# A Unified algorithm for Ballistic to Diffusion Limited Cluster-Cluster Aggregation.

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## Abstract

## Introduction

Fractal aggregates are encountered in many aggregation processes during nanomaterial production or combustion process. An aggregate is constituted of Np primary spheres whose ist radius is written Rpi. Thanks to the observations by Transmission Electron Microscope (TEM) or by analyzing the angular light scattering by these particles, it has been clearly demonstrated that number of primary spheres in an aggregates is in power law with aggregate size (equ. 1).

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|  | equ. |

In this equation called fractal law, Rg is called gyration radius and represents a purely geometrical size parameter (see equ. 2). In this equation, Li is the distance between the aggregate centre of mass and the centre of the ist primary sphere, considering here primary spheres of varying radii.

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In equ. 2, df and kf corresponds respectively to the fractal dimension and prefactor. These parameters are directly linked to the morphology of the “fractal” aggregates. The determination of df and kf for such particles is essential for understanding their physical behaviour (emissions, transport, coagulation, toxicological and environmental impact…). Indeed, realistic virtual generation of aggregates particles is essential for the evaluation of filtration efficiency, determination of nano-aggregates optical properties, kinetic of soot particle generation in flames, hydrodynamique properties… The fractal structure of aggregates is mainly dominated by the thermal Brownian motion of nano or submicronic particles. When particle mean free path λp in the surrounding gas is higher than distance between particles (di), aggregation is ballistic (BLA). On the contrary when λp< di aggregation is driven by diffusion motion (DLA : Diffusion Limited Aggregation). The two approaches are encountered to simulate aggregation. DLA or BLA codes are used to generate one aggregate of interest which is surrounded by primary spheres in thermal motion. More sophistically, aggregation of many clusters in the same volume of interest is called DLCA or BCA for Cluster aggregation. The use of DLCA or BLCA codes to simulate soot particles or colloids has been comforted by the fact that such generated aggregates respect the fractal law (equ. 1) with corresponding fractal dimension and prefactor similar to that ones determined experimentally (df≈1.8-2, kf≈1-2 ).

DLCA codes have common simple algorithms. At each iteration, a particle is arbitrary selected. The diffusion coefficient of the selected particle is evaluated using a simplified approach as D=D0mγ where D0 is a constant, *m* the particle mass and γ a constant used to take into account the fractal nature of aggregates.

Particles is displaced if D/Dmax>X where Dmax is the highest encountered diffusion parameter in the simulation and 0<X<1 an arbitrary fixed parameter. With that test, smallest particles (characterized by highest diffusion coefficients) are most often displaced than bigger ones taking into account their more intense Brownian motion. The particle displacement is generally considered constant and equal to the primary sphere diameter. That displacement can be 1D, 2D or 3D along an arbitrary orientation or in latticed configuration. In DLCA codes, when a contact occurs, aggregation is systematically associated. To simulate less intense attractive forces, aggregation can be considered after a certain number of contact (Raction Limited Aggregation), see Meakin (Review) for more information. In fact DLCA/RLCA or BLCA simple tools allowing the generation of realistic aggregates. Nevertheless these tools are limited by different aspects:

* Particle displacement is arbitrary fixed. That limitation does not permit to simulate a possible continuous transition between ballistic and diffusion aggregation BA-DLA that is suspected to occur as a function of particle concentration during aggregation process.
* Physical parameters as temperature T, pression P, gas nature, primary particle size are not explicitly taken into account.
* That modelisation of agglomeration process does not permit to evaluate a physical residence time.
* The taking into account of aggregate morphology for determining diffusion coefficient is limited to γ parameter in equ. 3. But how to choose this parameter? This expression of diffusion coefficient does not allow a taking into account of flow regime transition from molecular flow to continuum flow during particle growth.

In order to answer to the two first points Hayashi et al. (1999) proposed a code that attribute to each particle a displacement equal to its physically calculated mean free path (λp) explicitly taking into account of T, P. But, particles are randomly selected and displaced without taking into account that during this displacement, other particles of different sizes don’t move at the same velocity and thus can run numerous mean free path and thus should be selected more often. In consequence, time progression is different for each particle leading to a not physical global residence time (point 3). To answer to the point 4, (publics Sorensen) proposed different analyses in order to correlate the kinetic of agglomeration as a function of flow regime (Ballistic, Continuum, Epstein).

