Journal of Colloid and Interface Science 346 (2010) 23–31

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Geometrical determination of the lacunarity of agglomerates with integer fractal dimension

Magín Lapuerta [a,*], Francisco J. Martos [b], Gema Martín-González [b]

[a] Escuela Técnica Superior de Ingenieros Industriales, University of Castilla – La Mancha, Edificio Politécnico, Avda. Camilo José Cela, s/n, 13071 Ciudad Real, Spain

[b] Departamento de Máquinas y Motores Térmicos, University of Málaga, 29071 Málaga, Spain

ARTICLE INFO

Article history:
Received 8 October 2009
Accepted 9 February 2010
Available online 12 February 2010

Keywords:
Lacunarity
Agglomerates
Fractal dimension
Power-law relationship
Packing density

ABSTRACT

Different agglomerates composed by a variable number of spherical primary particles corresponding to extreme and intermediate values of fractal dimension ($D_f = 1$, $D_f = 2$ and $D_f = 3$) are analysed in this work. In each case, the moment of inertia, diameter of gyration and prefactor of the power-law relationship are determined as a function of the number of composing primary particles. The obtained results constitute the geometrical data base for the development of a method for the determination of the fractal dimension of individual agglomerates from their planar projections, although it is not the aim of this paper to describe the method itself. As a result of these calculations, the prefactor of the power-law relationship was shown not to be a constant parameter, but to tend asymptotically to a limit value with increasing number of primary particles. This limit value is closely related with the compactness of the initial geometrical arrangement in the agglomerate, this justifying the historical association of this parameter with the lacunarity of the agglomerate. A correlation for the determination of the prefactor as a function of the fractal dimension and the number of elementary structures is proposed and compared with other methods proposed in the literature.

1. Introduction

Agglomerates are often composed of contacting primary particles with geometries very similar to spheres which are almost uniform in size. This is, for example, the case of diesel soot agglomerates. The primary particles are disposed in the agglomerate as irregular clusters, with different size, compactness and apparent densities. As the irregularity of the agglomerates increases their surface increases (and so the adsorption of liquid substances such as water, hydrocarbons, etc.), their light extinction efficiency increases (and thus their opacity and global warming or dimming potential), their aerodynamic behaviour changes, their filtering efficiency increases, etc., all this changes contributing to modify their environmental impact. Since agglomerates are considered as fractal-like structures [1], it is acceptable to quantify their irregularity with the fractal dimension, D_f, as originally proposed by Mandelbrot [2], and it is also accepted that, in case of being composed by a sufficient number primary particles, they can be characterised by means of the power-law relationship [3]:

$$n_{po} = k_f \left(\frac{d_g}{d_{po}} \right)^{D_f} \tag{1}$$

where n_{po} is the number of primary particles (whose diameter is d_{po}), k_f is a dimensionless prefactor and d_g is the diameter of gyration of the agglomerate.

Two different approaches can be proposed to estimate the fractal dimension of a population of agglomerates, such as that flowing in the exhaust stream of a diesel engine:

- To obtain the slope of the regression line obtained when the number of primary particles is plotted in logarithmic coordinates against the ratio of diameters (agglomerate/primary particle) [4,5]. This method needs to collect data from a large number of agglomerates, and finally provides a mean fractal dimension characteristic of the whole particle population. At the same time as the fractal dimension, the prefactor of the power-law relationship is also obtained.
- To previously estimate the prefactor of the power-law relationship by means of agglomeration [6,7] or geometrical models [8,9], and then to solve for the fractal dimension of each of the individual agglomerate observed.

In both cases, the number of primary particles is an additional unknown, since the geometries of the agglomerates are observed from their planar projections. Usually, the images are obtained with Transmission Electron Microscopy from thermophoretic samples of diesel exhaust particles obtained following the procedure proposed by Dobbins and Megaridis [10] and later validated by

* Corresponding author. Fax: +34 926295361.
E-mail address: Magin.Lapuerta@uclm.es (M. Lapuerta).

0021-9797/$ - see front matter © 2010 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2010.02.016

Nomenclature

D	dimension	*Subscripts*	
d	diameter	bcc	body centre cubic
I	moment of inertia	f	fractal
k	prefactor	G	with respect to the centre of gravity
m	mass	g	gyration
N	number of elementary structures	hc	hexagonal close-pack
n	number	i	numeral of the primary particle in the agglomerate
p	packing density	p	agglomerate
r	radius or distance from the centre of gravity	po	primary particle
V	volume	sc	simple cubic
ρ	density		

Rosner et al. [11]. In these images, not every primary particle can be observed since many of them are totally or partially hidden each other. For the estimation of the number of primary particles an additional equation must be established. This equation calculates the overlapping among primary particles, and requires further modelling [12], but this is beyond the scope of this paper.

The geometrical determinations presented here are useful for the development of a new method, which is aimed to the determination of the fractal dimension of each individual agglomerate. This new method constitutes an improvement of that presented in reference [9], where the only case considered for $D_f = 1$ was a straight chain of spheres (not considering other possible configurations) and no solutions were proposed for $D_f = 2$.

2. The prefactor of the power-law relationship

The prefactor of the power-law relationship is a key parameter for the morphological characterisation of agglomerates. Agglomerates with similar size and fractal dimension may have different shapes, this difference being characterised by the prefactor. Whilst the fractal dimension accounts for the irregularity and the clusterization of the agglomerate structure (it is in fact an exponent), the prefactor expresses how the space is being filled up by the agglomerate mass, independently of its size (it is not an exponent but a factor), and how the primary particles are packed [13]. It has been associated with the lacunarity and with the porosity of the agglomerate [14]. A very wide dispersion of prefactor values has been found in the literature. Such a dispersion, which can be noted in Table 1, is probably associated with the corresponding dispersion in shapes, which proves the need to consider the prefactor as a variable to be modelled, similarly as the fractal dimension. However, very few of the reviewed authors were found to propose variation rules for the prefactor. Sorensen and Roberts [15], as well as Gmachowski [16] (who refers to it as structural coefficient), proposed variations for the prefactor as a function of the fractal dimension and the packing density (the former), and as a function of the fractal dimension (the latter). The equations proposed (in the former case assuming hexagonal close-pack) lead to the ranges indicated in Table 1.

