is assumed that the granules are rigid-plastic materials whereas in reality as previously stated, wet granular materials are complex visco-elastic-plastic materials with strain-rate and history dependent behaviour (Iveson et al., 2001a). Subsequent work by Iveson et al. (2001b) suggests that binder viscosity[20] needs to be included as a third independent parameter in the granule growth regime map thereby expanding the map into three dimensions. The regime map boundaries also suffer from the fact that it is associated with great difficulty of comparing different types of equipment using the regime map because of the uncertainty of the correct characteristic granule impact velocity (Iveson et al., 2001a). A suggestion for further work could be to develop an equipment specific regime map as not all regimes in the current maps are observed for all types of equipment.

Summary

The modelling of the different processes that occur during granulation at particle level may at first seem a too simplified approach in the process of being able to describe the entire granulating system. Much of the theory presented in the present text takes a starting point in the situation where only two particles interact and in addition only considers a situation in which only one of many types of processes occurs. Further, a lot of assumptions are associated with the theory, and a-priori knowledge is often needed in order to apply the equations quantitatively. The situation inside e.g. a fluid bed during granulation is obviously far more complex and many of the parameters needed in the micro-level equations cannot be determined easily or if they can, the single needed property may in fact consist of a wide distribution of values rather than a single value. That is e.g. the case with the particle collision velocities u_0 as previously emphasised. Hence, much of the theory presented may most likely not be applied readily for real granulating systems for other than qualitative purposes.

Micro-level modelling is nevertheless a vital tool towards a complete engineering of the granulation process at all scales. Although the introduced approaches are somewhat too simplified, they form a vital part in the process towards a fundamental understanding of the granulation process. Only by simplifications is it possible to study the various granulation processes and phenomena in detail. As it is the present case that meso-scale properties are still unknown, detailed micro-level theory is a prerequisite in the modelling of the granulation process at larger macro-level scale, and as it has been presented elsewhere (e.g. in Hede, 2006a), micro-level understanding play an important role in the different simulation techniques as well as population balance modelling of the fluid bed granulation process.

Table of symbols

Nomenclature		**Unit (SI-system)**
a	Internal coordinate	-
a'	Material constant	Dimensionless
a_d	Projected area of liquid binder droplets	m^2
a_{AE}	Fitting parameter	Dimensionless
a_n	Projected area of a nucleus granule	m^2
$\dot{A}$	Powder flux	m^2/s
A^*	Contact area between colliding granules	m^2
b	Internal coordinate	-
b_{AE}	Fitting parameter	Dimensionless
c	Cohesivity of dry particle mass	N/m^2
$d_{air\ distrib\ pl.}$	Air distribution plate diameter	m
d_b	Gas bubble diameter	m
d_{bed}	Fluidised bed diameter	m
d_d	Liquid droplet diameter	m
$d_{d,rel}$	Relative liquid droplet diameter	m
d_p	Particle diameter	m
$d_{orifices}$	Pitch orifice diameter	m
$d_{sp/sp}$	Interaction parameter of two spheres	m
d_v	Equivalent diameter of particles	m
d_{vessel}	Fluid bed vessel diameter	m
e	Particle coefficient of restitution	Dimensionless
E	Young modulus	N/m^2
E^*	Granule Young modulus	N/m^2
E_{elu}	Elutriation rate	-
$f_1(\mathbf{x}, \mathbf{r}, t)$	Average number density function	-
f_{bi}	Bi-variant average number density function	-
$f_{initial}$	Initial average number density function	-
f_{tetra}	Tetra-variant average number density function	-
$F_{pend.,bound.}$	Pendular force in the "boundary" method	N
$F_{pend.,eq\ sph.}$	Pendular force between two equally sized spheres	N
$F_{pend.,gorge.}$	Pendular force in the "gorge" method	N
F_{vis}	Viscous force	N

Nomenclature		**Unit (SI-system)**
$\mathbf{F}_i$	Net force vector acting on particle i	-
$\mathbf{F}_i\mathbf{H}$	Drag force vector	-
$\mathbf{F}_i\mathbf{E}$	Force vector accounting for external fields	-
$\mathbf{F}_i\mathbf{P}$	Force vector accounting for particle-particle interactions	-
g	Gravity	m/s^2
G($\mathbf{x}$, $\mathbf{r}$, t)	Rate of growth by layering	-
G_s	Mass flux of particles	m^2/s
h($\mathbf{x}$, $\mathbf{r}$, t)	Net generation rate of particles	-
h_0	Binder layer thickness covering colliding granules	m
h_a^+	Birth of particles due to aggregation	-
h_a^-	Death of particles due to aggregation	-
h_{asp}	Characteristic length scales of surface asperities	m
h_b^+	Birth of particles due to breakage	-
h_b^-	Death of particles due to breakage	-
h_{bed}	Bed height	m
H	Separation distance between two spheres	m
i	Summation parameter	-