The first aim of the present paper is to propose a new aggregation algorithm able to evaluate aggregate diffusion coefficient as a function of it gyration radius and thermodynamic conditions and allowing a transition between a ballistic and diffusion aggregation. This permits to take into account a possible change of flow regime and aggregation process during the clusters aggregation. As proposed by Hayashi et al. (1999), particles are displaced along their mean free path allowing a physically driven transition between BLCA to DLCA. In opposition to Hayashi et al., particles will be selected with a physically based weighting law different that one classically used in DLCA, allowing the determination of a more realistic residence time. So, in the present paper, a new algorithm is presented. Impact of volume fraction, primary particle size and polydispersion on aggregation kinetic, size distributions, particle morphology and residence time will be studied. Additionally to these algorithm enhancements and ensuing results, the second purpose of the present work is to propose a reference code for studied based on virtually conceived fractal aggregates. It is the reason why present code written in C++ can be freely download on the [www.coria.fr](http://www.coria.fr) website.

## DLCA algorithm

### Basis

First, N primary spheres are randomly positioned in a virtual cubic domain of size L.

The distribution of the primary spheres’ diameter can be normal (equ. 3) or log-normal (equ. 4) where Dpm and Dgeo are the modal diameters of the distributions and σ and σgeo respectively the standard deviation and geometric standard deviation of the distribution :

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In order to compare aggregation with same aggregates volume fraction, the box width L is determined by the following equation respectively in case of normal or lognormal primary sphere size distributions (equ. 5):

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| or | equ. |

Each primary sphere is labelized to simulate its affiliation to a given aggregate. Initially, before the beginning of aggregation, there are as many primary spheres as aggregates.

At time t, one of the Nagg clusters in the domain is selected respecting a law explained later. A randomly normalized vector is determined indicating the direction and the way of the particle displacement. Then, particle is displaced along the mean free path λp determined with equ. 6 where kB=1,38.10-23 N.m/K is the Boltzmann constant, T (K) is the surrounding gaz temperature, Cc the Cunningham slip factor, η the gaz viscosity, Dm the mobility diameter of the particle and  the aggregate speed.

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|  | equ. |

The Cunningham slip factor is expressed in equ. 7 with A=1.142, B=0.558 and C=0.999. That factor is used to take into account a possible change of flow regime (Kn) during the particle growth (equ. 8).

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| with | equ. |

In equ. 8, λg is the mean free path of the surrounding gaz at pressure P (Pa) and temperature T. It can be determined knowing the mean free path of the surrounding gaz λg,ref at a reference pressure and temperature (Pr = 101.3 kPa and Tr=293.15 K) with the Sutterland constant S=110 K.

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| with | equ. |

The viscosity of the gaz used in equ. 6 can be determined with equ. 9 where ηref is the gaz viscosity at a reference temperature.

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The aggregate velocity used in equ. 6 is evaluated by using equ. 10 with ma the aggregate mass and ρp the material density.

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| with | equ. |

If the particle displacement provokes a collision, a new aggregate is obtained. The new aggregate is analysed in terms of mass ma (equ. 10) and gyration radius Rg (equ. 2). The corresponding mobility diameter Dm has to be determined for calculation of the new mean free path λp (equ. 6) and velocity (equ. 10). The determination of a fractal aggregate mobility diameter is not simple. Indeed, contrarily to the gyration radius which is a purely geometrical parameter, mobility diameter also depends of thermodynamical parameters (P, T, surrounding gaz, flow regime…). The relation between the two size parameters has been investigated experimentally and numerically in the past. It has to be noted β=2Rg/Dm is known for a sphere (Np=1) : β0=√(5/3)=0.77. The β function increases with Np, it must depend on flow regime, primary particle size and fractal dimension. By selecting soot particles produced by a premixed ethene flame with a differential mobility analyser and analysing particles by Scanning Electron Microscopy, Chakrabarty et al. experimentally determined a simple relationship between Rg and Dm (equ. 11, with Rg and Dm expressed in nm).

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The combination of the fractal law (equ. 1) and equ. 11 enables the expression of β as a function of Np. This expression is finally constrained to respect β0=√(5/3). The resulting expression of β is given inequ. 12. In the work of Chakrabarty et al., by measuring df=1.7, it can be found α=0.50.