3. Preliminary definitions: moment of inertia and diameter of gyration

The moment of inertia of an agglomerate with respect to its centre of gravity, I_G, is an extension of the concept of moment of inertia with respect to an axis, and it is equivalent to half of the sum of the moments of inertia with respect to three orthogonal axis intersecting in the centre of gravity of the agglomerate [28]. It can be calculated as the sum of the contributions of all the solid elements composing the agglomerate:

$$I_G = \int r^2\,\mathrm{d}m \tag{2}$$

where r is the distance between any point belonging to the agglomerate and the centre of gravity, and m is the mass of the agglomerate. The radius of gyration of the agglomerate, r_g, is the radius of a ring with the same mass and moment of inertia as the agglomerate. Therefore, the diameter of gyration is:

$$I_G = m r_g^2 \rightarrow d_g = 2\sqrt{\frac{I_G}{m}} \tag{3}$$

The moment of inertia of a spherical primary particle of radius r_{po} with respect to its own centre of gravity is:

$$I_G = \int_0^{r_{po}} r^2\mathrm{d}m = \int_0^{r_{po}} r^2 \cdot \rho \cdot \mathrm{d}V = \int_0^{r_{po}} 4 \cdot \pi \cdot r^4 \cdot \rho \cdot \mathrm{dr} = \frac{4 \cdot \pi \cdot r_{po}^5 \cdot \rho}{5} \tag{4}$$

which can be also expressed as a function of its own mass, m_{po}:

$$m_{po} = \frac{4 \cdot \pi \cdot r_{po}^3 \cdot \rho}{3} \rightarrow I_G = \frac{3}{5} m_{po} r_{po}^2 \tag{5}$$

Substituting Eq. (5) into Eq. (3), the radius of gyration can be expressed as a function of the radius of the primary particle:

$$\frac{3}{5} m_{po} r_{po}^2 = m_{po} r_g^2 \rightarrow r_g = \sqrt{\frac{3}{5}} r_{po} \tag{6}$$

Since an agglomerate is composed by a finite number of primary particles (here assumed to be uniform in size and mass), the application of the Steiner theorem provides the following expression for the moment of inertia of the agglomerate:

$$I_p = m_{po} \cdot \sum_{i=1}^{n_{po}} \left(\frac{3}{5} r_{po}^2 + r_i^2\right) = m_{po} \cdot \left(\frac{3}{5} \cdot n_{po} \cdot r_{po}^2 + \sum_{i=1}^{n_{po}} r_i^2\right) \tag{7}$$

where r_i is the distance between the centre of gravity of each primary particle and that of the agglomerate. Substituting Eq. (7) into Eq. (3) an expression is obtained for the diameter of gyration of the agglomerate, which can be applied to agglomerates with known geometries:

$$d_g = 2 \cdot \sqrt{\frac{I_p}{m_p}} = 2 \cdot \sqrt{\frac{I_p}{n_{po} \cdot m_{po}}} = 2 \cdot \sqrt{\frac{3 \cdot r_{po}^2}{5} + \frac{\sum_{i=1}^{n_{po}} r_i^2}{n_{po}}} \tag{8}$$

Table 1
Literature revision of the prefactor of the power-law relationship.

References	Application	k_f	D_f
Meakin [17]	Simulations with agglomerates in general	1.05	1.74
Samson [18]	Experiments with soot from acetylene	3.49	1.40
		2.67	1.47
Mountain and Mulholland [19]	Soot simulations	5.80	1.90
Megaridis and Dobbins [20]	Experiments with soot from ethylene combustion	2.18	1.62
		1.80	1.74
Wu and Friedlander [13]	Simulations with agglomerates in general	1.30	1.84
Puri et al. [21]	Experiments with soot from ethane combustion	9.00	1.74
Cai et al. [5]	Experiments with soot from methane combustion	1.23	1.74
Köylü et al. [22]	Experiments with soot from combustion of acetylene, propylene, ethylene and propane	8.50	1.82
Sorensen and Roberts [15]	Soot simulations	1.57–1.81	1–3
Brasil et al. [23]	Soot simulations	1.27	1.82
Lee et al. [24]	Experiments with diesel soot	4.95	1.83
Gmachowski [16]	Simulations with agglomerates in general	0–2.15	1–3
Park et al. [25]	Experiments with diesel soot	1.91	1.75
Hu and Köylü [14]	Experiments with soot from combustion of acetylene	1.90	1.82
Neer and Köylü [26]	Experiments with diesel soot	1.90	1.77
Ouf et al. [27]	Experiments with soot combustion of acetylene, toluene and polymethyl metacrylate	2.44	1.78

4. Singular cases with $D_f = 1$

4.1. Straight-chain agglomerate

The elementary structure corresponding to $D_f = 1$ is the line, although, in the case of agglomerates, such an extreme value for the fractal dimension would also be reached by a long chain of primary particles. If the number of elementary structures composing the agglomerate is defined as N, a value of $N = 1$ is assigned to the type of agglomerates studied in this subsection. Chains with odd number of primary particles must be distinguished from those with even number before obtaining a general equation for straight agglomerates. Fig. 1 shows a straight-chain agglomerate with odd number (left) and even number (right) of primary particles.

In the case of odd number of primary particles, the summation included in Eq. (8) is extended from $i_1 = 1$ to $i_n = (n_{po} - 1)/2$ diameters at each side of the centre of gravity. In the case of even number of particles, it is extended from to $i_1 = 0.5$ to $i_n = (-n_{po} - 1)/2$ diameters at each side, in both cases with one diameter step:

$$d_g = 2 \cdot d_{po} \cdot \sqrt{\frac{3}{20} + \frac{2 \cdot \sum_{i=i_1}^{i_n} i^2}{n_{po}}} \tag{9}$$

The summation can be obtained by falling factorials, resulting, in both cases (with odd and with even number of particles):

$$\sum_{i=i_1}^{i_n} i^2 = \frac{i_n(i_n+1)(2i_n+1)}{6} - \frac{i_1(i_1-1)(2i_1-1)}{6} = \frac{n_{po}(n_{po}^2-1)}{24} \tag{10}$$

Substituting Eq. (10) into Eq. (9), the following expression is obtained for the diameter of gyration:

$$d_g = 2 \cdot d_{po} \cdot \sqrt{\frac{3}{20} + \frac{i_n(i_n+1)}{3}} = 2 \cdot d_{po} \cdot \sqrt{\frac{3}{20} + \frac{(n_{po}^2-1)}{12}} \tag{11}$$