Nomenclature		**Unit (SI-system)**
I_i	Moment of inertia	-
J	Nucleation ratio	Dimensionless
k	Proportionality constant	-
k´	Proportionality constant	-
k_{cn}	Coordination number	Dimensionless
K_a	Nucleation area ratio	Dimensionless
L	Characteristic length of particles	m
L_{bed}	Fluid bed length from distributor plate to exhaust exit	m
L_{slr}	Length scale ratio	Dimensionless
m	Mass	kg
m(**x**)	Mass of a particle of internal state **x**	
m_{aggl}	Agglomerate mass	kg
m_{bed}	Bed load	kg
m_{harm}	Harmonic mean granule mass	kg
$\dot{m}_{\text{nozzle air}}$	Spray rate from the nozzle	kg/s
$\dot{m}_{\text{spray}}$	Air flow rate through the nozzle	kg/s
$\mathbf{M}_i$	Net torque vector	-
n_{fi}	Flow index	Dimensionless
n(**x**, **r**, t)	Actual number density	-
$\dot{n}_0$	Nucleation rate	No. of particles/s
N(**r**, t)	Average total number of particles	-
N_T	Total number of particles	-
N_{T0}	Initial total number of particles	-
p	Summation number	Dimensionless
P	Pressure	Pa
P(**x**,**r**|**x**´,**r**´)	Probability density function	-
q	Discretisation number	Dimensionless
r	Radius	m
r_{aggl}	Radius of an agglomerate	m
r_{def}^*	Critical radius of an agglomerate after which def. occurs	m
r_{harm}	Harmonic mean granule radius	m
r_{neck}	Pendular bridge neck radius	m
$\bar{r}_g$	Mean granule size	m

Nomenclature		**Unit (SI-system)**
$\bar{r}_{g_0}$	Initial mean granule size	m
r_{neck}	Pendular bridge neck radius	m
$\mathbf{r}$	External coordinate vector	-
$\mathbf{r}'$	External coordinate vector	-
R	Radius	m
R_p	Particle radius	m
s_{max}	Maximum pore liquid saturation	Dimensionless
S	Distance	m
S_c	Saturation at transition funicular/capillary state	Dimensionless
S_d	Dry coating material feed rate	-
S_f	Saturation at transition pendular/funicular state	Dimensionless
S_{sat}	Amount of saturation	Dimensionless
St_{def}	Stokes deformation number	Dimensionless
St_{def}^*	Critical Stokes deformation number	Dimensionless
St_v	Viscous Stokes number	Dimensionless
St_v^*	Critical viscous Stokes number	Dimensionless
S_w	Wetting saturation	Dimensionless
S(q)	Summation function	-
$S_{Kolmogorov}$	Kolmogorov entropy	bits/s
t	Time	s
t_{coat}	Coating time	s
u	Granule velocity	m/s
u_0	Initial granule collision velocity	m/s
U	Fluidisation velocity	m/s
U_{br}	Bubble rise velocity for a fluid bed	m/s
U_{mf}	Minimum fluidisation velocity	m/s
U_s	Superficial gas velocity	m/s
$\mathbf{v}_i$	Velocity vector	-
v	Particle volume internal coordinate	-
$\bar{v}$	Average particle volume	m^3
v_L	Liquid binder volume internal coordinate	-
$\dot{V}$	Volumetric spray rate	m^3/s
V_{aggl}	Agglomerate volume	m^3
V_{bridge}	Liquid bridge volume	m^3

Nomenclature		**Unit (SI-system)**
$V\mathbf{r}$	Volume of external coordinates	-
$V\mathbf{x}$	Volume of internal coordinates	-
w	Granule volume parameter in coal. kernel expression	-
w^*	Critical average granule volume	-
w_{mr}	Mass ratio of liquid to solid	Dimensionless
W	Spray zone width	m
$\mathbf{x}$	Internal coordinate vector	-
$\mathbf{x}'$	Internal coordinate vector	-
x	Coordinate	m
y	Coordinate along the width of the spray zone	m
$\mathbf{Y}(\mathbf{r},t)$	Continuous phase vector	-
Y_d	Plastic yield stress	N/m^2
z	Counting number	Dimensionless

