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Fluidization of nanoparticles: A simple equation for estimating the size of agglomerates

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Abstract

In this work, we revise data published in the last decade on the size of agglomerates in gas-fluidized beds of nanoparticles. Experimental measurements reviewed are based on non-invasive techniques, mainly consisting of laser-based planar visualization of agglomerates in the splash zone and indirect derivation from the fit of bed expansion, settling, and/or minimum fluidization velocity data to empirical correlations. Special attention is focused on the effect of fluidization aids such as vibration, magnetic assistance, sound excitation or centrifugation. Independent measurements performed by diverse authors or by the same authors using different techniques are confronted. Empirical models proposed to predict agglomerate size are also reviewed. Most of these models are difficult to apply in practice because they rely on parameters that need to be measured in the fluidization experiment or assumed. We propose a simple equation to estimate agglomerate size derived from the balance between the local shear force on the particle attached at the outer layer of the agglomerate and the interparticle adhesion force. In general, the results predicted by this equation are in satisfactory agreement with the reviewed experimental data.

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1. Introduction

Newly developed powder production and synthesis methods have stressed the role of nanopowders in powder-based processing innovations. These particles, which are only about 1–100 nm in size, provide controlled functionality and greater reactivity, thus delivering relevant advantages over traditional materials in numerous industrial applications. A part of the current nanopowder research is focused on a better understanding of nanoparticle behavior within fluidized beds [1], which have been used for years in many industrial processes on micron-scale particles [2]. A number of reports have appeared showing that some nanopowders can be fluidized homogeneously, with large bed expansion and absence of appreciable gas bubbles [3–13]. Even in certain cases, as for example in fluidization of silica nanoparticles, the bubbling regime commonly observed for micron-scale and larger particles above a critical gas velocity, is fully suppressed and the fluidized bed of nanoparticles transits directly to elutriation [13].

The condition of non-bubbling fluidization has been related to the formation of large porous agglomerates of several hundred microns in size in the fluidized state, thus this type of fluidization has been termed as agglomerate particulate fluidization (APF). Some studies have suggested that fluidized agglomerates of nanoparticles have a fractal structure with a fractal dimension D_a close to 2.5, in agreement with the diffusion-limited agglomeration (DLA) model [4,12]. However, in certain processes, like agglomeration due to dipole–dipole interaction in the presence of externally applied magnetic or electric fields, the agglomerates can adopt anisotropic shapes with a fractal dimension differing from the DLA value [14,15]. The study of these anisotropic agglomerates is outside the scope of this paper.

2. Experimental measurements of agglomerate sizes

Because of the great enhancement of gas–solid contact surface, bubbling suppression is of particular interest to the use of fluidized beds of nanoparticles as catalysts. However it is known that fractal agglomerates screen the external gas flow quite effectively [16], thus hindering the efficiency of gas–solid mixing. In the last years, several works have focused on estimating the size of nanoparticle agglomerates. At the beginning, these included

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Nomenclature

A	Hamaker constant
Ar	complex-agglomerate Arquimedes number, $Ar=(d^{**})^3\rho_f(\rho^{**}-\rho_f)g/\mu^2$
ABF	agglomerate bubbling fluidization
APF	agglomerate particulate fluidization
Bo_g	granular Bond number $\mathrm{Bo}_g=F_0/W_p$
Bo_g^*	ratio of attractive force between simple-agglomerates to simple-agglomerate weight
d	sub-agglomerate size
d_{as}	typical size of surface asperities
d_p	primary particle size
d^*	simple-agglomerate size
d^{**}	complex-agglomerate size
D	fractal dimension of a simple-agglomerate, $D=\ln N/\ln k$
D_0	fractal dimension of a sub-agglomerate, $D_0=\ln N_0/\ln k_0$
D_a	general fractal dimension of a complex-agglomerate, $D_a=\ln N_a/\ln k_a$
D_s	general fractal dimension of a simple-agglomerate, $D_s=\ln N_s/\ln k_s$
D^*	fractal dimension of a complex-agglomerate, $D^*=\ln N^*/\ln k^*$
F	attractive force between sub-agglomerates
F_0	interparticle attractive force
F_c	interparticle capillary force
F_s	local shear force
F_{vdW}	interparticle van der Waals' force
F^*	attractive force between simple-agglomerates
g	gravity acceleration
g_{ef}	effective acceleration
k	ratio of simple-agglomerate size to sub-agglomerate size, $k=d^*/d$
k_0	ratio of sub-agglomerate size to primary particle size, $k_0=d/d_p$
k_a	ratio of complex-agglomerate size to primary nanoparticle size, $k_a=d^{**}/d_p$
k_s	ratio of simple-agglomerate size to primary particle size, $k_s=d^*/d_p$
k^*	ratio of complex-agglomerate size to simple-agglomerate size, $k=d^{**}/d^*$
n	Richardson–Zaki exponent
N	number of sub-agglomerates in a simple-agglomerate
N_0	number of primary nanoparticles in sub-agglomerate
N_a	number of primary nanoparticles in a complex-agglomerate
N_s	number of primary nanoparticles in a simple-agglomerate
N^*	number of simple-agglomerates in a complex-agglomerate
Re	particle Reynolds number, $Re=\rho_f v_{p0} d_p/\mu$
SEM	scanning electron microscopy
v_g	superficial gas velocity
v_{p0}	terminal settling velocity of an individual primary particle
v^*	terminal settling velocity of an individual simple-agglomerate
v^{**}	terminal settling velocity of an individual complex-agglomerate
W_p	primary particle weight
z	minimum of intermolecular distance to estimate van der Waals' force