The prefactor of the power-law relationship can be obtained substituting Eq. (11) into Eq. (1):

$$k_f(D_f \approx 1) = \frac{n_{po} d_{po}}{d_g} = \frac{n_{po}}{2\sqrt{\frac{3}{20} + \frac{(n_{po}-1)(n_{po}+1)}{12}}} = \frac{n_{po}}{\sqrt{\frac{3}{5} + \frac{1}{3}(n_{po}^2-1)}} \tag{12}$$

But this straight-chain agglomerate would only strictly correspond to $D_f = 1$ when the number of primary particles tends to infinite. In this case, the size of the primary particles becomes negligible in front of the length of the agglomerate:

$$k_f(D_f = 1) = \lim_{n_{po}\to\infty} k_f = \sqrt{3} \tag{13}$$

4.2. Square cross agglomerate

The case of a square cross agglomerate (Fig. 2) is also an example of $D_f = 1$, since the volume occupied increases linearly as the external diameter of the agglomerate increases. In this case, $N = 2$. Again, the cases with odd or even number of primary particles must be distinguished.

In both cases (odd and even number of particles) the diameter of gyration can be obtained from Eq. (8). The summation is extended from $i_1 = 1$ to $i_n = (n_{po} - 1)/4$ at each of the four branches, in the case of odd number, and from $i_1 = \sqrt{2}/2$ to $i_n = (n_{po} - 4)/4 + \sqrt{2}/2$ at each of the four branches, in the case of even number of particles, in both cases with one diameter step.

$$d_g = 2 \cdot d_{po} \cdot \sqrt{\frac{3}{20} + \frac{4 \cdot \sum_{i=i_1}^{i_n} i^2}{n_{po}}} \tag{14}$$

Substituting Eq. (10) into Eq. (14), the resulting equation is different for odd and even numbers:

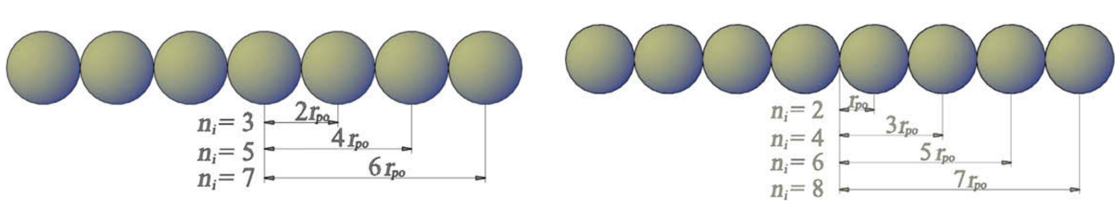

Fig. 1. Straight-chain agglomerate with odd number (left) and with even number (right) of primary particles.

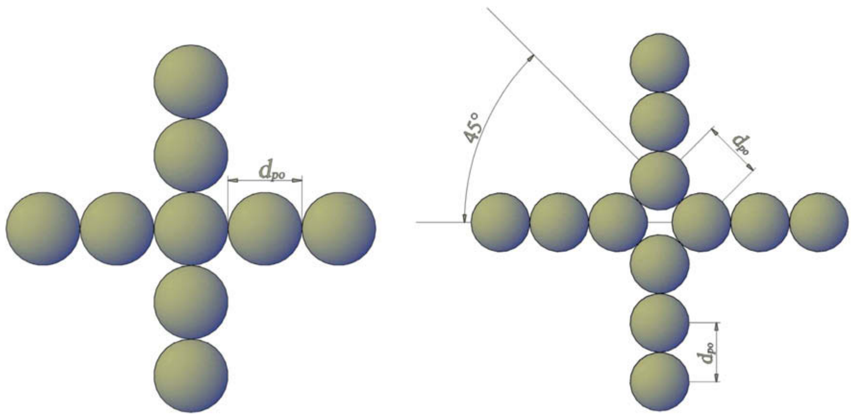

Fig. 2. Square cross agglomerate with odd number (left) and with even number (right) of primary particles.

$$d_g = 2 \cdot d_{po} \cdot \sqrt{\frac{3}{20} + \frac{2i_n(i_n+1)(2i_n+1)}{3(4i_n+1)}} = 2 \cdot d_{po} \cdot \sqrt{\frac{3}{20} + \frac{(n_{po}^2-1)(n_{po}+3)}{48n_{po}}} \quad (n_{po} \text{ odd}) \tag{15}$$

$$d_g = 2 \cdot d_{po}\sqrt{\frac{3}{20} + \frac{4 \cdot \left(\frac{i_n(i_n+1)(2i_n+1)}{6} + \frac{\sqrt{2}}{6} - \frac{1}{4}\right)}{4 - 2 \cdot \sqrt{2} + 4 \cdot i_n}}$$
$$= 2 \cdot d_{po}\sqrt{\frac{3}{20} + \frac{(n_{po}+2\sqrt{2}-4)(n_{po}+2\sqrt{2}) + 2\sqrt{2}-2) - 8\sqrt{2}(\sqrt{2}-2)(\sqrt{2}-1)}{48n_{po}}}$$
$$(n_{po} \text{ even}) \tag{16}$$

The prefactor of the power-law relationship can be obtained substituting Eqs. (15), (16) into Eq. (1):

$$k_f(D_f \approx 1) = \frac{n_{po}d_{po}}{d_g} = \frac{n_{po}}{\sqrt{\frac{3}{5} + \frac{(n_{po}^2-1)(n_{po}+3)}{12n_{po}}}} \quad (n_{po} \text{ odd}) \tag{17}$$

$$k_f(D_f \approx 1) = \frac{n_{po}}{\sqrt{\frac{3}{5} + \frac{(n_{po}+2\sqrt{2}-4)(n_{po}+2\sqrt{2})(n_{po}+2\sqrt{2}-2) - 8\sqrt{2}(\sqrt{2}-2)(\sqrt{2}-1)}{12n_{po}}}} \quad (n_{po} \text{ even}) \tag{18}$$

Again, this square cross agglomerate would only strictly correspond to $D_f = 1$ when the number of primary particles tends to infinite. In both cases the limit tends to the same value:

$$k_f(D_f = 1) = \lim_{n_{po}\to\infty} k_f = 2\sqrt{3} \tag{19}$$

4.3. Triple-branched cross agglomerate

The following approach ($N = 3$) could correspond to two different cases: An orthogonal three-dimensional cross and a two-dimensional star with six branches shifted 60° each other (dimensions referred here to the Euclidean space). The approach is only presented for a cross with a central particle (odd number of particles), but in case that no particle occupies the central position (even number of particles), the same limit would be reached, as proved in the previous case (see Fig. 3).