Nomenclature		**Unit (SI-system)**
Greek		
β	Coalescence kernel	-
β_0	Rate constant	-
β_{dt}	Aggregation probability in time interval dt	-
β_{id}	Coefficient of interphase drag	Dimensionless
β^*	Coalescence kernel expression	-
δ	Dimensionless bubble spacing	Dimensionless
δ_{pdef}	Extent of permanent plastic deformation	Dimensionless
μ_f	Coefficient of internal friction	Dimensionless
μ_{mean}	Mean in the Gaussian distribution	m
σ_f	Macroscopic shear stress at failure	Pa
σ_n	Macroscopic normal stress	Pa
σ_{width}	Standard deviation	m
$\sigma_{t,f}$	Funicular bridge static tensile strength	N/m^2
$\sigma_{t,p}$	Pendular bridge static tensile strength	N/m^2
$\sigma_{t,c}$	Capillary bridge static tensile strength	N/m^2
$\sigma(\dot{\gamma})$	Characteristic stress in an agglomerate	N/m^2
σ_y	Yield stress/strength	N/m^2
τ_c	Average particle circulation time	s
τ_d	Droplet penetration time	s
ψ_a	Dimensionless spray flux	Dimensionless
$\psi_n(y)$	Dimensionless nuclei distribution function	Dimensionless
ψ_n	Dimensionless spray number	Dimensionless
ζ	Particle shape factor (sphericity)	Dimensionless
λ	Dimensionless parameter in the dynamic strength eq.	Dimensionless
φ	Half filling radius	°
Θ	Contact angle	°
ν	Poisson ratio	Dimensionless
$\nu(\mathbf{x}',\mathbf{r}',\mathbf{Y},t)$	Average number of particles formed from break up	-
ε	Particle voidage (void fraction)	%
$\varepsilon_{longitudinal}$	Longitudinal extension strain	Dimensionless
ε_{min}	Minimum porosity	%
ε_{trans}	Transverse contraction strain	Dimensionless
$\bar{\varepsilon}_g$	Mean granule porosity (void fraction)	%

Nomenclature		Unit (SI-system)
γ_{lv}	Interfacial surface tension between liquid and vapour	N/m
$\dot{\gamma}$	Shear rate	s^{-1}
ρ	Density	kg/m^3
ρ_b	Binder liquid density	kg/m^3
ρ_g	Granule density	kg/m^3
ρ_p	Particle density	kg/m^3
η_{app}	Apparent viscosity	kg s /m
η_{liq}	Liquid (binder/coating) viscosity	kg s /m
ω_i	Angular velocity vector	-
Ω_H	Hounslow discretisation parameter	-
$\Omega\mathbf{r}$	Domain of external coordinates	Dimensionless
$\Omega\mathbf{x}$	Domain of internal coordinates	Dimensionless

