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► **To cite this version:**

Michel Cournil, Frédéric Gruy, Patrick Cugniet, Pascal Gardin, Hubert Saint Raymond. Model of aggregation of solid particles in nonwetting liquid medium. Angelo Chianese. 15th International Symposium on Industrial Crystallization, Sep 2002, Sorrento, Italy. European Federation of Chemical Engineering ; American Institute of Chemical Engineers ; Associazione italiana di ingegneria chimica, Non paginé, 2002. <hal-00625663>

**HAL Id: hal-00625663**

**<https://hal.archives-ouvertes.fr/hal-00625663>**

Submitted on 22 Sep 2011

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# MODEL OF AGGREGATION OF SOLID PARTICLES IN NON-WETTING LIQUID MEDIUM

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Problem of modelling solid particles aggregation in non-wetting liquids is in close relation with the problem of interactions between hydrophobic particles in water. Hydrophobic aggregation is discussed from a thermodynamic point of view, then the main aspects of aggregation dynamics are envisaged in the particular conditions created by non-wetting. Consequences on aggregation and fragmentation kernels are studied. An experimental illustration is provided.

## 1. INTRODUCTION

In spite of many complex aspects, aggregation dynamics is relatively well understood (De Boer et al., 1989). However, some physical situations were little studied and deserve further works. This is the case of aggregation in non wetting liquid media. An important application of this problem is found in the processing of liquid steel. Solid inclusions-typically alumina ( $\text{Al}_2\text{O}_3$ ), 3 to 20  $\mu\text{m}$  particles- are present in the baths and gather to form clusters of 50 to 300  $\mu\text{m}$ . For lack of systematic studies -due to the conditions of a molten bath (2000 K)- many aspects of the phenomenon still remain obscure. Importance of non-wetting of the solid particles by the liquid phase was acknowledged as essential element of understanding in (Kozakévitch and Lucas, 1968). According to these authors, the liquid phase is spontaneously drained off from the contact zone between two solid inclusions; this results in the formation of a gaseous bridge which ensures a stronger cohesion of the particle doublet.

In several points, this situation suggests analogies with the *hydrophobic interactions* which have been known for many years, however in different physical contexts. Many experimental works, indeed, have definitely proved the existence of very strong and long range attractive forces between hydrophobic surfaces in water or more generally surfaces separated by non-wetting medium (Yaminsky et al., 1983, Yushchenko et al., 1983, Parker et al., 1994). This hydrophobic interaction was measured and proved to be much larger than the van der Waals forces. Several works mention the existence of gas cavities between particles in close interaction. After a long period of controversies, it seems that the interpretations of hydrophobic forces are now convergent. Hydrophobicity results in reducing the solvent density down to possible local evaporation near the solid surface (Forsman et al., 1997). Ruckenstein and Churaev (1991), Yaminski and Niham (1993), and Ruckenstein (1997) calculated interactions between surfaces covered with gaseous gaps, however separated by a liquid layer.

To our knowledge, aggregation dynamics of solid particles in non-wetting medium has never been studied extensively in spite of the interest of some experimental works (Zhou et al, 1996; Song and Lopez Valdivieso, 1999) on particular points. The aim of this work is to re-examine and, if need be, to adapt or modify several elements of aggregation modelling in case of non-wetting. The main static and thermodynamic aspects of aggregation are presented first, then, dynamic aspects are studied; in particular, the aggregation kernel factors (collision frequency and efficiency) are calculated and principles of fragmentation kernel determination are given.

## 2. STATIC ASPECTS OF AGGREGATION IN NON-WETTING MEDIA

In case of non-wetting, equilibrium of the contact line between the three phases gas-liquid-solid (when it exists) imposes the Young relation between the respective interfacial tensions  $\mathbf{g}$  (G = gas phase; L = liquid phase; S = solid phase):

$$\mathbf{g}_G - \mathbf{g}_L = \mathbf{g}_G \cos \mathbf{q} \quad (1)$$

where  $\mathbf{q}$  is the contact angle. Larger than  $90^\circ$   $\mathbf{q}$  values correspond to non-wetting situations. In the case of the alumina - liquid steel - air system,  $\mathbf{q}=140^\circ$  (2.44 radians). Possibility of existence and development of different gas-liquid-solid configurations can be judged from the sign and variations of their Gibbs enthalpy of formation  $\mathbf{D}\mathbf{G}_n$ :

$$\mathbf{D}\mathbf{G}_n = n (\mathbf{m}(T, P_{\text{ext}}) - \mathbf{m}(T, P_{\text{ext}})) + \mathbf{g}_G \mathbf{D}\mathbf{S}_{LG} + \mathbf{g}_G \mathbf{D}\mathbf{S}_{SG} + \mathbf{g}_L \mathbf{D}\mathbf{S}_{SL} \quad (2)$$