Greek symbols

β	half-filling angle for estimation of capillary force
γ	liquid surface tension
Λ	ratio of effective acceleration to gravity acceleration $\Lambda=g_{ef}/g$
μ	gas viscosity
ρ_b	bulk density
ρ_f	fluid density
ρ_p	particle density
ρ_T	tapped bed density
ρ^*	simple-agglomerate density
ρ^{**}	complex-agglomerate density
ϕ	particle volume fraction
ϕ^*	volume fraction of simple-agglomerates
ϕ^{**}	volume fraction of complex-agglomerates

invasive techniques in which samples were aspirated out from the bed and later analyzed by electronic microscopy [3,4].

To avoid the serious problem of sample distortion, some other techniques have been developed such as laser-based planar imaging, in which in situ images of the fluidized agglomerates are obtained with the aid of a laser source focused on the fluidized bed surface [4,7–9,11,13]. It must be warned however that, even though this technique has the advantage of being non-invasive, its effectiveness can be limited by stratification of the agglomerates due to size dispersion. It is well known that fluidized beds of polydisperse units are generally stratified [2]. In the stratified bed the largest agglomerates would be at the bottom and the successive layers toward the top would be composed of agglomerates of ever decreasing sizes, with the smallest ones preponderant at the very top, some of them being elutriated with the gas. In this way the agglomerate samples recorded in the images close to the bed free surface could be biased towards smaller sizes.

Another method that has been used to obtain information about agglomerate size is to fit bed expansion data to the Richardson–Zaki (RZ) empirical equation [17]:

$$\frac{v_g}{v_{p0}}=(1-\phi)^n \tag{1}$$

where v_g is the superficial gas velocity, ϕ the particle volume fraction, the RZ exponent is $n\approx 5$ in the viscous limit, and v_{p0}

is the terminal settling velocity of a single particle:

$$v_{\mathrm{p0}} = \frac{1}{18}\frac{\rho_{\mathrm{p}} g d_{\mathrm{p}}^2}{\mu} \quad (2)$$

where ρ_{p} is the particle density, g the gravity field, d_{p} the particle size, and μ is the viscosity of the gas, and fluid density and inertia have been neglected. Originally the RZ equation was conceived to describe the expansion of beds of non-agglomerated particles uniformly fluidized with liquids [17]. In their pioneer experimental work, Richardson and Zaki related n with the particle Reynolds number, $Re = \rho_{\mathrm{f}} v_{\mathrm{p0}} d_{\mathrm{p}}/\mu$, where ρ_{f} is the fluid density. Richardson and Zaki obtained $n \simeq 4.65$ for Reynolds numbers $Re < 0.2$, n had a constant value of 2.39 at Reynolds numbers larger than about 500, and n was correlated with Re in the intermediate flow regime.

Particle agglomeration changes the internal effective particle size, which turns to be determined by the agglomerate size d^{**}. Thus, the velocity scale in the RZ equation for fluidized beds of agglomerates should be changed to the terminal settling velocity of the fluidizing units v^{**}, namely the agglomerates. Yao et al. [3] fitted their experimental data to the modified equation:

$$\frac{v_{\mathrm{g}}}{v^{**}} = (1-\phi)^n \quad (3)$$

By considering v^{**} and n as fitting parameters and writing $v^{**} \approx (1/18)\rho^{**} g (d^{**})^2/\mu$, where the agglomerate density ρ^{**} was approximated to the bulk density of the nanopowder ρ_{b}, Yao et al. inferred the agglomerated sizes in fluidized beds of several nanopowders. However this derivation has a main inconvenient. Screening of the gas flow by the agglomerates should be also taken into account in the modified RZ equation [18]. Moreover, the Reynolds number in fluidized beds of nanoparticles is typically small [9], thus the RZ exponent cannot deviate too much from $n \approx 5$, while Yao et al. obtained values of n as low as 3, typically reported for turbulent conditions in liquid-fluidized beds of non-agglomerated particles [17].

A straightforward approach to consider gas flow screening by the agglomerates is to assume that the agglomerate hydrodynamic radius can be approximated to its gyration radius, thus we can use the agglomerate volume fraction ϕ^{**} instead of the particle volume fraction ϕ in the modified RZ equation [18]:

$$\frac{v_{\mathrm{g}}}{v^{**}} = (1-\phi^{**})^n \quad (4)$$

This equation has been used in several works to derive the agglomerate size in fluidized beds of micron-scale particles [18-20] and also in fluidized beds of nanoparticles [4,9,13].

Matsuda et al. [5] have inferred the agglomerate size from data on the minimum fluidization velocity and empirical correlations with the Reynolds and Arquimedes ($Ar = (d^{**})^3 \rho_{\mathrm{f}} (\rho^{**} - \rho_{\mathrm{f}}) g/\mu^2$) numbers. In their derivation, they assumed that the agglomerate density ρ^{**} can be approximated by the tapped density of the bed ρ_{T}. These results must be analyzed with caution since agglomerates are likely broken and compacted by tapping, thus it should be $\rho_{\mathrm{T}} > \rho^{**}$ [21].