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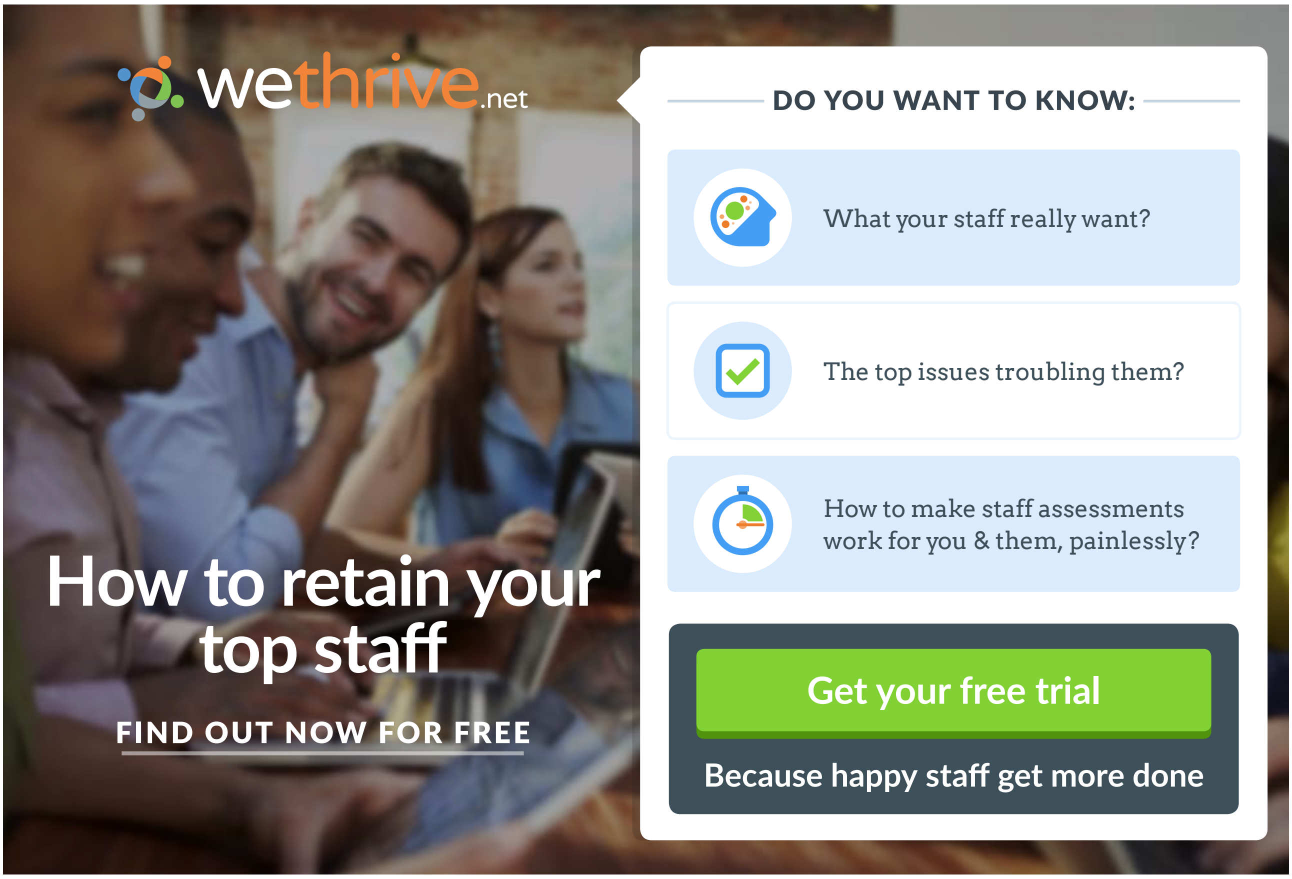

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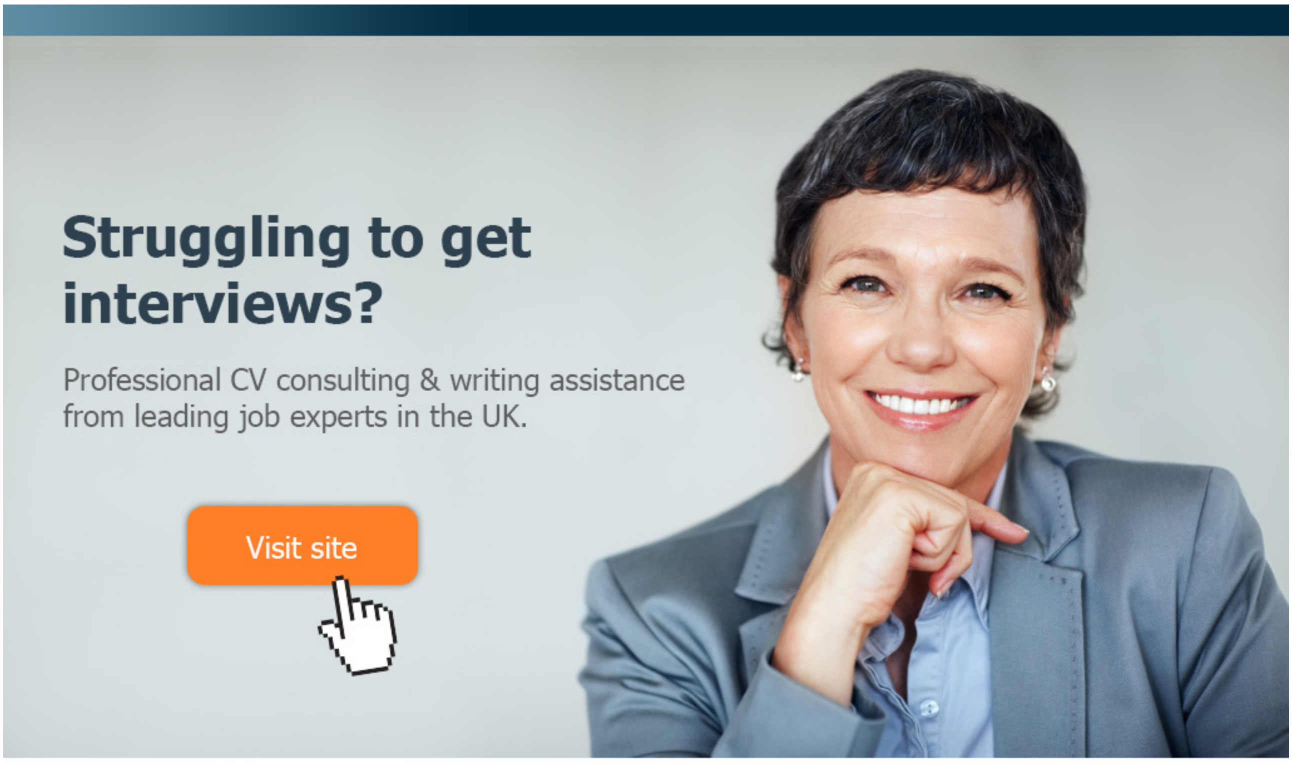

