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The fractal scaling of fluidized nanoparticle agglomerates

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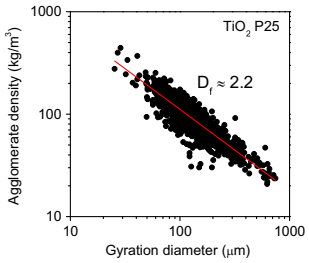
HIGHLIGHTS

- Complex fluidized nanoparticle agglomerates have multiple fractal dimensions.
- Fractal dimension found in the scale of 30–400 μm is about 2.
- Prefactor relating size of agglomerate and nanoparticle can greatly differ from one.
- Commonly reported dimension of 2.5 might be an artefact from using a prefactor unity.

GRAPHICAL ABSTRACT



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ABSTRACT

It is widely reported in the literature that fluidized nanoparticle agglomerates have a mass fractal dimension of about 2.5. In this paper, we question the current methods reported in the literature to calculate the fractal dimension for fluidized nanoparticle agglomerates, which assume a prefactor one in the fractal scaling law. The fractal dimension 2.5 obtained with a prefactor one approximates the density of the agglomerates in a limited range of sizes but does not describe the scaling of the agglomerate density (or agglomerate mass) with the agglomerate size, which is the ultimate meaning of a mass fractal dimension. By studying the settling of fluidized agglomerates, we have found that the prefactor of the fractal scaling law for large fluidized agglomerates can be up to two orders of magnitude larger than one. We show with a simple equation that this large prefactor comes from the multidimensional nature of fluidized nanoparticle agglomerates, revealing that the assumption of a prefactor one can lead to an erroneous fractal dimension when studying multidimensional structures. The fractal dimension found for agglomerates larger than 40 μm without imposing a value for the prefactor, this is, from the fitting log(density) vs. log(size) is about two.

1. Introduction

Fluidization is an attractive method to process nanoparticles, for instance, to produce coated nanoparticles (Hakim et al., 2005; Goulas and van Ommen, 2013). Nanoparticles, peculiarly, do not fluidize individually but form agglomerates as a result of van der Waals forces (van Ommen et al., 2012; Shabanian et al., 2012), capillary bridges (Israelachvili, 2011) or hydrogen bond formation (Tahmasebpoor et al., 2013). Although nanoparticle fluidization has been extensively studied in the last decade, the interplay between nanoparticle and agglomerate properties, and fluidization dynamics is still not fully resolved. A reason is the lack of knowledge about the agglomerate structure.

The agglomerate structure is commonly described by means of fractal geometry (Vicsek, 1992; Friedlander, 2000; van Ommen et al., 2012; Shabanian et al., 2012). In a mass fractal cluster formed

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by monodisperse particles of size d_p, the number of particles N_p or agglomerate density ρ_a scales to the power of the ratio d_a/d_p according to

$$N_p = k_n\left(\frac{d_a}{d_p}\right)^{D_f} \quad \text{or} \quad \rho_a = \rho_p k_n\left(\frac{d_a}{d_p}\right)^{D_f-3} \tag{1}$$

where d_a is the agglomerate diameter (gyration, maximum or hydrodynamic diameter, Bushell et al., 2002), ρ_p is the particle density, k_n is a prefactor and D_f is the mass fractal dimension, from now on denoted as "fractal dimension".

The popularity of the fractal dimension arises from the large amount of information deduced from it. It describes the agglomerate structure, necessary to model diffusion processes inside the agglomerates and agglomerate breakage, and it also gives information about the growth mechanism of the agglomerates (Vicsek, 1992; Friedlander, 2000). The cluster–cluster diffusion limited aggregation (DLA) mechanism forms open clusters with fractal dimension D_f=1.80, whereas D_f=2.50 would indicate dominant particle–cluster diffusion limited aggregation. A fractal dimension 3.0 is found in clusters formed by a particle–cluster ballistic aggregation and reaction limited aggregation with low sticking coefficient (Fig. 1).

It is extensively reported that fluidized nanoparticle agglomerates have a fractal dimension of about 2.5, obtained from Eq. (1) with k_n=1 (Nam et al., 2004; Quevedo et al., 2006; Valverde and Castellanos, 2006; Wang et al., 2006a; Valverde and Castellanos, 2007; Valverde et al., 2008; Valverde and Castellanos, 2008; Nakamura and Watano, 2008; Quintanilla et al., 2008; Shabanian et al., 2012; Espin et al., 2009; To et al., 2009; Ammendola et al., 2011; van Ommen et al., 2012). Many of these studies associate this dimension with a dominant DLA mechanism for fluidized nanoparticle agglomerates. It is important to note that Eq. (1) implicitly considers that the building block that forms the agglomerate of size d_a with fractal dimension 2.5 is the nanoparticle d_p, not any preexisting aggregate; otherwise, the size of the preexisting aggregate should go to the denominator. Therefore, any claim about a DLA mechanism based on the dimension 2.5 obtained from Eq. (1) with k_n=1 refers to DLA agglomeration of individual nanoparticles. This contradicts the well known fact that nanoparticles fluidize as agglomerates, not individually (van Ommen et al., 2012; Shabanian et al., 2012). Moreover, nanoparticles produced in flame reactors, such as commercial nanoparticles typically used in fluidization studies, already form sintered aggregates with cluster–cluster mechanism during their synthesis (Hyeon-Lee et al., 1998; Kammler et al., 2004). Thus, to claim that large fluidized nanoparticle agglomerates are formed by a particle–cluster mechanism is, at least, questionable. If there is a dominant mechanism in the formation of large fluidized agglomerates, it seems to be more logical to expect a cluster–cluster mechanism.