The diameter of gyration can be obtained from Eq. (8), the summation being extended from $i_1 = 1$ to $i_n = (n_{po} - 1)/6$ at each of the six branches with one diameter step.

$$d_g = 2 \cdot d_{po} \cdot \sqrt{\frac{3}{20} + \frac{6 \cdot \sum_{i=i_1}^{i_n} i^2}{n_{po}}} \tag{20}$$

Substituting Eq. (10) into Eq. (20), the resulting equation is:

$$d_g = 2 \cdot d_{po} \cdot \sqrt{\frac{3}{20} + \frac{i_n(i_n+1)(2i_n+1)}{(6i_n+1)}}$$
$$= 2 \cdot d_{po} \cdot \sqrt{\frac{3}{20} + \frac{(n_{po}-1)(n_{po}+5)(n_{po}+2)}{108n_{po}}} \tag{21}$$

Substituting in Eq. (1), the prefactor of the power-law relationship becomes:

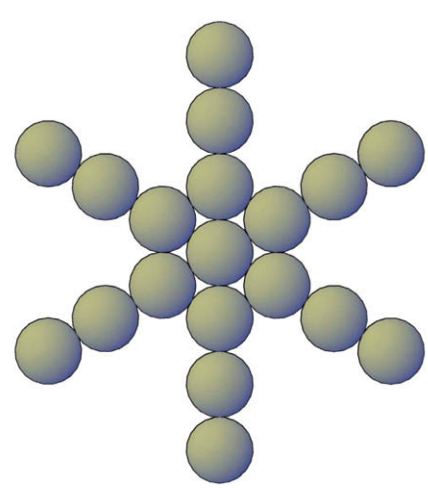

Fig. 3. Triple-branched cross agglomerate.

$$k_f(D_f \approx 1) = \frac{n_{po}}{\sqrt{\frac{3}{5} + \frac{(n_{po}-1)(n_{po}+5)(n_{po}+2)}{27n_{po}}}} \tag{22}$$

Again, this square cross agglomerate would only strictly correspond to $D_f = 1$ when the number of primary particles tends to infinite:

$$k_f(D_f = 1) = \lim_{n_{po}\to\infty} k_f = \frac{1}{\sqrt{\frac{1}{27}}} = 3\sqrt{3} \tag{23}$$

5. Singular cases with $D_f = 2$

5.1. Plane hexagonal close-pack agglomerate

A plane agglomerate (Fig. 4) composed by particles packed with hexagonal close pack has been considered as the elementary structure of $D_f = 2$, since the volume occupied increases linearly as the square of the external diameter of the agglomerate increases. In the case of a single plane, again $N = 1$.

The number of particles can be obtained from the following summation:

$$n_{po} = 1 + \sum_{i=1}^{i_n} 6 \cdot i = 1 + 6\frac{i_n(i_n+1)}{2} = 1 + 3i_n(i_n+1) \tag{24}$$

The limit of the summation can then be expressed as a function of the number of particles of the agglomerate:

$$i_n = -\frac{1}{2} + \sqrt{\frac{n_{po}}{3} - \frac{1}{12}} = \frac{\sqrt{4n_{po}-1}}{2\sqrt{3}} - \frac{1}{2} \tag{25}$$

Once more, the diameter of gyration can be obtained from Eq. (8), the summation being extended from $i = 1$ to i_n with one diameter step. It can be proved that the summation to be solve in this case is:

$$d_g = 2 \cdot d_{po} \cdot \sqrt{\frac{3}{20} + \frac{6\sum_{i=1}^{i_n}\sum_{j=0}^{i-1}(i^2 + j^2 - i \cdot j)}{n_{po}}} \tag{26}$$

The solution of this double summation can also be derived from falling factorials and considering the result provided in Eq. (25), this leading to:

$$\sum_{i=1}^{i_n}\sum_{j=0}^{i-1}(i^2 + j^2 - ij) = \frac{5}{24}i_n^4 + \frac{5}{12}i_n^3 + \frac{7}{24}i_n^2 + \frac{1}{12}i_n = \frac{10n_{po}^2 - 8n_{po} - 47}{432} \tag{27}$$

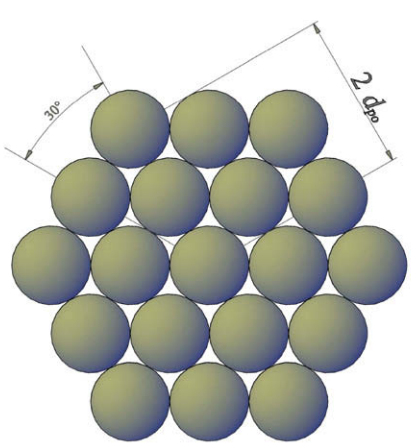

Fig. 4. Plane agglomerate with hexagonal close-pack arrangement.

The diameter of gyration and the prefactor are then:

$$d_g = 2 \cdot d_{po} \cdot \sqrt{\frac{3}{20} + \frac{10n_{po}^2 - 8n_{po} - 47}{72n_{po}}} \tag{28}$$

$$k_f(D_f \approx 2) = \frac{n_{po}d_{po}^2}{d_g^2} = \frac{n_{po}}{\frac{3}{5} + \frac{10n_{po}^2 - 8n_{po} - 47}{18n_{po}}} \tag{29}$$

This plane agglomerate would only strictly correspond to $D_f = 2$ when the number of primary particles tends to infinite, since in this case the width of the particles could be neglected in front of the size of the agglomerate:

$$k_f(D_f = 2) = \lim_{n_{po}\to\infty} k_f = \frac{1}{\frac{10}{18}} = 1.8 \tag{30}$$

5.2. Agglomerate formed by two orthogonal plane hexagonal close-pack agglomerates

All couples of plane hexagonal close-pack agglomerates growing up from its central particle constitute cases of $D_f = 2$, since their volume increase linearly with the square of their external diameters. As an example, the agglomerate formed by two orthogonal planes ($N = 2$) was chosen (Fig. 5).

