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Modeling the size distribution in a fluidized bed of nanopowder

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ABSTRACT

Fluidization is a technique used to process large quantities of nanopowder with no solvent waste and a large gas–solid contact area. Nonetheless, nanoparticles in the gas phase form clusters, called agglomerates, due to the relatively large adhesion forces. The dynamics within the fluidized bed influence the mechanism of formation, and thus, the morphology of the agglomerates. There are many theoretical models to predict the average size of fluidized agglomerates; however, these estimates of the average lack information on the whole size range. Here, we predict the agglomerate size distribution within the fluidized bed by estimating the mode and width using a force balance model. The model was tested for titania (TiO_2), alumina (Al_2O_3), and silica (SiO_2) nanopowders, which were studied experimentally. An *in-situ* method was used to record the fluidized agglomerates for size analysis and model validation.

1. Introduction

A balance between adhesion and separation forces (or energies) is a settled theoretic framework to predict the average agglomerate size of fluidized nanopowders [1–8]. The average agglomerate size is usually assumed to be that at which the adhesion and separation forces balance each other; however, predictions of agglomerate size distributions are absent. It is well known that cohesive powders form agglomerates with a very wide, typically log-normal, size distribution [9–12]. The purpose of the present paper is to explore a conceptual model to predict the width of the distribution using a force balance approach.

Fluidization is a common method to process nanoparticles [11,13-15], which fluidize as agglomerates due to the relatively strong attractive interactions, particularly van der Waals and capillary forces [13,16-19]. As the stable structures of the fluidized powder, the properties of the agglomerates are directly linked to the fluidization dynamics [13]. Nanopowder fluidization depends on the agglomerate properties and can be classified as agglomerate particulate fluidization (APF) or agglomerate bubbling fluidization (ABF) [20]. APF is characterized by uniform, non-bubbly behavior, good solid–gas contact, and homogeneous distribution of powder throughout the bed. On the other hand, ABF shows a small bed expansion with channels, bubbles, and non-uniform powder distribution [9,15]. The fluidization type and agglomerate properties are co-dependent. As a key property distinguishing the two forms of fluidization, various studies have focused on the theoretical and experimental estimation of the fluidized agglomerate size.

Visualization techniques for the fluidized nano and micron size scales include the *ex situ* Transmission and Scanning Electron Microscopies (TEM and SEM, respectively), and multiple camera systems for *in situ* measurements. Sample extraction and preparation of the fragile fluidized agglomerates for SEM and TEM have led to images of agglomerate sizes smaller than those expected inside the fluidized bed [21]. This indicates the need of *in situ* techniques for more accurate results [21,22]. A common *in situ* method used to measure the fluidized agglomerate size involves laser illumination and a digital CCD camera [15]. Average agglomerate sizes between 70 μm and 900 μm have been measured with this technique for Aerosil R974, Aeroxide TiO_2, fumed silica, zirconia, and iron oxide nanopowders [10,11,13,21-24]. Furthermore, the laser/CCD camera system was also used for size distribution measurements at the splash zone of the Aerosil R974 fluidized bed with mode at approximately 140 μm [10] or 200 μm [11], or a positive skewed distribution in the size range 40–600 μm [22]. Another visualization technique, the Lasentec Focused Beam Reflectance Method/Particle Vision Measurement system, showed a log-normal size distributions of Aerosil R974 and Aerosil 90 [9,25]. More recently, de Martin et al. [4] developed a settling tube technique for the analysis of agglomerate size distribution, among other properties, at the splash zone of the fluidized bed.

Knowledge of the fluidized agglomerate size distribution is crucial for proper understanding of the dynamic processes within the fluidized bed, which are of great importance in nanopowder

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processing and applications such as in medicine, optics, and solar cells [26,27]. Even though the tools to experimentally determine the agglomerate size distribution are available, most of the studies only focus on the average size values. These measured sizes are mainly used for qualitative analysis or comparison based on different fluidization conditions or powder properties, with no further description of the size distribution. This includes the limited use of force (energy) balances to estimate the mean agglomerate size only.

In this work, we predict the mode and width of the log-normal fluidized agglomerate size distribution from a simple force balance. The attractive and repulsive forces were calculated theoretically to identify the dominating interactions. This model is simple, and provides a good prediction of the size distribution based on a novel interpretation of the conventional force balance concept. Simplification of the final expression obtained from the balance shows that the size distribution of fluidized nanoparticle agglomerates is self-similar. The calculated size distribution is validated by *in situ* experiments using oxide nanopowders showing either APF or ABF behavior.

2. Material and methods

The nanopowders used in this study were bought from Evonik. The characteristics given by the supplier are shown in Table 1. The powder selection involves both fluidization behaviors, APF and ABF. As mentioned in literature, Al_2O_3 and TiO_2 show bubbling, while SiO_2 fluidized homogeneously [9,11,28]. All nanopowders are sieved using a 450 μm mesh to remove large agglomerates that would prevent proper fluidization. The powders are fluidized in a 15 cm high quartz column with a square cross-section of 4.5×4.5 cm using pure nitrogen gas at 0.13 m/s, which enters the column through a distributor plate. The gas leaving the setup is sent to a water bubbler and HEPA filter to remove any entrained particles.