Papers claiming a fractal dimension of about 2.5 assume that the number of particles in the agglomerate, N_p, is related to the ratio d_a/d_p like in Eq. (1), with k_n=1. Some papers use image analysis (Nam et al., 2004; Wang et al., 2006b; Quintanilla et al., 2012) whereas others perform bed expansion studies (Valverde and Castellanos, 2006; Quintanilla et al., 2008; Espin et al., 2009). However, due to the difficulty of studying *in situ* the properties of the small fluidized agglomerates, say, smaller than a few dozens of micrometers, most of these studies are limited to the characterization of the large fluidized agglomerates, say, larger than ~80 μm. In these studies, the fractal dimension is related to the density and size of the fluidized agglomerates or bed expansion, which in turn depends on the average agglomerate density and size. Thus, the fractal dimensions reported in the literature so far is the exponent of Eq. (1) that explains the density of the very large fluidized agglomerates for k_n=1. The question is, does the value 2.5 describe the power-law scaling of the agglomerate density with the agglomerate size? because this is the ultimate meaning of a fractal dimension (Mandelbrot, 1982).

Let us discuss the assumption k_n=1 in detail. According to Sorensen and Roberts (1997), the prefactor of fractal clusters has a value so that Eq. (1) has the correct N_p=3 limit, and that limit is a linear arrangement of three monomers. According to Jiang and Logan (1991), for an Euclidean object, k_n is a function of the packing factor and the ratio of the shape factors of the aggregate and the primary particles. The prefactor of the agglomerates generated by the six mechanisms displayed in Fig. 2 is well known. Although the prefactor can be affected by the overlap of particles due to sintering (Brasil et al., 1999) or polydispersity (Eggersdorfer and Pratsinis, 2012), most of the real agglomerates have a prefactor between 0.5 and 3 (Sorensen and Roberts, 1997; Bushell et al., 2002). Ehrl et al. (2009) studied the geometry of simulated clusters formed by rigid monodisperse primary particles with a fractal dimension in the range from 2.2 to 3. They propose a correlation for the prefactor with the form $k_n = 4.46D_f^{-2.08}$, which gives a prefactor $k_n \sim 1$ for D_f=2.0 when using particle radius and agglomerate gyration radius in Eq. (1).

Therefore, without further information, the assumption k_n=1 seems to be a reasonable starting point. However, all previous studies report prefactors for mono-dimensional clusters; that is, clusters in which the building unit is the particle and all the scales are described by a unique fractal dimension. This might be the case of agglomerates formed by micron-sized particles, but does not

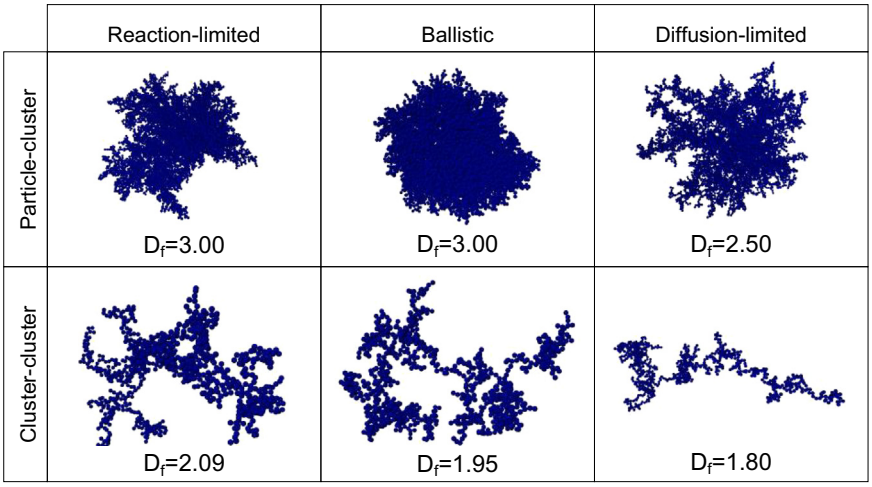

Fig. 1. Kinetic growth models in a 3D embedding space and fractal dimensions associated (based on Friedlander, 2000).