$T$  is the temperature,  $P_{\text{ext}}$ , the pressure in the liquid phase,  $n$ , the vapour mole number;  $\mathbf{m}$  and  $\mathbf{m}$  are respectively the chemical potentials of the gas and the liquid;  $\mathbf{D}\mathbf{S}_{LG}$ ,  $\mathbf{D}\mathbf{S}_{SG}$  and  $\mathbf{D}\mathbf{S}_{SL}$ , the changes in liquid-gas, solid-gas and solid-liquid interfacial areas.

From these criteria, we find the following results:

- *gas cavities in pores*

Gas cavities can spontaneous appear and grow in most of the pores, holes or crevices of the inclusion surface and fill them to reach the external surface. Thus, the surface of a solid particle immersed in a non-wetting liquid is partially covered with a gas layer which consists of the top of different cavities filled with gas (Figure 1).

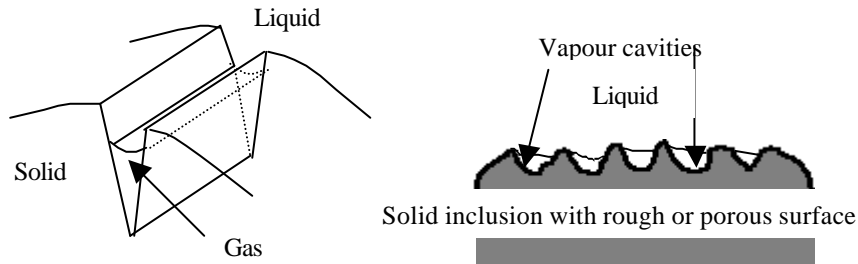


Fig. 1: Gas cavity in a crevice; solid-liquid interface with gas cavities

- *gas bridge between two solid surfaces*

In Fig. 2 is shown a gas bridge between two close flat surfaces. From thermodynamic criteria, it appears that this bridge can spontaneous appear only if the surfaces are in contact, otherwise, an activation is necessary. Once gas bridge is formed, it can

spontaneously evolve by lateral growth and axial shrinkage till surfaces are in contact. Thus, surface bridging via pores filled with gas is spontaneous and constitutes a quite plausible mechanism. Gas is either vaporized liquid or gas desorbed from liquid.

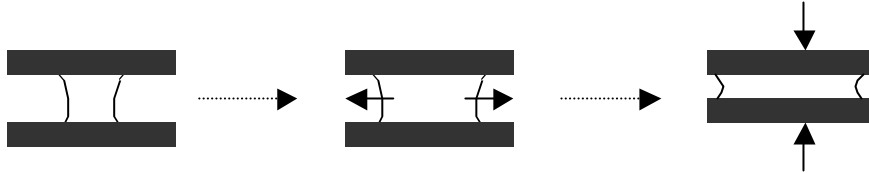


Fig.2: Spontaneous evolution of a gas bridge between two flat interfaces

▪ *forces between particles in a non-wetting medium*

Hydrophilic particles in interaction in a fluid medium are submitted to the well-known *DLVO forces* (De Boer et al., 1989). In a non-wetting and non-aqueous medium, van der Waals forces are still active, whereas electrochemical forces are irrelevant. Presence of gas bubbles or cavities at or between the particle surfaces results in attractive forces:

i) *van der Waals force*: for two plane surfaces, force  $f_w$  per unit area is given by:

$$f_w = \frac{A}{6\pi h^3} \quad (3)$$

$A$  is the Hamaker constant,  $h$  the separation between the surfaces.

ii) *hydrophobic force (absence of gaseous bridge)*: (Ruckenstein, 1997) evaluated the interaction force  $f_R$  due to the hydrodynamic interaction force between pulsating gas bubbles located on hydrophobic surfaces in water:

$$f_R \approx \frac{1}{h^3} \quad (4)$$

Dependence of  $f_w$  and  $f_R$  against separation  $h$  is the same ( $\approx 1/h^3$ ). Numerical comparison is difficult because of unknown parameters in (4). However, experiments prove that coefficient of  $1/h^3$  is much larger in  $f_R$  than in  $f_w$ .

iii) *forces due to the gaseous bridge*: Problem of determination of forces due to the presence of a mass bridge between solid particles was studied in (Simmons et al., 1994; Yaminski et al., 1983). Capillary binding forces  $F_G$  can be compared to van der Waals force  $F_w$ , for alumina in liquid steel (Cournil et al., 2002):  $F_w / F_G = 1.4 \times 10^{-10}/r_1^2$  where  $r_1$ , radius of the gas bridge, is expressed in  $\mu\text{m}$ . Thus, van der Waals forces are negligible, once the gas bridge is established and cohesion force of the doublet of particles is considerably higher than in case of aggregation in wetting conditions.