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Nevertheless, it has to be noted that α is suspected to change with the flow regime. For example the results by Wang and Sorensen (1999), in free molecular flow regime corresponds to αmol=0.44. By using the multipole expansion technique, Kätzel et al. determined the aerodynamic force acting on aggregates in continuum flow regime as a function of the fractal dimension. Fortunately, their results are compatible with equ. 12 and corresponding αcont parameter is done in equ. 13.

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|  | equ. |

In the present study, in order to be able to evaluate the mobility diameter of each aggregate as a function of its morphology, number of primary spheres and for any flow regimes (αmol < α < αcont), the Danheke approach is used. This method as also been used by Naumann, it consists in determining the mobility radius Rm that satisfies equ. 14 where β is determined by using equ. 12 with α = 0.44 for the estimation of βmol in free molecular flow regime and with α given by equ. 13 for calculation of βcont, in continuum flow regime.

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Since after contact aggregation is taken into account, a new particle is selected following the method described hereafter.

### Method for particles selection and residence time

As explained in introduction, if a “physical” residence time is wanted, particles cannot be selected purely randomly. The reason is duration time  for a particle displacement along its mean free path is not the same for all particles. Noting that τmax is the longest duration time for a particle to move along its mean free path, the ratio ns(i)= τmax/τi indicates the number of successive displacements done by the ist aggregates along its mean free path during the elapsed time τmax. In consequence, the ist aggregates has to be selected ns times more than particles with longest duration τmax. So, at each new aggregation, the distribution of the duration time τ is calculated and is used to select particles statically in respect of the physical residence time progression. That statistical approach also permits to evaluate the total number of particles that must be called nt=∑ ns(i) for a residence time progression equal to τmax. In consequence, when a particle is selected, the global residence time is incremented of τmax/nt.

## Results

In the present paper, in order to illustrate the ability of the proposed algorithm to take into account some physical effects, some parameters have been changed: the primary particle size (from 10 to 50 nm), the volume fraction (from 1 to 105 ppm), the primary particle size polydisersion ( from 1 to 2). The thermodynamical conditions are fixed to P = 1 atm, for air at T = 1500 K not so for from soot formation conditions on in flames. The primary particle density is fixed to 1800 kg/cm3. In the following, classical analyses are reported and some new insights are presented.

### Aggregation kinetic and residence time

The main interest of the proposed algorithm lies in its ability to take into account simultaneously the variation of flow regime in regard of aggregate growth (*Figure 1*, x abscissa) and the continuous transition from ballistic to diffusional aggregation (*Figure 1*, y abscissa). The Knudsen number (equ. 7) is reported on X axis showing a transition from molecular flow regime for small particles (Kn>1) at beginning of the aggregation process to continuum flow regime (Kn🡪0) when particles become bigger. The Y axis presents the ratio λp / *dist* where λp is the mean free path of the particles (based on equ. 6) and *dist* represents the mean edge to edge distance between two aggregates. This parameter is higher than 1 when aggregation process is in average ballistic and, to the contrary, corresponds to a diffusion process when this ratio is lower than 1. In case of diluted aerosol (fv < 1000 ppm), *Figure 1* shows a power law between the two parameters (slope of ≈1.5 in log-log plot). For higher concentrations, the relationship is shown to be more complex. Change of primary particle size is observable in terms of initial Knudsen values but effects are more reduced concerning the ballistic to diffusion transition.

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| Transition_regime |
| *Figure 1 : Illustration of the taking into account of the flow regime changing during aggregation and of a possible transition from Ballistic to Diffusion aggregation* |

The second originality of the present aggregation code is its ability to evaluate a physical residence time. In Figure 2, the inverse of the particle number concentration is presented as a function of the residence for 3 different volume fractions. It is naturally observed that the more the volume fraction is, the more aggregation is quick. At the beginning of the process, when the majority of the population is composed of 1 or 2 primary particles, agglomeration can be considered as coalescing process. In this case, from Smoluchowski equation, the theoretical behaviour is given by :

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| Dynamique_tempo |
| *Figure 2 : Kinetic of aggregation and residence time evaluation accuracy (Dp=30 nm, σgeo=1.0)* |