Using some of the above-mentioned experimental methods the agglomerate size in gas-fluidized beds of nanoparticles have been obtained by several authors as affected by parameters such as:

- particle size and density [3,8,9,13],
- initial vibration [4],
- particle wettability [8,9],
- pretreatment of vessel walls to minimize its electrostatic interaction with the particles [8],
- effective acceleration in a centrifugal fluidized bed [5,10],
- ultrasound excitation [6],
- premixing with magnetic beads excited by an oscillating magnetic field [7],
- superficial gas velocity [11],
- gas viscosity [13].

Recent experimental results on the size of agglomerates measured in fluidized beds of nanoparticles using non-invasive techniques are summarized in Table 1. The gas used in most of the fluidization experiments is either dry nitrogen or air unless otherwise stated. We show results directly obtained from laser-based planar imaging in one column and in other column results indirectly derived from fitting data on bed expansion, settling or minimum fluidization velocity to empirical equations.

3. Prediction of agglomerate sizes

Some of the empirical models proposed in the past to predict agglomerate size are reviewed by Yang [1]. We give here a brief review on these models and also include others not included in the review by Yang [1].

Chaouki et al. [22] proposed that agglomerates in the fluidized bed are clusters of the fixed bed previous to fluidization, and that the size of the agglomerate could be inferred from the balance between the attractive van der Waals' force between particles and the agglomerate weight, which should be equal to the drag force on the agglomerate at minimum fluidization. Morooka et al. [23] proposed an energy balance model for estimating agglomerate size, in which the energy generated by laminar shear plus the kinetic energy of agglomerate was equated to the energy required to break the agglomerate. Iwadate and Horio [24] presented a model to predict agglomerate size in a bubbling bed. In their model, Iwadate and Horio postulated that the adhesive force between agglomerates was balanced by the expansion force caused by bubbles, yet this model cannot be applied to uniform non-bubbling fluidization generally observed for nanoparticles. Zhou and Li [25] have proposed an equation in which the joint action of the drag and collision forces is balanced by the gravitational and cohesive force. As pointed out by Yang [1], the approach by Zhou and Li [25] is only valid at high Reynolds number (turbulent flow), while typical values of the Reynolds number around the agglomerate in fluidized beds of nanoparticles are small (viscous flow) [9]. Mawatary et al. [26] wrote a force balance between the van der Waals' attractive force and the separation forces, including gravity, drag force, and vibration if present. Matsuda et al. [5] have proposed an energy balance equation based on the assumption that there exists an attainable energy for disintegration of agglomerates proportional

Table 1
Agglomerate size d^{**} measured in nanofluidization experiments reported in the literature

Source	Trade no.	Material	ρ_p (kg/m^3)	d_p (nm)	Fluidization aid	d^{**}_{exp} (μm)	d^{**}_{exp} (μm)	d^{**}_{th} (μm)
Zhu [9]$^{(+)}$	R974	SiO_2	2560	12		315	211	172
Yu [7]$^{(+)}$	R974	SiO_2	2560	12	Magnetic excitation	196	95	172
Valverde [13,15]$^{(0)}$	R974	SiO_2	2560	12	Initial shaking	180	309	172
Valverde [13,15]$^{(0)}$	R974	SiO_2	2560	12	Initial shaking (neon)	176	373	172
Zhu [6]	R974	SiO_2	2560	12	Sound excitation	100–400		172
Wang [11]	R974	SiO_2	2200	12		220		182
Wang [12]	R974	SiO_2	2200	12		168		182
Nam [4]$^{(+)}$	R974	SiO_2	2200	12	Initial vibration	185	160	182
Hakim [8]	A300	SiO_2 hydrophilic	2200	7		320		307
Yao [2]$^{(+)}$	A300	SiO_2 hydrophilic	2560	7			286	290
Zhu [9]$^{(+)}$	A300	SiO_2 hydrophilic	2560	7		585	296	290
Hakim [8]	A300	SiO_2 hydrophilic	2200	7	Walls pretreated	300		307
Hakim [8]	A300	SiO_2 hydrophilic	2200	7	Preheating	240		188
Hakim [8]	A150	SiO_2 hydrophilic	2200	14		430		297
Yao [2]$^{(+)}$	A150	SiO_2 hydrophilic	2560	14			331	280
Hakim [8]	A150	SiO_2 hydrophilic	2200	14	Walls pretreated	320		297
Hakim [8]	A150	SiO_2 hydrophilic	2200	14	Preheating	290		180
Yao [2]$^{(+)}$	R972	SiO_2	2560	16			277	170
Zhu [9]$^{(+)}$	R972	SiO_2	2560	16		422	195	170
Quevedo [10]$^{(+)}$	R972	SiO_2	2560	16	Centrifugal field 10 × g		120	101
Quevedo [10]$^{(+)}$	R972	SiO_2	2560	16	Centrifugal field 20 × g		214	87
Hakim [8]	OX50	SiO_2 hydrophilic	2200	40		200		280
Hakim [8]	OX50	SiO_2 hydrophilic	2200	40	Walls pretreated	100		280
Hakim [8]	OX50	SiO_2 hydrophilic	2200	40	Preheating	120		170
Zhu [9]	P25	TiO_2 hydrophilic	4500	21		195		224
Valverde [13,15]$^{(0)}$	P25	TiO_2 hydrophilic	4500	21	Initial shaking	165	146	224
Valverde [13,15]$^{(0)}$	P25	TiO_2 hydrophilic	4500	21	Initial shaking (neon)	194	193	224
Matsuda [5]$^{(x)}$		TiO_2 hydrophilic	4000	7	Centrifugal field 5 × g		373	180
Matsuda [5]$^{(x)}$		TiO_2 hydrophilic	4000	7	Centrifugal field 7 × g		353	161
Matsuda [5]$^{(x)}$		TiO_2 hydrophilic	4000	7	Centrifugal field 10 × g		285	148
Matsuda [5]$^{(x)}$		TiO_2 hydrophilic	4000	7	Centrifugal field 17 × g		257	132
Matsuda [5]$^{(x)}$		TiO_2 hydrophilic	4000	7	Centrifugal field 26 × g		205	120
Matsuda [5]$^{(x)}$		TiO_2 hydrophilic	4000	7	Centrifugal field 37 × g		168	111
Matsuda [5]$^{(x)}$		TiO_2 hydrophilic	4000	7	Centrifugal field 51 × g		136	103
Matsuda [5]$^{(x)}$		TiO_2 hydrophilic	4000	7	Centrifugal field 82 × g		100	93
Zhu [9]$^{(+)}$	R805	SiO_2	2560	12		218	279	172
Zhu [9]$^{(+)}$	R104	SiO_2	2560	12		226	245	172
Zhu [9]$^{(+)}$	R711	SiO_2	2560	12		274	207	172
Zhu [9]$^{(+)}$	CoK84	SiO_2-Al_2O_3	2740	12		320	316	171
Zhu [9]$^{(+)}$	R106	SiO_2	2560	7		172	201	176
Zhu [9]	A90	SiO_2 hydrophilic	2560	20		896		276
Yao [2]$^{(+)}$	R812s	SiO_2	2560	7			230	177
Yao [2]$^{(+)}$	TS530	SiO_2	2560	9			277	174
Yao [2]$^{(+)}$	R504	SiO_2	2560	12			238	172