### 3. DYNAMICAL ASPECTS OF AGGREGATION IN NON-WETTING MEDIA

In this section, we will successively examine the effect of non-wetting and connected phenomena on the aggregation and fragmentation kernels.

#### 3.1 Aggregation kernels

We consider solid grains of typical size  $5 \mu\text{m}$  in a turbulent medium of Kolmogorov scale of about  $50 \mu\text{m}$ . At the eddy scale, the solid particles can be considered as submitted mainly to a local laminar flow characterised by a velocity gradient  $\dot{g}$ .

In a suspension consisting of classes of particles or aggregates (mean radius  $R_i$  and density by number  $n_i$ ), the collision frequency of particle  $i$  can be calculated as follows (Saffman and Turner, 1956):  $J_{ij}^0 = \frac{4}{3} \dot{g} (a_i + a_j)^3 n_j$  with  $\dot{g} \approx \left( \frac{\mathbf{r}\mathbf{e}}{\mathbf{m}} \right)^{1/2}$ ;  $\mathbf{e}$  is the turbulent energy dissipation rate per unit mass,  $\mathbf{r}$ ; the liquid density, and  $\mathbf{m}$  the dynamic viscosity. Aggregation models should take into account the effects of the interaction forces between particles. Some of them also exist in motionless system; others appear only with motion (fluid drainage). These effects modify the collision frequency as follows:

$$J_{ij} = \mathbf{a}_j J_{ij}^0 \quad (5)$$

where  $\mathbf{a}_j$  is the collision efficiency coefficient. In case of wetting liquid, when no-slip condition is fulfilled,  $\mathbf{a}_j$  is calculated from (Highashitani, 1982). In case of non-wetting, presence of gas pockets at the interface may result in slip of the liquid. Slip conditions have been already considered in the vicinity of solid interfaces (Vinogradova, 1995). Collision efficiency between two particles in non-wetting media has been calculated by us in (Cournil et al., 2002). For common values of the energy dissipation rate ( $10^{-3} \text{ m}^2 \cdot \text{s}^{-3} < \mathbf{e} < 1 \text{ m}^2 \cdot \text{s}^{-3}$ ),  $\dot{g}$  is ranging between 18.9 and 598  $\text{s}^{-1}$ . For particles radius of 5  $\mu\text{m}$  and van der Waals-like interactions,  $\mathbf{a}_j$  is little sensitive to the Hamaker constant (2). For instance, for hundred or thousand times as large Hamaker constants,  $\mathbf{a}_j$  values would not change. As interaction forces due to the presence of gas cavities (3) are of the same form as van der Waals forces, previous  $\mathbf{a}_j$  calculations are valid in this case too. In the common case of wetting,  $\mathbf{a}_j = 0.15$ ; in case of non-wetting  $\mathbf{a}_j = 0.38$ . Thus, non-wetting results in an increase of the collision efficiency, thus of the aggregation rate.

### 3.2 Fragmentation

The occurrence of break-up depends on the balance between the disaggregation effects due to the action of the fluid and the overall cohesion of the aggregate due to the interactions between primary particles. In case of non-wetting, the situation of fragmentation is quite new because the different particles are linked by gas bridges. This problem has not been studied yet. Here, we only examine the fragmentation conditions of a doublet of identical spherical particles just after the collision between the particles and later when the gas bridge is built up.