The number of particles is double than that of the plane hexagonal close-pack agglomerate minus those composing the intersecting chain:

$$n_{po} = 2 \cdot (1 + 3 \cdot i_n + 3 \cdot i_n^2) - (1 + 2 \cdot i_n) = 1 + 4 \cdot i_n + 6 \cdot i_n^2 \tag{31}$$

Similarly, the diameter of gyration can be obtained modifying Eq. (26) correspondingly:

$$d_g = 2 \cdot d_{po} \cdot \sqrt{\frac{3}{20} + \frac{12\sum_{i=1}^{i_n}\sum_{j=0}^{i-1}(i^2 + j^2 - i \cdot j) - 2\sum_{i=1}^{i_n} i^2}{n_{po}}} \tag{32}$$

Substituting Eqs. (27) and (31) in Eq. (32), the diameter of gyration and the prefactor can be obtained as a function of the number of particles:

$$d_g = 2 \cdot d_{po} \cdot \sqrt{\frac{3}{20} + \frac{4(9n_{po} - 13)\sqrt{6n_{po} - 2} + 45n_{po}^2 + 24n_{po} - 17}{648n_{po}^2}} \tag{33}$$

$$k_f(D_f \approx 2) = \frac{n_{po}d_{po}^2}{d_g^2} = \frac{n_{po}}{\frac{3}{5} + \frac{4(9n_{po}-13)\sqrt{6n_{po}-2} + 45n_{po}^2 + 24n_{po} - 17}{162n_{po}}} \tag{34}$$

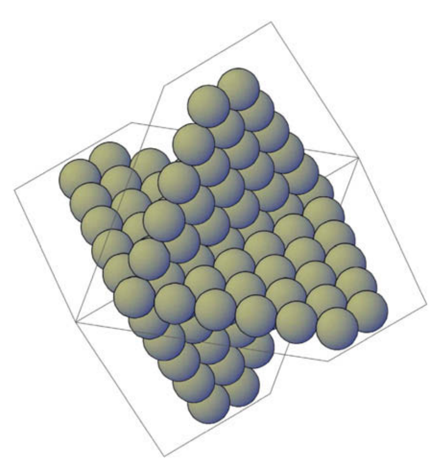

Fig. 5. Agglomerate composed by two plane hexagonal close-pack structures orthogonally disposed.

As in the previous case, this double-plane agglomerate would only strictly correspond to $D_f = 2$ when the number of primary particles tends to infinite:

$$k_f(D_f = 2) = \lim_{n_{po}\to\infty} k_f(n_{po}) = \frac{1}{\frac{45}{162}} = 3.6 \tag{35}$$

5.3. Agglomerate formed by three orthogonal plane hexagonal close-pack agglomerates

Another example of $D_f = 2$ is the agglomerate formed by three orthogonal planes ($N = 3$), such as that shown in Fig. 6.

The number of particles is triple than that of the plane hexagonal close-pack agglomerate minus twice those composing the intersecting chain:

$$\begin{aligned} n_{po} &= 3 \cdot (1 + 3 \cdot i_n + 3 \cdot i_n^2) - 2 \cdot (1 + 2 \cdot i_n) \\ &= 1 + 5 \cdot i_n + 9 \cdot i_n^2 \end{aligned} \tag{36}$$

The diameter of gyration can be obtained modifying Eq. (26) correspondingly:

$$d_g = 2 \cdot d_{po} \cdot \sqrt{\frac{3}{20} + \frac{18\sum_{i=1}^{i_n}\sum_{j=0}^{i-1}(i^2 + j^2 - i \cdot j) - 4\sum_{i=1}^{i_n} i^2}{n_{po}}} \tag{37}$$

Substituting Eqs. (27) and (36) in Eq. (37), the diameter of gyration and the prefactor can be obtained as a function of the number of particles:

$$d_g = 2 \cdot d_{po} \cdot \sqrt{\frac{3}{20} + \frac{(108n_{po} + 32)\sqrt{36n_{po} - 11} + 405n_{po}^2 - 396n_{po} - 144}{8748n_{po}^2}} \tag{38}$$

$$k_f(D_f \approx 2) = \frac{n_{po}d_{po}^2}{d_g^2} = \frac{n_{po}}{\frac{3}{5} + \frac{(108n_{po}+32)\sqrt{36n_{po}-11}+405n_{po}^2-396n_{po}-144}{2187n_{po}}} \tag{39}$$

As in the previous case, this triple-plane agglomerate would only strictly correspond to $D_f = 2$ when the number of primary particles tends to infinite:

$$k_f(D_f = 2) = \lim_{n_{po}\to\infty} k_f(n_{po}) = \frac{1}{\frac{405}{2187}} = 5.4 \tag{40}$$

6. Singular case with $D_f = 3$

The agglomerate with fractal dimension closest to 3 is that composed of particles forming a sphere with hexagonal close-pack structure. This case is essentially different to the previous ones, since no substructures can be distinguished. The packing fraction, defined as the ratio between the volume occupied by the material and that of the external sphere of diameter d_p, in the hexagonal close-pack case, has been proved to be:

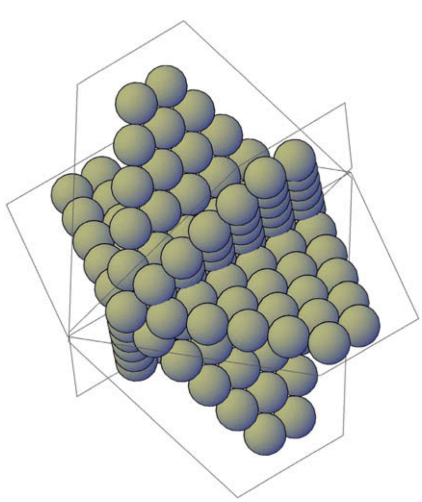

Fig. 6. Agglomerate composed by three plane hexagonal close-pack structures.

$$p_{hc} = n_{po} \cdot \left(\frac{d_{po}}{d_p}\right)^3 = \frac{\pi}{\sqrt{18}} \rightarrow n_{po} = \frac{\pi}{\sqrt{18}}\frac{d_p^3}{d_{po}^3} \tag{41}$$