The first column shows data directly obtained from laser-based planar imaging. The second column shows data indirectly derived from fitting bed expansion $^{(+)}$ or settling velocity$^{(0)}$ data to RZ equation and also from data on minimum fluidization velocity$^{(x)}$. The last column shows the prediction by Eq. (10). Unless otherwise stated the particle surface is modified to render it hydrophobic wettability, and the fluidization gas is nitrogen or air.

to a power law of the effective acceleration, with an exponent that is adjusted to fit the model prediction to experimental results.

Generally, the predictions by these models were checked by the authors with a limited number of experimental results, usually only those obtained by themselves. Moreover the predictive equations are functions of variables that need to be measured, assumed or indirectly estimated from experimental observations on the fluidized bed, which precludes them from a straightforward crosschecking. These variables include:

- minimum fluidization gas velocity [23],
- bed porosity [25,26],
- gas velocity for channel breakage [26],
- relative agglomerate velocity [25],
- agglomerate voidage or density [22–25],
- bubble size [24],
- particle pressure in the bubbling bed [24],
- coordination number of agglomerates at minimum fluidization [24],
- fitting parameters [5].

To date a simple predictive equation has not been formulated that is satisfactorily crosschecked with the extensive data already available in the literature from diverse authors. Thus there is a lack of a simple tool for estimating the size of the agglomerates from primary parameters such as particle size, particle density, and interparticle attractive force without the need of additional information from the fluidization experiment or the introduction of other fitting parameters to be assumed.

4. A simple predictive equation for estimating agglomerate sizes

4.1. Agglomeration of micron-scale particles in fluidized beds

In Ref. [27], we proposed a simple predictive equation to find agglomerate size in fluidized beds of micron-scale particles by studying the limit of mechanical stability of the agglomerate suspended in the gas flow field. We reproduce here this equation that was derived from a model inspired in a previous study on the limits to gelation in the clustering of a thermal colloidal particles [28,29]. In the fluidized state micron-scale primary particles agglomerate due to the action of the interparticle attractive force F_0. The weight force of the agglomerate, which acts uniformly through the agglomerate body, is compensated by the hydrodynamic friction from the surrounding gas, which acts mainly at its surface due to the flow screening effect [16]. As a consequence shear forces appear distributed across the cluster. These shear forces grow as the cluster size increases and eventually curtail its growth. According to the model proposed in Ref. [27], the response of the agglomerate resembles that of a spring subjected to a typical strain $\gamma_s \sim N_a W_p/(K_a R_a)$, where N_a is the number of particles in the aglomerate, W_p the particle weight, K_a the agglomerate spring constant and R_a is the aglomerate radius. The spring constant K_a was given by ζ_0/k_a^{β}, where ζ_0 is the interparticle force constant, k_a the ratio of the agglomerate size d_a to particle size d_p, and β is the elasticity exponent ($\beta = 3$ for 3D) [27]. The local shear force acting on the agglomerate surface was thus estimated as $F_s \sim \zeta_0 \gamma_s d_p/2 \sim W_p N_a k_a^2$. Particles would continue adhering to the agglomerate as long as the interparticle attractive force F_0 is larger than F_s. Thus the condition $F_0 = F_s$ served us to find an equation to predict the agglomerate size:

$$Bo_g \sim k_a^{D_a+2} \tag{5}$$

where $D_a = \ln N_a/\ln k_a$ is the fractal dimension of the aglomerate and Bo_g is the granular Bond number, defined as the ratio of interparticle attractive force to particle weight ($\mathrm{Bo}_g = F_0/W_p$).