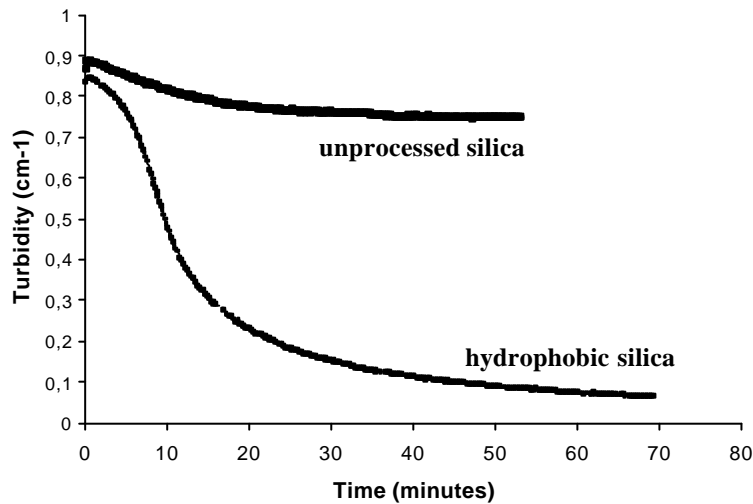
*Particle "sticking"*: we assume that gas cavities pre-exist at or under the surface of the solid particles. Building up of a gaseous bridge requires that the two colliding particles stay close to each other for a minimum time. Similar situations have been envisaged for agglomeration from supersaturated solutions (David et al., 1991, Mumtaz et al., 1997, Hounslow et al., 1998). Models generally consist in comparing time  $t_b$  needed to form the bridge and time  $t_p$  spent by the particles in close proximity. For particles smaller than Kolmogorov microscale,  $t_p$  is currently taken equal to  $\dot{g}^{-1}$ , thus:  $t_p \approx \left( \frac{\mathbf{n}}{\mathbf{e}} \right)^{1/2} \cdot t_b$ , is the drainage time of the liquid film located in the slit between the two inclusion surfaces. Motion of the liquid gas meniscus is due to the difference of pressure between the gas and the liquid phase. For the system of reference,  $t_b \approx 8 \times 10^{-7} \text{ s}$  and  $t_p \approx 10^{-2} \text{ s}$  (see details in (Cournil et al., 2002)). As the

time needed to build up a gas bridge is considerably shorter than the duration of the contact, the sticking probability of the two inclusions is close to 1.

#### *Doublet rupture*

Competition between the disaggregation and the cohesion effects can be judged from the value of ratio  $E_c/E_t$ ;  $E_c$  and  $E_t$  are respectively the aggregate cohesion energy and the turbulent energy acting on this aggregate. Breakage rate is

proportional to  $g e^{-\frac{E_c}{E_t}}$ . From analogy with rupture of pendular (liquid) bridges between particles (Simmons et al., 1994), energy  $e_c$  per unit volume of the doublet is: found equal to:  $2.53 \times 10^4 \text{ J.m}^{-3}$ . This value can be compared to the turbulent energy  $e_t$  dissipated per unit volume during action time:  $t_p$ .  $e_t$  ranges between 0.35 and  $12 \text{ J.m}^{-3}$ . This fluid turbulent energy is much lower than the required breakage energy and gaseous bridge fragmentation by the liquid flow is highly unlikely. Thus, very large aggregates can be met in aggregation in non-wetting media.



*Fig. 3: Comparison of aggregation in water of two silica samples : unprocessed silica and hydrophobic silica (monitoring by turbidimetry)*

### **3.3 Experimental aspects**

The previous theoretical approach is qualitatively confirmed in the case of alumina inclusions in liquid steel. Another validation comes from the experimental study of aggregation of hydrophobic silica in water. Aggregation is followed in situ and continuously using a turbidity probe. Turbidity of a suspension depends indeed on the number, the size and the morphology of the particles it contains and therefore may be very sensitive to a process such as agglomeration. In Fig. 3, we present an example of turbidity evolution with time during aggregation for two silica samples of same weight: one of them has been made hydrophobic by grafting of silanol groups at the surface of the grains ( $1.5 \mu\text{m}$  in diameter), the other consists of unprocessed silica In (Saint-Raymond et al, 1998), we explain how to interpret this sort of curves. Initial decrease in turbidity is due to aggregation whereas the final

plateau height strongly depends on the fragmentation intensity. The higher this plateau, the more intense the aggregate fragmentation. From Figure 3, it appears that initial aggregation is a little weaker for unprocessed silica than for hydrophobized silica. The effect of hydrophobicity on fragmentation is however much stronger. The near zero asymptotic value of turbidity reached for hydrophobized silica proves that large aggregates have been formed. On the contrary, in the absence of hydrophobizing process, the aggregates remain small, probably because their size is reduced by fragmentation. These two features of the aggregation process exactly correspond to the predictions of the previous discussions. In the same hydrodynamic conditions, non-wetting slightly increases the collision efficiency, thus the aggregation rate, whereas it practically suppresses fragmentation.

#### 4. CONCLUSION

From preliminary thermodynamic study, conditions of aggregation of solid particles in a non-wetting medium are defined: presence and role of gaseous cavities are justified as well as the expressions of interaction forces, whether the particles are in contact or not. From theoretical and experimental studies of aggregation processes, it appears that, in the same hydrodynamic conditions, non-wetting affects both aggregate formation and fragmentation, however much more the latter than the former phenomenon.

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