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Full Paper

Population Balance Modeling of Aggregation and Coalescence in Colloidal Systems

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Abstract

A complex interplay between aggregation and coalescence occurs in many colloidal polymeric systems and determines the morphology of the final clusters of primary particles. To describe this process a 2-D population balance equation (PBE) based on cluster mass and fractal dimension is solved, employing the Gaussian basis functions as discretization technique. To prove the general reliability of the model and to show its potential, parametric simulations are performed employing both DLCA and RLCA kernels and different coalescence rates. It turns out that in both DLCA and RLCA regimes a faster coalescence leads to smaller sized and more compact clusters, whereas a slow coalescence promotes the formation of highly reactive fractals, resulting in larger aggregates.

1 Introduction

Colloidal systems are typically defined as kinetically stable,¹ meaning that the dispersed phase will eventually separate from the continuous one in which it is suspended. Two of the key phenomena leading to such a destabilization are aggregation and coalescence of the primary particles originally present in the suspension. It is known that pure aggregation leads to clusters of fractal nature,² whereas pure coalescence (e.g. of bubbles or liquid droplets) typically leads to spherical clusters.^{3, 4} In several systems of practical interest, simultaneous aggregation and coalescence are identified, such as aerosols, soft polymer colloids, liquid-liquid dispersions.^{5, 6} Moreover, in heterogeneous polymerizations such as suspension, emulsion or mini-emulsion free-radical polymerization, coalescence and aggregation play an important role, causing the ideal approximation of monodisperse and stable primary particles to become unrealistic and affecting the produced latex properties.⁷ Also in more complex processes, such as the reactive gelation one,⁸ the interplay of coalescence and aggregation strongly determines the final material properties. The concurrent occurrence of these two phenomena leads namely to a continuous reshaping of the aggregate, driven towards a fractal cluster or a spherical one, according to the relative importance of the two interplaying phenomena.

Modeling approaches aimed to describe the dynamic evolution of the particle size distribution (PSD) in destabilized colloidal systems can be subdivided into two main classes: MonteCarlo (MC) models and deterministic models based on population balance equations (PBEs). MC models allow enucleating physical laws and understanding specific mechanistic aspects,⁹⁻¹¹ while they fail in describing the full evolution of a real system due to their high computational costs. Deterministic models, on the other hand, are typically based on population balance equations and allow accounting for the evolution of the PSD in time. As a

downside, they are mean-field approaches, hence not working in all conditions, e.g. in crowded systems or close to the percolation limit.^{12, 13}

When modeling systems of industrial interest where the knowledge of the complete PSD is needed, the natural choice is to employ PBE. In order to account for the evolution of the particle size distribution (PSD) at least two internal coordinates are necessary: the first internal coordinate accounts for the cluster mass (affected by aggregation), whereas the second one for its shape (affected by coalescence). The second internal coordinate gives information on the shape of the cluster and is therefore essential, as the spatial organization of a cluster strongly affects its reactivity.¹⁴ Typically, for aggregating-coalescing systems, cluster mass (x) (or volume v) and cluster area (a) are employed.^{15, 16}

To mathematically describe the aggregation-coalescence process, an aggregation kernel is needed. Well-accepted kernels for aggregation in the literature are the diffusion-limited-cluster aggregation (DLCA) kernel and the reaction-limited-cluster-aggregation (RLCA), just to mention some of the most popular ones.¹⁴ These kernels depend on cluster mass and fractal dimension (d_f), therefore the choice of x and d_f as internal coordinates is the most convenient. An additional advantage of using these internal coordinates, is that further mechanisms (besides aggregation and coalescence) can be accounted for with minor effort. Restructuring and breakage for instance modify the fractal dimension of the clusters, but not their area. Hence they could be easily introduced in a 2-D PBE with x and d_f as internal coordinates (and with appropriate kinetic laws describing the rate of d_f variation), but not as easily using x and a . Finally, it should be mentioned that detailed solution of 2-D PBE having x and a as internal coordinates have already been proposed.^{6, 16} Using d_f instead of

a represents a more challenging task, as the internal coordinates are not simply additive as in the case of x and a . Kostoglou et al.^{17, 18} solved these equations in the case of aggregation and restructuring with MC stating that the numerical integration is “really a formidable task”.

In this frame, the aim of this paper is to provide the solution of the 2-D PBE employing cluster mass and fractal dimension as internal coordinates. The model is solved by employing a discretization method based on Gaussian basis functions (GBF), already employed and validated elsewhere.¹⁹ This specific method was selected because especially effective in dealing with convolution integrals, which typically occur in coalescing-aggregating systems. The presented model is able to capture the physics of such systems, as shown by parametric simulations performed employing two kernels, the DLCA and the RLCA one, and different rates of coalescence.

2 The model

As mentioned in the introduction, two internal coordinates were chosen to describe the unknown distribution of particles clusters. In particular, the clusters are defined by their cluster mass x and fractal dimension y . Notably, both internal coordinates have been assumed to be continuous. This is clearly an approximation, especially at low cluster masses; nevertheless, the error introduced this way becomes negligible after few aggregation steps and has been considered acceptable. The first index represents the number of particles per cluster, with boundaries $[1, \infty)$, whereas the fractal dimension has boundaries $[1, 3]$ and accounts for the clusters spatial occupancy.