As a consequence, because Figure 2 is a log-log plot, the beginning of aggregation process is supposed to be a straight line whose slope is 1 and Y-intercept is governed by primary particle diameter and thermodynamical conditions. This theoretical behaviour is presented in dash line in Figure 2. It can be observed that theoretical initial slope is respected whatever the volume fraction indicating a physical evaluation of the residence time. However, a slight decay with the theoretical Y-intercept is observed indicating an overestimation of the calculated residence time by a factor ≈5. That informs us about the limitation of the present code to evaluate precisely the residence time. The extensive use of mean parameters (mean free path or velocity) may explain this decay. Nevertheless this error remains low in comparison of the residence time order of magnitude covered. When aggregation is no more governed by coalescence, a change of slope is observed in Figure 2 and reported in Tab 1. For example, in diluted configuration, rate of agglomeration z=0.85 is lower than z=2.79 observed in ballistic aggregation (high fv).

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| |  |  |  |  |  |  | | --- | --- | --- | --- | --- | --- | | *fv = 1000 ppm, σgeo=1.0* | *z* | *Dp = 30 nm, σgeo=1.0* | *z* | *fv = 1000 ppm,*  *Dp = 30 nm* | *z* | | *Dp = 10 nm* | *1.066* | *fv = 1 ppm* | *0.852* | *σgeo=1.00* | *0.897* | | *Dp = 20 nm* | *0.922* | *fv = 10 ppm* | *0.820* | *σgeo=1.25* | *0.893* | | *Dp = 30 nm* | *0.897* | *fv = 100 ppm* | *0.806* | *σgeo=1.50* | *0.881* | | *Dp = 40 nm* | *0.916* | *fv = 1000 ppm* | *0.897* | *σgeo=1.75* | *0.858* | | *Dp = 50 nm* | *0.908* | *fv = 10000 ppm* | *1.269* | *σgeo=2.00* | *0.870* | |  |  | *fv = 100000 ppm* | *2.787* |  |  | |
| *Table 1 : Rate of agglomeration as a function of physical parameters (T=1500 K, P = 1 atm and ρ=1800 kg/cm3* |

This behaviour has been studied by Pierce and Sorensen (2006) who shown that z=2.2 in ballistic regimes, 1-1.28 in continuum regime and 0.73-0.88 in Epstein regime. These values are in good agreement with present results. The dependence of the z parameter (rate of agglomeration) is clearly illustrated in *Figure 1* observing the time evolution of Y axis. Indeed, during aggregation, when λp / *dist* becomes <<1 (low volume fraction) the probability for two particles to aggregate themself decreases and thus rate of agglomeration z is reduced. From a theoretical point of view, this behaviour can also be related to the aggregation collision kernel K in the Smoluchowski equation.

### Size distributions

According to Oh and Sorensen (1997), for fractal aggregation, the kernel is expected to be a homogeneous function of its variables. This hypothesis conducted the authors to define a general form of the aggregates size distribution called “self-preserving” (equ. 16) where n(Np,t) is the number of aggregates made of Np primary spheres,  is the mean number of primary particles by aggregate at a given time t, and λ the homogenous scaling constant.

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The self-preserving function is a description of the particles size distribution completely governed by the λ parameter. This parameter is supposed to be theoretically connected to the z parameter: λ = 1-1/z. In the present study, the convergence toward a self-preserving law and the relation between λ and z are verified (Figure 3).

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| self-preserving |
| *Figure 3 : Verification of the self-preserving size distribution (case Dp=30 nm, σgeo=1.0, fv = 1000 ppm). The continuous curve is obtained by using the self-preserving function with z=0.9* |

### Aggregates morphology

The DLCA codes are known to generate aggregates that respect the well-known fractal law (equ. 1) with characteristics fractal dimension about df = 1.7-1.8 whereas ballistic aggregation is known to generate more compact clusters (df>2). This behaviour is illustrated in Figure 4 and Figure 5 when comparing the determined fractal dimension in regard of the corresponding volume fraction. Indeed, for higher volume fraction (convergence toward a ballistic aggregation), higher fractal dimension is observed (slope of the curve in Figure 4) corresponding to more compact particles (Figure 5). In classical representation, fractal law (Figure 4) is characterized by an important dispersion of dots. This phenomena explains the dispersion of fractal prefactors found in the literature and has been recently correlated to the clusters anisotropy (Sorensen et al. ?). To overcome this effect, a mean temporally define fractal law is also presented in Figure 4. The temporal fractal law is defined by observing the temporal evolution of the mean number of primary particles as a function of the corresponding mean gyration radius normalised by the mean radius of the primary particles. The so defined temporal fractal dimension dft and prefactor kft are found to be deferent than classical ones (df and kf, see *Table 2*). This difference can be explained by the dependence of the temporally defined fractal law to the distribution of aggregates’ gyration radius:

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|  | equ. |

Then, the difference between df and dft (respectively between kf and kft) is directly connected to the spread of the size distribution.