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Endnotes

1. Please refer to Hede (2005) section 4.2.3.
2. More on Monte Carlo techniques may be found in Hede (2006a).
3. Please refer to Hede (2005) section 4.2.4.
4. The time it takes for a particle to circulate a complete wetting-drying cycle. It depends primarily on the fluidisation velocity and bed height, as it was presented in Hede (2005 & 2006b).
5. Please refer to equation 4.11 in Hede (2005).
6. It can be shown mathematically that this does not affect the density of binder liquid along the width of the spray zone (Wildeboer et al., 2005).
7. There may obviously also be buoyancy force due to the partial submersion of the particle spheres but Princen (1968) showed that this is negligible for particle spheres with diameters less than 1 mm.
8. Only large liquid bridges are affected by gravitational distortion (Simons et al., 1994).
9. Sometimes also referred to as the capillary suction pressure (Iveson et al., 2001a).
10. Ennis & Sunshine (1993) suggest a value for kcn of 1.1.
11. Please refer to equation 1.29.
12. Equation 1.22 has not yet been fully verified (Iveson et al., 2002).
13. The Herschel-Bulkley model is often preferred to power law or Bingham relationships as it results in more accurate models on Non-Newtonian behaviour when adequate experimental data is available (London, 2005).
14. Please note that this assumption is basically the same assumption presented by Ennis et al. (1991) in which the collision velocity is based on the bubble rise velocity Ubr, bubble diameter db, radius of the agglomerate raggl and the axial fluid bed bubble spacing δ. Please refer to Hede (2005), pp. 22 for further information.
15. The coefficient of restitution is the ratio of the difference in velocity before and after the collision. In the case of two colliding particles it is the difference in the velocities of the two colliding particles after the collision divided by the difference in their velocity prior to collision. Perfect elastic collisions has $e = 1$ (Christensen et al., 2000). The coefficient of restitution e thereby accounts for the viscous dissipation in the binder phase being sufficient to dissipate the energy of collision (Liu et al., 2000).
16. Please refer to appendix A4 in Hede (2006b) to see the derivation of equation 1.27 and equation 1.28.
17. For instance that there exists a uniform granule collision velocity or that in coalescence, capillary forces can be neglected (Ennis et al., 1991). Ennis et al. (1991) justified neglecting capillary forces on the basis that the energy added during liquid bridge formation and granule approach is cancelled by the energy dissipated during granule separation and liquid bridge rupture. This is a rough assumption as that dynamic energy of the pendular bridge and the rupture energy are equal only if the collision has a coefficient of restitution equal to one, which is almost never the case (Liu et al., 2000). Especially the difficulty of determining a precise collision velocity u0 makes the viscous Stokes theory difficult to exploit fully in practice (Abbott, 2002).

18. Poissons ratio is the ratio of transverse contraction strain to longitudinal extension strain in the direction of the stretching force. Tensile deformation is considered positive and the compressive deformation is considered negative. Hence, the Poisson ration is defined as: $\nu = -\varepsilon\mathrm{trans} / \varepsilon\mathrm{longitudinal}$ (Wisconsin, 2005).
19. Please note that the superstructure of equation 1.36 in fact is the same as equation 1.23 in which the harmonic mean mass has been substituted with the mass of the agglomerate, the harmonic mean radius with the volume of the agglomerate and the plastic yield stress with the characteristic stress in the agglomerate.
20. Characterised by the viscous Stokes number Stv (Iveson et al., 2001b).