The diameter of gyration can be obtained from Eq. (6), because if the number of composing primary particles is large enough ($n_{po} \to \infty$), the spherical agglomerate can be considered to be homogeneous, the holes contributing to reduce its density with respect to that of the material (soot in the case of diesel agglomerates). Therefore, the prefactor can be obtained as a function of the packing density:

$$k_f(D_f = 3) = \frac{n_{po}d_{po}^3}{d_g^3} = p\left(\frac{5}{3}\right)^{\frac{3}{2}} \tag{42}$$

which in the case of the hexagonal close-pack gives:

$$k_f(D_f = 3) = \frac{\pi}{\sqrt{18}}\left(\frac{5}{3}\right)^{\frac{3}{2}} = 1.5933 \tag{43}$$

7. Summarised results

The results presented in previous sections provide limit values for the prefactor of the power-law relationship describing isotropically orientated agglomerates, composed of spherical particles. Any deviation with respect to the sphericity of the composing primary particles (as a consequence, for example, of sintering) [7] or with respect to the isotropic orientation of the agglomerate (as a consequence, for example, of the aggregation regime associated with the aerosol dynamics) [29] would lead to increased or to decreased values for the prefactor, respectively.

The obtained equations are plotted as a function of the number of primary particles in Fig. 7. The asymptotic approximation to the limit corresponding to large agglomerates shows, in all cases, that the effect of the number of particles decreases as the size of the agglomerate increases, the prefactor becoming a parameter useful to describe the structure of the agglomerate independently of its size.

The mentioned limit values are shown in Fig. 8 by means of isolated spots. This figure shows that the limit reached by the prefactor when the number of particles composing the agglomerate is large enough is proportional to the number of elementary structures (N), and therefore, to the compactness of the agglomerate, even if the fractal dimension remains unchanged. This justifies the prefactor to be expressed as "lacunarity". Finally, the range of variation of the prefactor decreases as the fractal dimension increases, reaching a unique value for the case of $D_f = 3$. This convergence to a unique value of the prefactor is justified because, in the 3D space, if an agglomerate composed of different substructures becomes tighter (its fractal dimension tending to 3), such substructures would become more and more indistinguishable. Finally, when the space becomes completely or uniformly filled, no distinction of the initial substructures would be possible. The results of the whole collection of singular cases have been fitted to the following two-parameter square polynomial correlation:

$$\begin{aligned} k_f &= (0.7967 - 0.934N)D_f^2 + (-2.38985 + 2.86985N)D_f \\ &\quad + (1.59325 - 0.20385N) \end{aligned} \tag{44}$$

This correlation, which is also plotted in Fig. 8, provides values for the prefactor in the ranges $N \geqslant 1$ and $1 \leqslant D_f \leqslant 3$ which are consistent with the proposed values for the studied cases, and could then be used for the determination of the prefactor of real agglomerates with noninteger fractal dimensions.

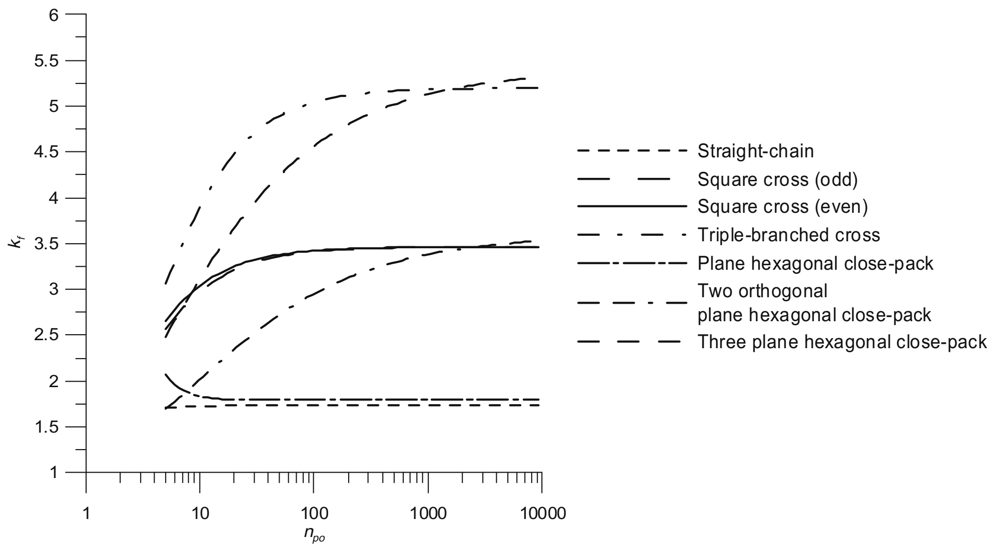

Fig. 7. Prefactor of the power-law relationship as a function of the number of particles for different geometrical configurations.

The results from the methods proposed by Sorensen and Roberts [15] and by Gmachowski [16] have also been plotted in the figure. In the first case, the hexagonal close-pack arrangement was taken, considering spatial dimension = 2 for agglomerates with fractal dimension below 2 and identifying spatial and fractal dimensions for $D_f > 2$ as suggested by the authors. The results show a good agreement with those presented here (especially in the range of high fractal dimensions), although no variability was considered by these authors to account for the different lacunarities which could take place for a given fractal dimension. In the case of Gmachowski's method, the agreement is quite worse throughout the whole range, although this author considered homogeneous packing ($p = 1$), which in the case of $D_f = 3$ (Eqs. (41) and (42)) would lead to the same result ($k_f = 2.15$). In this case, again, no variability was considered by the author to account for the different lacunarities for a given fractal dimension.

8. Extension to other packing configurations

Although the hexagonal close-pack configuration is the closest one to the a purely homogeneous plane or sphere in case of non-infinite agglomerate, other less dense configurations should be considered as well, because they also tend to $D_f = 2$ or to $D_f = 3$ respectively when the size of the agglomerate (with respect to that of the primary particle) tends to infinite.