It must be stressed that Eq. (5) has been derived from a balance of local forces (shear and adhesion) on a particle at the outer layer of the agglomerate. This is a relevant difference from apparently similar force balance equations such as the one proposed by Chaouki et al. [22], who equated the local interparticle attractive force to the global drag force on the agglomerate. It is important to remark also that our model is strictly applicable to history-independent samples, for which fluidization (or aided fluidization if needed) is able to break interparticle contacts down to the level of individual particle, thus erasing memory on previous processes.

4.2. Agglomeration of nanoparticles in fluidized beds

The in situ images of nanoparticle agglomerates obtained by Hakim et al. [8] by laser-based planar imaging offer evidence of a dynamic agglomeration behavior. Agglomerates are seen to form, break apart, and reform dynamically as they change size and shape during the process [8]. According to the SEM analysis by Yao et al. [3], the primary nanoparticles form multi-stage agglomerates (MSA) by three steps. Firstly, primary nanoparticles agglomerate into 3D net-like structures (let us call them sub-agglomerates). Secondly, the sub-agglomerates agglomerate into simple-agglomerates existing before fluidization. When fluidized, the pre-existing simple-agglomerates further join into complex-agglomerates. Thus, agglomeration of nanoparticles in fluidized beds needs for a special treatment. In a formulation of a modified Eq. (5) we considered pre-existing simple-agglomerates as effective particles [21]. Thus Eq. (5) was rewritten as

$$\mathrm{Bo}_g^* \sim (k^*)^{D^*+2} \tag{6}$$

where $\mathrm{Bo}_g^* = F^*/(N_s W_p)$ is the ratio of the attractive force between simple-agglomerates F^* to the weight of a simple-agglomerate, N_s the number of primary nanoparticles in each simple-agglomerate, k^* the ratio of complex-agglomerate size d^{**} to simple-agglomerate size d^* ($k^* = d^{**}/d^{**}$), $D^* = \ln N^*/\ln k^*$ the fractal dimension of the complex-agglomerates, and N^* is the number of simple-agglomerates in the complex-agglomerate. Eq. (6) was used in Ref. [21] to predict the size of agglomerates of hydrophobic silica nanoparticles used by Nam et al. [4], finding good agreement with the experimental measurements. In our study, [21] we calculated F^* from the van der Waals' attractive force:

$$F_{\mathrm{vdW}} \simeq \frac{A d_{\mathrm{as}}}{24 z^2} \tag{7}$$

where A is the Hamaker constant ($A \simeq 1.5 \times 10^{-19}$) for silica [30]), z the minimum intermolecular distance ($z \simeq 4$ Å [32]) and d_{as} is the typical surface asperity size of the simple-agglomerates at contact. For the size of the simple-agglomerates we used $d^* = 35$ μm as it could be inferred from SEM measurements by Nam et al. [4]. N_s was derived from the size of the simple-agglomerates, $N_s = k_s^{D_s}$, where $k_s = d^*/d_p$. We assumed for the fractal dimensions $D_s = D^* \simeq 2.5$ as suggested by the fit of Nam et al. [4] bed expansion data to the modified RZ equation (Eq. (4)). The prediction by Eq. (6) conformed to the measured complex-agglomerate size for $d_{\mathrm{as}} \approx 0.2$ μm, which was the value used by Chaouki [22] and coincides with the typical asperity size of micron-scale powder particles [33].

The main obstacle for applying Eq. (6) in practice is that the size of the simple-agglomerates needs to be known a priori. Moreover it does not account for the previous steps of formation of sub- and simple-agglomerates. Nevertheless, although Eq. (5) for the agglomeration of individual particles was applied to a gas-fluidized bed system, it was originally derived from a more general framework on the mechanical stability of tenuous objects [28] that has been also applied to other problems such as to find the limits to gelation in colloidal agglomeration. In this work, our proposal is to use Eq. (5) in each one of the steps of formation of nanoparticle agglomerates [3].

In the first step, primary nanoparticles of size d_p agglomerate to form the so-called sub-agglomerates of size d. According to our model we would have

$$d = d_\mathrm{p}\left(\frac{F_0}{(1/6)\pi\rho_\mathrm{p} g d_\mathrm{p}^3}\right)^{1/(D_0+2)} \tag{8}$$

where F_0 is the attractive force between primary nanoparticles, ρ_p the nanoparticle density, $g = 9.81\,\mathrm{m/s^2}$ the acceleration due to gravity, and $D_0 = \ln N_0/\ln k_0$ is the fractal dimension of the sub-agglomerates, being N_0 the number of nanoparticles in each sub-agglomerate and $k_0 = d/d_\mathrm{p}$.

In the second step, sub-agglomerates agglomerate to form simple-agglomerates of size d^*, which would be given by the equation:

$$d^* = d\left(\frac{F}{k_0^{D_0}(1/6)\pi\rho_\mathrm{p} g d_\mathrm{p}^3}\right)^{1/(D+2)} \tag{9}$$

where F is the attractive force between sub-agglomerates and $D = \ln N/\ln k$ is the fractal dimension of the simple-agglomerates, being N the number of sub-agglomerates in each simple-agglomerate and $k = d^*/d$.