The fluidized agglomerates are recorded while falling through a settling tube placed in the splash zone. As was demonstrated by Wang et al. [22], agglomerates present in the splash zone are representative of those found in the bed. Additionally, the gas velocity used for fluidization is large enough for the agglomerates to follow the gas flow by keeping their Stokes number below one. The settling tube is a black box with an opening at the top to catch falling agglomerates, and two openings on the side for agglomerate recording and tube cleaning purposes (Fig. 1). A rigid borescope (Olympus R040-021-000-60 S5) and high speed camera (Phantom v9.1) system are used for the recordings, enabling a visible size range from 30 μm to 4 mm [29].

The videos are taken 10 min after starting fluidization to reach an observable steady state. The movies are analyzed using a MATLAB script by dividing them into frames, and later processing each frame for light correction, and agglomerate recognition, tracking, filtering, and measurements. More details on the technique can be found in the papers by de Martin et al. [29,30].

An important feature of nanoparticle agglomerates is the solid fraction, which can be estimated from their density. The agglomerate density can be calculated from the settling velocity and size obtained from the videos. The size distribution is taken directly from the images, assuming the agglomerates to be spherical [30]. The diameter used to describe the size of the agglomerate is the area equivalent diameter; the diameter of a circle with the same area as the region recognized from image processing. Other works suggest the use of volume–surface diameter for fluidized agglomerate sizing from 2D images as a better representation of the fluid–particle interaction [22]. However, the error propagation from image analysis is increased in this case.

Table 1
Properties of the fluidized nanopowders as provided by the manufacturer.

Powder	Surface	d_p (nm)	ρ_p (kg/m^3)	ρ_{Tamped} (kg/m^3)
TiO_2 P25	Hydrophilic	21	4000	100–180
Al_2O_3 AluC	Hydrophilic	13	3800	50
SiO_2 A130	Hydrophilic	16	2200	50

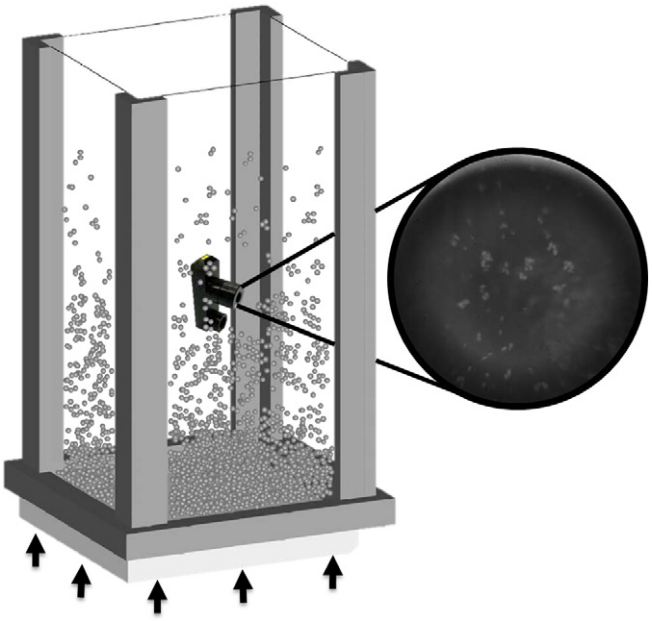

Fig. 1. *In-situ* analysis of fluidized agglomerates. Nanopowder is fluidized in a square column with the settling tube placed at the splash zone. A sample frame from a recorded video is shown.

The settling velocity is also directly calculated from the images since the frame rate is known, and agglomerate displacement between frames is obtained from the agglomerate recognition step. Settling velocity and agglomerate size are used to calculate the Reynolds number, which is used to estimate the drag coefficient, thus completing the list of parameters needed to determine the agglomerate density.

3. Theory

The forces acting on a fluidized agglomerate are divided into two categories: adhesion (those keeping ensembles of particles together) and separation (those breaking particle ensembles). The forces to be considered, and their classification into the two groups varies in literature. Van der Waals, capillary, and electrostatic are regularly in the adhesion group, while gravity–buoyancy sometimes is classified as cohesive [2,3] and sometimes as a separation force [7]. Here, gravity–buoyancy is classified as a separation force. Bed expansion, drag, and collision forces belong to the group of separation forces. The gravity–buoyancy force is evaluated with the effective density of the agglomerate. The bed expansion force is that exerted on nanoparticles by the bubbles inside the bed, which depends on bubble size, agglomerate pressure around a spherical bubble, gravity, agglomerate size and density, and coordination number [1]. The drag force calculation includes a shape factor of 0.9 in the denominator, representing the agglomerate sphericity. Finally, capillary force is estimated as the maximum force assuming the formation of a liquid bridge between two highly porous spherical agglomerates. Fig. 2 presents a comparison of the forces for TiO_2 P25 with properties as shown in Table 1, contact distance of 0.4 nm, Hamaker coefficient of 1.02×10^{-19} J, Young's modulus of 234 GPa, and work of adhesion of 0.8 J/m^2, with fluidizing gas velocity of 13 cm/s. It