In the case of plane agglomerates, the integration along the radius of the agglomerate leads to the following relationship between the radius of gyration and the external radius of the agglomerate, r_p:

$$r_g = \frac{r_p}{\sqrt{2}} \tag{45}$$

Therefore, as the packing density can be determined as the ratio between the area occupied by the material and that of the external circle of diameter d_p, the combination with Eq. (1) leads to the following relationship between the packing density and the prefactor:

$$p = n_{po} \cdot \left(\frac{d_{po}}{d_p}\right)^2 = \frac{k_f(D_f = 2)}{2} \tag{46}$$

The general equations for the simple cubic (identified with subscript *sc*) and body centre cubic (identified with *bcc*) packing densities are (Γ being the Gamma function) [15]:

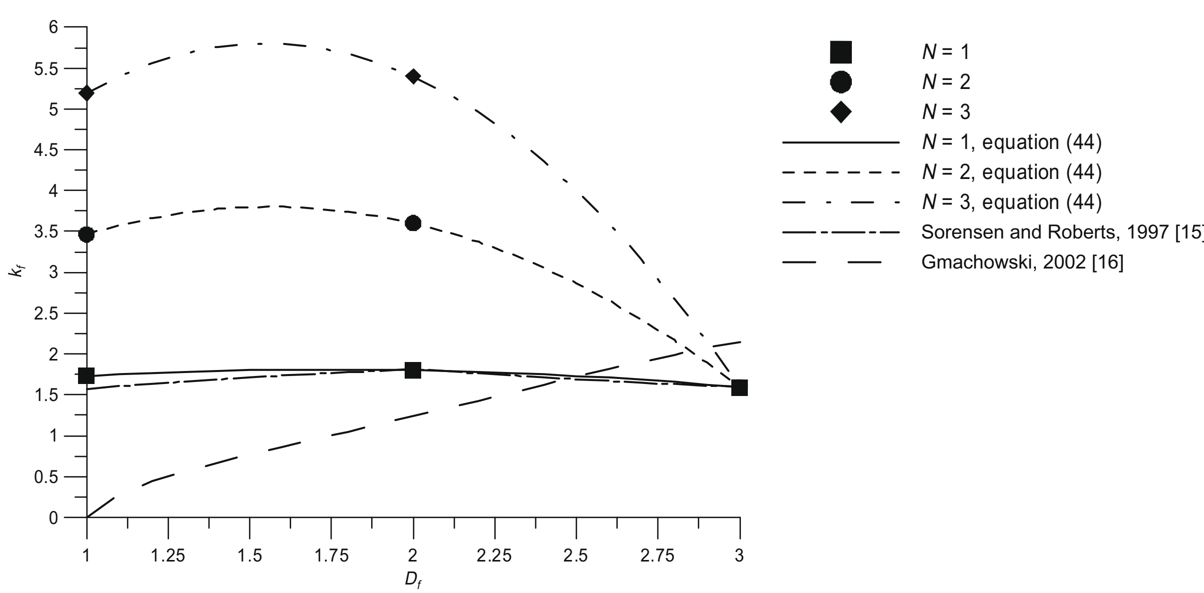

Fig. 8. Values for the prefactor, obtained from the geometrical method and from correlations, as a function of the fractal dimension.

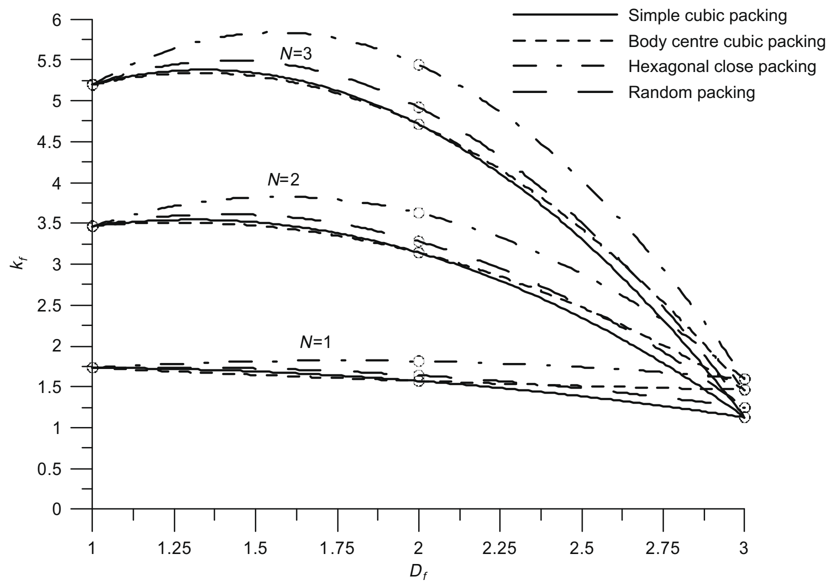

Fig. 9. Values for the prefactor as a function of the fractal dimension and the packing configuration.

$$p_{sc}(D_f) = \frac{\pi^{D_f/2}}{2^{D_f}\Gamma(1+D_f/2)}; \quad p_{bcc}(D_f) = \left(\frac{D_f\pi}{16}\right)^{D_f/2}\frac{2}{\Gamma(1+D_f/2)} \tag{47}$$

These equations lead to the following values for the plane and the spherical agglomerates:

$$p_{sc}(D_f=2) = \frac{\pi}{4\Gamma(2)} = \frac{\pi}{4} = 0.7854; \quad p_{sc}(D_f=3) = \frac{\pi^{3/2}}{8\Gamma(5/2)} = \frac{\pi}{6} = 0.5236 \tag{48}$$

$$p_{bcc}(D_f=2) = \frac{\pi}{8}\frac{2}{\Gamma(2)} = \frac{\pi}{4} = 0.7854; \quad p_{bcc}(D_f=3) = \left(\frac{3\pi}{16}\right)^{3/2}\frac{2}{\Gamma(5/2)} = \frac{\sqrt{3}\pi}{8} = 0.6802 \tag{49}$$

For the random packing arrangement (identified with r), in the case of plane circles ($D_f = 2$), a packing density $p_r = 0.82$ has been obtained from the literature [30] [31]. In the case of spherical monosize particles, although a lot of literature can be found proposing different values, a random packing density $p_r = 0.578$ has finally been chosen following the latest modelling work by Shi and Zhang [32].