Finally, in the fluidized bed simple-agglomerates agglomerate to form complex-agglomerates of size d^{**} that could be derived from the equation:

$$d^{**} = d^*\left(\frac{F^*}{k^D k_0^{D_0}(1/6)\pi\rho_\mathrm{p} g_\mathrm{ef} d_\mathrm{p}^3}\right)^{1/(D^*+2)} \tag{10}$$

where F^* is the attractive force between simple-agglomerates and $D^* = \ln N^*/\ln k^*$ is the fractal dimension of the complex-agglomerates, being N^* the number of simple-agglomerates in each complex-agglomerate and $k^* = d^{**}/d^*$. In Eq. (10) we have included the possibility that the fluidized bed is operated in an environment of effective acceleration g_ef different form the gravitational acceleration as for example in centrifugation or microgravity experiments. Note also that the properties of the fluidizing gas do not intervene in Eqs. (8–10).

It is also important to note that in our model we have considered perfectly spherical agglomerates. Although this can give us a simple estimation it must be admitted that in practice agglomerates are not spherical. Wang et al. have observed that the sphericity of the aggregates exhibits a wide distribution with a mean sphericity of approximately 0.7. The influence of this effect needs still to be addressed.

5. Comparison with experimental data

Unknown parameters a priori intervening in Eq. (10) to predict agglomerate size are the attractive forces and fractal dimensions of the agglomerates formes at each stage.

Concerning attractive forces we must consider the wettability character of the nanoparticles. For surface treated hydrophobic and uncharged nanoparticles the main contribution to the attractive force is the van der Waals' short-ranged force [32]. In the first step of agglomeration of individual nanoparticles to form sub-agglomerates the van der Waals' interparticle attractive force F_0 would be given by [33]

$$F_0 \simeq \frac{A d_\mathrm{p}}{24 z^2} \tag{11}$$

where we have used particle size d_p, which for nanometric particles is below the typical range of action of the van der Waals' force. For most solids, the Hamaker constant is around 10^{-19} J [30]. In our calculations, we will use $A \approx 1.5 \times 10^{-19}$ J, which is a typical value for titania and silica [30,31] mainly used in nanofluidization experiments. A typical value of F is $F \simeq 0.4$ nN ($A \approx 1.5 \times 10^{-19}$ J, $z = 4$ Å, $d_\mathrm{p} = 10$ nm). In the following steps of agglomeration between agglomerates there will be multiple contacts between primary particles belonging to each one of the agglomerates at contact. To account for the existence of a multiple number of contacts we will use Eq. (7) for the attractive forces $F^* = F = F_\mathrm{vdW}$ assuming a typical size $d_\mathrm{as} \simeq 0.2\,\mu\mathrm{m}$ for the surface asperities of the micron-scale agglomerates in contact [21]. This gives a typical value $F_\mathrm{vdW} \simeq 0.2$ nN.

Capillary forces will not be considered for nanoparticles with surface modification to render it strong hydrophobicity. In the case of unmodified hydrophilic particles we should take into account also the possibility of moisture condensation at the contacting surfaces that increases the total adhesion force. The capillary force between two equal spheres of radius R can be approximated by $F_\mathrm{c} \simeq \pi\gamma R^2\beta/S$, where γ is the liquid surface tension, β the half-filling angle and S is the separation distance [34]. For small liquid bridges $S \sim R\beta$, thus we can write:

$$F_\mathrm{c} \simeq \pi\gamma R \tag{12}$$

where $R = d_\mathrm{p}/2$ for the contact between individual particles and we will assume $R \sim d_\mathrm{as}/2 \simeq 0.1\,\mu\mathrm{m}$ for the contact between micron-scale agglomerates. Eq. (12) is similar to the equation proposed by Massimilla and Donsi [35] and recently reviewed by Yang [1], $F_\mathrm{c} = 2C\gamma R$, where C is the shape factor of the liquid bridge. According to Eq. (12) the estimated capillary adhesive force is $F_\mathrm{c} \simeq 1$ nN between 10 nm particles and $F_\mathrm{c} \simeq 20$ nN between agglomerates, thus representing a relevant contribution to the total attractive force. The work of Yao et al. [3] illustrates also the necessity to include capillary forces in the case of hydrophilic particles without surface modification, such as the Aerosil 300 and Aerosil 150. Yao et al. [3] found that the fluidization behavior was affected by surface modification of the nanoparticles.

Even though we have used only van der Waals' and capillary forces to illustrate the model, other interaction if present at any agglomeration stage, such as electrostatic or magnetic forces should be considered in the calculation of the attractive force. It must be noted also that the dynamics of agglomeration at each stage could be different, which would yield different values of the fractal dimensions. Thus it is not possible in general to define a general fractal dimension for the complex-agglomerate as $D_\mathrm{a} = \ln N_\mathrm{a}/\ln k_\mathrm{a}$, where $N_\mathrm{a} = N^* N N_0$ is the total number of primary particles in the complex-agglomerate and

$k_a = k^* k k_0 = d^{**}/d_p$ is the ratio of complex-agglomerate size to primary nanoparticle size. This definition has a physical meaning only if we assume $D^* = D = D_0$. In this case, we may formulate a simple equation to predict complex-agglomerate size:

$$d^{**} = d_p^{D_a(D_a+1)/(D_a+2)^2} d_{as}^{(D_a+4)/(D_a+2)^2} \times \Lambda^{-1/(D+2)} \mathrm{Bo}_g^{(D_a^2+6(D_a+2))/(D_a+2)^3} \tag{13}$$

being $\Lambda = g_{ef}/g$ and Bo_g the nanoparticle Bond number calculated as the attractive force between primary nanoparticles over the weight of the primary nanoparticles:

$$\mathrm{Bo}_g = \frac{F_0}{(1/6)\pi\rho_p g d_p^3}, \quad \text{where } F_0 = \frac{A d_p}{24 z^2} + \frac{\pi\gamma d_p}{2} \tag{14}$$