Nevertheless, this temporal representation clearly shows a similar behaviour at the beginning of agglomeration process (Np,mean<10) whatever the volume fraction and initial physical conditions, followed by a morphological distinction appearing when aggregates becomes larger. The physical explanation could be that number of spatial arrangements of a few monomers in an aggregate is reduced comparing to the one when higher number of primary particles. This observation is interesting because it indicates that every fractal curves have a common “pivot point” on the fractal plot (Rg\*/Rp, Np\*). In the present study, by observing the impact of the different varied physical parameters, it is found Rg\*/Rp=2.51 and Np\*=7.4 (red square in Figure 4). As observed pivot point corresponds to the beginning of the aggregation process, one could argue that particles size distribution remains principally monodisperse and corresponding pivot point must be unchanged when considering classically defined fractal law. In consequence, a relationship between df and kf can be explained:

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|  | equ. |

This relationship is in very good accordance with Ehrl at al. (Lattuada…) and presents similar trends with Ouf et al. By using equ. 18 with classical df = 1.8, kf is found to be 1.4 that is in good agreement with results of (???). Surprisingly, the fractal dimension and prefactor seem not to be strongly affected by the primary sphere polydispersity as long as mean primary particles (Rp,mean) is taken into account. For example, when primary spheres polydispersity is fixed to =1.75 (Figure 5-c), df  is found to be 1.75 and corresponding prefactor is kf = 1.52, in respect with equ. 18.

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| Loi_fractale |
| *Figure 4 : Population based fractal law: classical (upper) and temporal (lower) approached. Fractal dimension dependence to the volume fraction (right part)* |

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| Illustration_fv1ppm_Agg27_Np325 | Illustration_100000ppm_Agg16_Np331 | Illustration_lognorm175_Agg8_Np338 |
| Low volume fraction  (1 ppm), Np=325 | High volume fraction  (100 ppk), Np=331 | High primary sphere polydispersity  (=1.75), Np=338 |
| *Figure 5 : Examples of generated aggregates* | | |

The classical or temporally defined fractal laws are relevant of the aggregates morphology of the *population* of aggregates. But fractal morphology can also be found in the structure of one aggregate. The corresponding “intrinsic” fractal dimension is defined by density autocorrelation function:

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|  | equ. 19 |

where is the density function i.e. the material density for each spatial position. Indeed, after having averaged this function over isotropic orientations, it is commonly admitted that autocorrelation function decreases as a power law and depending on the intrinsic fractal dimension dfi :

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|  | equ. 20 |

In this equation, hc is the cutoff function. The autocorrelation function has been calculated for a set of clusters generated in the present study for aggregates of Np ≈ 600 (upper graph of the Figure 6). For distance r>Rp on could observe in log-log representation a linear behaviour. The corresponding slope allows the determination of the intrinsic fractal dimension (dfi in *Table 2*). Accordingly to the previous observations, the intrinsic fractal dimension of aggregates generated in case of high volume fractions are significantly higher than in case of reference case. It is also observed that intrinsic fractal dimension are similar to the classical definition (fractal law). Temporally defined fractal dimension is systematically lower than two other fractal dimensions.