Solving for the prefactor from Eq. (46) in the plane case and from Eq. (42) in the spherical case:

$$k_{f,sc}(D_f=2) = 2p_{sc}(D_f=2) = 1.5708; \quad k_{f,sc}(D_f=3) = \left(\frac{5}{3}\right)^{\frac{3}{2}} p_{sc}(D_f=3) = 1.1266 \tag{50}$$

$$k_{f,bcc}(D_f=2) = 2p_{bcc}(D_f=2) = 1.5708; \quad k_{f,bcc}(D_f=3) = \left(\frac{5}{3}\right)^{\frac{3}{2}} p_{bcc}(D_f=3) = 1.4635 \tag{51}$$

$$k_{f,r}(D_f=2) = 2p_r(D_f=2) = 1.64; \quad k_{f,r}(D_f=3) = \left(\frac{5}{3}\right)^{\frac{3}{2}} p_r(D_f=3) = 1.2437 \tag{52}$$

These values and their extensions to the whole range $1 \leqslant D_f \leqslant 3$ and to higher number of elementary structures ($N \geqslant 1$) have been plotted in Fig. 9, together with the results previously obtained for the hexagonal close-pack configuration. It is expected that the prefactor for any other packing configuration should remain within these limits: below the values corresponding to the hexagonal close-pack and above those corresponding to the simple cubic configuration. However, it is also expected that sintering could lead to prefactor values even higher than those obtained for the hexagonal close-pack configuration, and that anisotropic orientations could lead to values below those obtained for the cubic arrangements.

9. Conclusions

The geometrical approach presented here, based on the calculation of the moment of inertia of different configurations of contacting sphere chains and on the application of the power-law relationship to singular cases with integer values of the fractal dimension, prove that increasing numerical values proportional to the number of growing elementary structures must be given to the prefactor of the power-law relationship (which is supposed to govern the shape-size relationship of fractal agglomerates). This result is consistent with the concept of lacunarity usually associated to this prefactor.

The results obtained (initially considering a hexagonal close-pack configuration for the plane and spherical agglomerates, but finally being extended to other packing configurations) constitute the basis for a geometrical model for calculating the fractal dimension of individual agglomerates. Although further work must be developed for estimating the prefactor values for intermediate fractal dimensions, a correlation is proposed which could be used for a preliminary estimation of the prefactor of real agglomerates. This correlation proves that the functions proposed in the literature for estimating the prefactor variations usually lead to underestimation of the prefactor and are not flexible enough to account for differences in lacunarity for a given fractal dimension.

Finally, if the information available about these particles comes from planar images, further work must also be developed to estimate the overlapping among primary particles.

References

[1] G. Skillas, S. Künzel, H. Burtscher, U. Baltensperger, K. Siegmann, J. Aerosol Sci. 29 (1998) 411–419.
[2] B.B. Mandelbrot, The Fractal Geometry of Nature, W.H. Freeman & Co., New York, 1983.

[3] P.A. Bonczyk, R.J. Hall, Langmuir 7 (1991) 1274–1280.
[4] K.O. Lee, R. Cole, R. Sekar, M.Y. Choi, J. Zhu, J. Kang, C. Bae, Detailed characterization of morphology and dimensions of diesel particulates via thermophoretic sampling. SAE paper, 2001-01-3572, 2001.
[5] J. Cai, N. Lu, C.M. Sorensen, J. Colloid Interface Sci. 171 (1995) 470–473.
[6] C. Artelt, H.J. Schmid, W. Peukert, J. Aerosol Sci. 34 (2003) 511–534.
[7] G. Yang, P. Biswas, J. Colloid Interface Sci. 211 (1999) 142–150.
[8] M. Lattuada, H. Wu, M. Morbidelli, J. Colloid Interface Sci. 268 (2003) 106–120.
[9] M. Lapuerta, R. Ballesteros, F.J. Martos, J. Colloid Interface Sci. 303 (2006) 149–158.
[10] R.A. Dobbins, C.M. Megaridis, Langmuir 3 (1987) 254–259.
[11] D.E. Rosner, D.W. Mackowski, P.L. García-Ybarra, Combust. Sci. Technol. 80 (1991) 87–101.
[12] C. Oh, C.M. Sorensen, J. Aerosol Sci. 28 (1997) 937–957.
[13] M.K. Wu, S.K. Friedlander, J. Colloid Interface Sci. 159 (1993) 246–248.
[14] B. Hu, U.O. Koylu, Aerosol Sci. Technol. 38 (2004) 1009–1018.
[15] C.M. Sorensen, G.C. Roberts, J. Colloid Interface Sci. 186 (1997) 447–452.
[16] L. Gmachowski, Colloids Surf., A: Physicochem. Eng. Aspects 211 (2002) 197–203.
[17] P. Meakin, J. Colloid Interface Sci. 102 (1984) 491–504.
[18] R.J. Samson, G.W. Mulholland, J.W. Gentry, Langmuir 3 (1987) 272–281.
[19] R.D. Mountain, G.W. Mulholland, Langmuir 4 (1988) 1321–1326.
[20] C.M. Megaridis, R.A. Dobbins, Combust. Sci. Technol. 71 (1990) 95–109.
[21] R. Puri, T.F. Richardson, R.J. Santoro, R.A. Dobbins, Combust. Flame 92 (1993) 320–333.
[22] Ü.Ö. Köylü, G.M. Faeth, T.L. Farias, M.G. Carvalho, Combust. Flame 100 (1995) 621–633.
[23] A.M. Brasil, T.L. Farias, M.G. Carvalho, Aerosol Sci. Technol. 33 (2000) 440–454.
[24] K.O. Lee, R. Cole, R. Sekar, M.Y. Choi, J. Kang, C. Bae, H. Shin, Proc. Combust. Inst. 29 (2002) 647–653.
[25] K. Park, D.B. Kittelson, P.H. McMurry, Aerosol Sci. Technol. 38 (2004) 881–889.
[26] A. Neer, U.O. Koylu, Combust. Flame 146 (2006) 142–154.
[27] F.-X. Ouf, J. Vendel, A. Coppalle, M. Weill, J. Yon, Combust. Sci. Technol. 180 (2008) 674–698.
[28] H. Harrison, T. Neltleton, Advanced Engineering Dynamics, Butterworth Heinemann, Oxford, 1997.
[29] D. Fry, A. Mohammad, A. Chakrabarti, C.M. Sorensen, Langmuir 20 (2004) 7871–7879.
[30] H.H. Kausch, D.G. Fesko, N.W. Tschoegl, J. Colloid Interface Sci. 37 (1971) 603–611.
[31] D.N. Sutherland, J. Colloid Interface Sci. 60 (1977) 96–102.
[32] Y. Shi, Y.W. Zhang, Appl. Phys. A: Mater. Sci. Process. 92 (2008) 621–626.