Wang et al. [12] have recently used particle image velocimetry analysis and laser-based planar imaging to measure the terminal settling velocity and size of single agglomerates of nanoparticles formed in the fluidized bed. By relating both measurements they have obtained that the fractal dimension of the agglomerates was centered around 2.5. Nam et al. [4] fitted their experimental results on bed expansion to the modified RZ equation for fractal agglomerates and obtained a fractal dimension of 2.57. In our calculations we will assume $D_a = D^* = D = D_0$, and $D_a = 2.5$ according to these experimental observations, albeit the predicted results do not change significatively if the fractal dimensions are independently varied around 2.5. Under these assumptions we obtain:

$$d^{**} = d_p^{0.679} d_{as}^{0.321} d^{-0.222} \mathrm{Bo}_g^{0.365} \quad \text{with } d_{as} \simeq 0.2\,\mu\text{m} \tag{15}$$

Complex-agglomerate sizes predicted by Eq. (13) are shown in Table 1. As a general comment it can be seen that the sizes predicted are comparable to the reported ones in the literature from experimental measurements. In some cases, for which independent measurements on the same nanopowder are available, the difference between the reported values is similar to the deviation of the predicted value to the experimental ones. This is remarkable since Eq. (13) can be used without any additional information from the fluidization experiment. Remind that the parameters involved in Eq. (13) are only particle density and size, fractal dimension and attractive force.

6. Effect of fluidization aids

Fluidization aids used in some of the experiments serve to break strongly consolidated agglomerates that may have been generated during previous processes such as packing, storage, and transportation. It can be seen in Table 1 that the measured size of the complex-agglomerates in assisted fluidization is smaller than the size measured for the same material in unassisted fluidization. For example, the mean agglomerate size measured by laser-based planar imaging in unassisted fluidization of silica R974 nanopowder was 315 μm [9]. Applying initial vibration the average values measured using the same technique were 185 μm [4], 180 μm [13], and 176 μm [13] (the latter one using neon as fluidizing gas). With the assistance of magnetic beads premixed with the nanoparticles and application of an oscillating magnetic field to the fluidized bed, the agglomerate size measured for the same nanopowder was 196 μm [7]. Zhu et al. [6] observed also a decrease of the agglomerate size (in the range 100–400 μm) when the fluidized bed was subjected to sound excitation, although the authors do not report a value of the average size. The predicted values by Eq. (13) are 172 μm if we use $\rho_p = 2560\,\text{kg/m}^3$ (reported in Ref. [9]) and 182 μm if we use $\rho_p = 2200\,\text{kg/m}^3$ (reported in Ref. [4]), which are in closer agreement with the measured values in the fluidization-assisted experiments. In two separated papers, Wang et al. have reported for the same system mean agglomerate sizes of 220 μm [11] and 168 μm [12] obtained by laser-based planar imaging. (Even though Wang et al. did not use external assistance they achieved good-quality fluidization thanks to special preparation methods of the sample and vessel [11].) It is worth noting also that Wang et al. [11] found a slight dependence of the agglomerate size on the superficial gas velocity v_g, decreasing from 262 to 189 μm as v_g was increased from 1.18 to 1.81 cm/s due to the increase in the fraction of relatively small aggregates in the splash zone where agglomerates are visualized. To our point of view, this phenomenon can be a consequence of stratification induced by polydispersity, which is promoted at high gas velocities. In fact the amount of agglomerates elutriated increases in parallel to the increase of the gas velocity, thus it is plausible that the fraction of relatively small agglomerates visualized in the splash zone must also increase as the gas velocity is increased.

The influence of preconditioning techniques on fluidization is also apparent from measurements of agglomerate size in fluidized beds of silica A300 nanoparticles (hydrophilic). Using laser-based planar imaging, Hakim et al. [8] and Zhu et al. [9] reported mean values of 320 and 585 μm for unassisted fluidization, respectively. When Hakim et al. applied an anti-static surfactant on the inside surface of the vessel to reduce electrostatic interactions between particles and the wall, the average agglomerate size decreased down to $d^{**} = 300$ μm. The predicted values by Eq. (13), including the capillary adhesive force, are $d^{**} = 307$ μm (using $\rho_p = 2200\,\text{kg/m}^3$ reported in Ref. [8]) and 290 μm (using $\rho_p = 2560\,\text{kg/m}^3$ reported in Ref. [9]), which are in closer agreement with the result reported by Hakim et al. after pretreatment. These predicted values are in accordance also with data obtained from indirect measurements [3,9]. By fitting bed expansion measurements to the original RZ equation (Eq. (3)), Yao et al. derived $d^{**} = 286$ μm, which is similar to the value inferred by Zhu et al. (d^{**} =296 μm [9]) by fitting their results to the modified RZ equation (Eq. (4)). After preheating/drying the particles in order to remove surface moisture, Hakim et al. [8] observed that the agglomerate size decreased down to d^{**} =240 μm. The value predicted by Eq. (13), in the absence of the capillary adhesive force, is d^{**} =188 μm. Similar effects of the prior use of anti-static surfactant and particle preheating/drying is found for silica A150 hydrophilic nanoparticles.