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| |  |  |  |  | | --- | --- | --- | --- | | *Fractal dimension* | *fv = 1000 ppm, σgeo=1.0, Dp = 30 nm*  *(reference case)* | *fv = 100000 ppm, σgeo=1.0, Dp = 30 nm* | *fv = 1000 ppm, σgeo=1.25, Dp = 30 nm* | | *dfi (deduced from A(r))* | *1.85* | *2.24* | *1.76* | | *df (classical definition)* | *1.82* | *2.68* | *1.81* | | *dft (temporal definition)* | *1.72* | *2.14* | *1.64* | |
| *Table 2 : Rate of agglomeration as a function of physical parameters (T=1500 K, P = 1 atm and ρ=1800 kg/cm3* |

The intrinsic fractal dimension can also be determined by observing the aggregate structure factor. This property is used to interpret angular light scattering measurements [??] in the power-law regime. By neglecting the multi-scattering of the light, the structure factor can be theoretically derived from the autocorrelation function [review Sorensen]:

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|  | equ. 21 |

where λ is the wavelength. The lower part of the Figure 6 presents calculated structure factors on the set of aggregates presented in the upper part of the figure, for λ=532 nm. The plain curves correspond to application of equ. 21 on determined autocorrelation functions and the dash curves result of the application of equ. 21 on the theoretical form of autocorrelation function (equ. 20) by injecting the intrinsic fractal dimension reported in Table 2. As predicted by the theory, the dash curves clearly present a linear part in log-log plot corresponding to the power-law regime with a slope opposite to the intrinsic fractal dimension. These dashed curves show that compact aggregates generated when volume fraction is high are characterized by higher values of the intrinsic optical fractal dimension. Concerning the plain curves, even if the global tendency is respected, ripples make the determination of the intrinsic fractal dimension by this approach more difficult and consequently less reliable. This is especially the case for primary sphere polydispersion and high volume fraction. In fact, the main difference between the plain and dash curves is due to the taken into account (plain curves) or not (dash curves) of the primary spheres autocorrelation (for distance r<Rp).

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| *Figure 6 : structural fractal dimension of aggregates determined by pair-autocorrelation and structure factor calculation.* |

### Aggregate size

In the fractal law, the size parameter of aggregates is the gyration radius defined in equ. 2. It can be shown that parameter can also be derived from density autocorrelation function:

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|  | equ. 22 |

where Rgeo is the radius of a sphere centred at aggregate mass centre and with the minimum radius that permits to contain the aggregates. This parameter is better soundly speaking that gyration radius because it permits to evaluate the spatial occupation by the aggregates and it is naturally linked to the ξ parameter in the cutoff function in equ. 20. In a classical approach, the relation between Rg and Rgeo can be theoretically determined by integrating equ. 22 using theoretical expression of the density autocorrelation function (equ. 20) without taking into account the cutoff function.

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|  | equ. 23 |

The same reasoning is used to find a relation between Rg and Rg2D (equ. 24) in order to determine the fractal law from 2D images (TEM).

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|  | equ. 24 |

With that approach, Rgeo and Rg2D are proportional to Rg and these relations have been extensively used in the past [citer ref]. For classical fractal dimension df=1.8, this approach yields to Rgeo/Rg=1.45 whereas for a sphere (Np=1), on can calculates from equ. 2 Rgeo/Rg=1.29 whatever the fractal dimension. This indicates a transition between these two asymptotic ratios that much depends on the number of primary particles. The left part of the Figure 7 presents the time evolution of the ratio between mean geometric radius and mean gyration radius as a function of the mean number of primary spheres per aggregate. It can be shown that needed number of primary particles in order to converge toward a constant ratio is important (≈100) and corresponding asymptotic ratio is 1.84, i.e. 27% higher than theoretical estimation by using equ. 23. Moreover, it is found that ratio does not depend on the radius of the primary spheres and volume fraction. As volume fraction has been shown to have an impact on fractal dimension, one can conclude that Rgeo/Rg does not depend on fractal dimension and theoretical approach leading to equ. 23 (and by extension equ. 24) are probably not adapted. Contrarily to the volume fraction and size of primary sphere, it must be noted that the lower part of the figure shows a dependence of the ratio Rgeo/Rg to the primary sphere polydispsersion.

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| *Figure 7 : Relation between radius of the surrounding sphere Rgeo with gyration and mobility radius and their dependency to the number of primary spheres* |

The right part of the ***Figure 7*** presents the time evolution of the ratio between mean geometric radius and mean mobility radius as a function of the mean number of primary spheres per aggregate. As for ratio Rgeo/Rg, Rgeo/Rm does not show a noticeable dependence on the size of the primary spheres and to the volume fraction (excepted the highest studied volume fraction 100 000 ppm) and it also depends on the primary spheres polydispersion. Contrarily to the ratio Rgeo/Rg , ratio Rgeo/Rm increases with Np without converging toward a constant.

## Conclusion

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