In Table 1 we summarize also the results from diverse studies on fluidized beds of OX50 silica and P25 titania nanoparticles. In general preconditioning methods help to improve the quality of fluidization for these powders and reduce the measured agglomerate size directly visualized or indirectly inferred. However these results must be cautiously considered since these powders do not exhibit homogeneous fluidization but bubble vigorously soon after the minimum fluidization velocity is reached [9].

The agreement between experimental results and predicted values by Eq. (13) for other types of silicas, for which there are not comparative studies, is also reasonable as can be seen in Table 1. An exception is the unassisted fluidization of hydrophilic A90 silica for which Zhu et al. report an unexpectedly large value of d^{**} =896 μm. In spite that Zhu et al. pre-sieved this highly cohesive nanopowder using a shaker and a 500 μm sieve opening, it is likely that large agglomerates formed on previous processes are preserved in fluidization since only bubbling fluidization (ABF) could be observed. In the bubbling fluidization regime the gas bypasses the bed through large bubbles. Thus fluidization is not able to break agglomerates of strongly adhered particles formed during consolidation processes previous to fluidization. It would be interesting to check also on this powder the ability of assisted fluidization on erasing powder memory and consequently decrease agglomerate size.

Usually the simple way of obtaining the average diameter from the laser-based planar imaging was to calculate the arithmetic mean diameter (number-length mean diameter $d^{**}_{\rm nl}$). Another option is to calculate the volume–surface or Sauter mean diameter $d^{**}_{\rm sv}$, expressing the average ratio between the volume and the surface area of the units ($d^{**}_{\rm sv} = \sum n_i {d_i}^3 / \sum n_i d_i^2$), which is especially important in calculations where the active surface area is important. Thus the Sauter mean diameter would be the most appropriate mean diameter to represent the size distribution in fluidization. In spite of this the distinction between number-length mean and surface–volume mean diameters has been addressed only recently by Wang et al. [11], who found an appreciable difference between both means that they attributed to the wide size distribution (they obtained $d^{**}_{\rm nl} \approx 130$ μm, while $d^{**}_{\rm sv} \approx 220$ μm). This difference has been noted also by Valverde et al. [13] and should therefore be considered in future protocols.

7. Influence of effective acceleration and type of fluidizing gas

According to the proposed equation (Eq. (13)) the properties of the environmental gas, such as gas viscosity, should not affect agglomerate size. This has been checked in a recent work in which the mean size of agglomerates was obtained directly from laser-based planar imaging and indirectly derived from bed expansion data fit to the modified RZ equation for fluidization with nitrogen and neon of titania P25 and silica R94 nanoparticles. It can be seen in Table 1 that the results did not change significantly, as predicted by Eq. (13), when the high viscosity neon was employed.

The effective acceleration $g_{\rm ef}$ of the fluidized bed can be altered in the centrifugal fluidized bed (CFB) setup [5,10]. According to our model, $g_{\rm ef}$ plays a relevant role on Eq. (13), the agglomerate size predicted decreases as $g_{\rm ef}$ is increased. Matsuda et al. [5] carried out an extensive series of CFB experiments on hydrophilic titania nanoparticles, in which the agglomerate size was inferred from the fit of measurements of the minimum fluidization velocity to empirical correlations with the agglomerate Arquimedes and Reynolds numbers [5]. It can be seen that the values predicted by Eq. (13) converge to the values derived by Matsuda et al. [5] as $g_{\rm ef}$ is increased, which can be attributed to the reported progressive improvement of fluidization uniformity, and thus the consequent decline of history dependence (we remind that titania nanopowder exhibits bubbling fluidization in the conventional fluidized bed [9]). Furthermore, in their derivation of agglomerate size, Matsuda et al. [5] assumed that the agglomerate density ρ^{**} could be approximated by the tapped density of the bed $\rho_{\rm T}$. As discussed in Ref. [21] a better agreement with our model would be obtained if ρ^{**}, which is related to agglomerate size, were used instead. Nonetheless we have preferred to list in Table 1 the agglomerate sizes derived by Matsuda et al. in their original derivation. On the other hand, recent experiments by Quevedo et al. [10] do not show a clear trend of the results with the effective acceleration (see Table 1). At $g_{\rm ef} = 10 \times g$, the fit of bed expansion data to the modified RZ equation yields smaller agglomerate size when compared to the prediction of the agglomerate size for a conventional fluidized bed, but at $g_{\rm ef} = 20 \times g$ the reverse result is surprisingly derived (see Table 1), in contrast to the results reported by Matsuda et al. [5]. Quevedo et al. point out that, besides of the increase of normal acceleration, tangential momentum effects should play a role in the CFB system. To our opinion additional data points would help to clear up this apparently controverted result (Quevedo et al. were able to obtain only three data points for the expansion curve of the rotated fluidized bed at $g_{\rm ef} = 20 \times g$).

A relevant result predicted by Eq. (13), but to our knowledge unobserved experimentally in fluidized beds, is the increase of agglomerate size as the effective acceleration is decreased. Eventually fluidization of nanoparticles at microgravity conditions may lead to the formation of fractal and extremely porous jammed solids. Thus our work might provide insight into the understanding of the first stage pre-planetary dust agglomeration leading to the formation of planetesimals [36].

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