Let us define the cluster density function $f(x, y, t)$ such that $f(x, y, t)dx dy dt$ represents the concentration of clusters consisting of x to $x + dx$ primary particles and having fractal dimension from y to $y + dy$ in the time interval $t + dt$. Only two phenomena are considered to affect this density function, aggregation and coalescence: accordingly, the evolution of $f(x, y, t)$ in time is described by the following 2-D PBE:

$$\begin{aligned} \frac{\partial f(x, y, t)}{\partial t} + \underbrace{\frac{\partial}{\partial y}(f(x, y, t)v(x, y))}_{\mathcal{I}_A} = \\ - \underbrace{f(x, y, t) \int_1^\infty \int_{y_m}^{y_M} \beta(x, x_1, y, y_1) f(x_1, y_1, t) dy_1 dx_1}_{\mathcal{I}_B} \\ + \underbrace{\frac{1}{2} \int_1^\infty \int_1^\infty \int_{y_m}^{y_M} \int_{y_m}^{y_M} \beta(x_1, x_2, y_1, y_2) f(x_1, y_1, t) f(x_2, y_2, t) \mu dy_1 dy_2 dx_1 dx_2}_{\mathcal{I}_C} \end{aligned} \quad (1)$$

$$\mu = \delta(x - g_1(x_1, x_2)) \delta(y - g_2(x_1, x_2, y_1, y_2)) \quad (2)$$

Where y_m is the minimum fractal dimension (the value established in the case of pure aggregation, hence defined through the aggregation regime), whereas y_M is the maximum fractal dimension, corresponding to full coalescence, ($y_M = 3$).

The influence of coalescence on the PBE can be appreciated in term $\mathcal{I}_A$, which accounts for the variation of the cluster population due to the rate of variation in time of its fractal dimension, $v(x, y)$. In other words, term $\mathcal{I}_A$ is a Liouville term, as already detailed by Koch and Friedlander.¹⁵ Term $\mathcal{I}_B$, in equation (1), accounts for the disappearance of x -sized clusters with fractal dimension y aggregating with clusters of any other size and fractal dimension. The formation of x -sized clusters with fractal dimension y (term $\mathcal{I}_C$) on the other hand, is obtained by aggregation of two clusters satisfying the constitutive laws defined in equation (2).

Before solving the 2-D PBE, one needs to choose an aggregation kernel (present in terms $\mathcal{I}_B$ and $\mathcal{I}_C$), to define the constitutive laws g_1 and g_2 ¹⁷ (term $\mathcal{I}_C$) and to introduce an equation describing the time-variation of the fractal dimension, $v(x, y)$ (occurring in term $\mathcal{I}_A$).

Concerning the aggregation Kernel, $\beta(x_1, x_2, y_1, y_2)$, both the DLCA (equation (3)) and the RLCA (equation (4)) will be employed:

$$\beta(x_1, x_2, y_1, y_2) = \frac{2}{3} \frac{k_B T}{\eta} (x_1^{1/y_1} + x_2^{1/y_2}) (x_1^{-1/y_1} + x_2^{-1/y_2}) \quad (3)$$

$$\beta(x_1, x_2, y_1, y_2) = \frac{2}{3} \frac{k_B T}{\eta} \frac{(x_1 x_2)^\gamma}{W} (x_1^{1/y_1} + x_2^{1/y_2}) (x_2^{-1/y_1} + x_2^{-1/y_2}) \quad (4)$$

Note that for the RLCA Kernel the formulation suggested by Family et al.²⁰ has been selected, but any other one (e.g. Odriozola et al.²¹ or Ball et al.²²) could have been chosen with no impact on the numerical aspects, as detailed in the subsequent section.

The aim of the constitutive laws g_1 and g_2 in term $\mathcal{I}_C$ is to select among all possible cluster combinations only those actually forming a cluster of the desired size x and fractal dimension y . They are defined as:

$$g_1(x_1, x_2) = x_1 + x_2 \quad (5)$$

$$g_2(x_1, x_2, y_1, y_2) = \frac{y_m \ln(x_1 + x_2)}{\ln(x_1^{y_m/y_1} + x_2^{y_m/y_2})} \quad (6)$$

The first constitutive law (equation (5)) is simply an additive law, indicating that if a cluster of size x is sought, the cluster masses of the combining clusters x_1 and x_2 added up have to give x . As the fractal dimension is not an additive property, a more complex constitutive law (g_2 , equation (6)) was employed, as suggested in previous works.^{17, 18} In particular, the fractal dimension of a cluster formed by aggregation of two clusters having different fractal dimensions, is a function of their cluster masses (x_1 and x_2) and their fractal dimensions (y_1 and y_2) as well as of the aggregation regime, which defines the minimum fractal dimension, y_m . For the DLCA case, $y_m = 1.8$, while for RLCA, $y_m = 2.1$, as these are representative fractal dimensions for these regimes.² Note that, when $y_1 = y_2 = y_m$ the constitutive law is always satisfied, as g_2 is always equal to y_m (equation (6)).

Finally, let us discuss the rate of coalescence $\nu(x, y)$, i.e. the time-variation of the fractal dimension appearing in term $\mathcal{I}_A$ of equation (1). In this frame the fractal dimension is

changing due to coalescence only, as in the limit of pure aggregation no variation in fractal dimension occurs, once the aggregation regime is defined. Therefore, the required function needs to be in the form of a relaxation law, i.e. a growing function approaching an asymptotic value, as coalescence is a process in which the primary particles constituting a cluster inter-diffuse in one another and eventually turn into a single, compact sphere, reaching thus the maximum fractal dimension of 3. The oversimplified equation (7) fulfills the aforementioned criterion:

$$v(x, y) = \frac{1}{\tau_c(x)} (y_M - y) \quad (7)$$

As long as the fractal dimension is smaller than the maximum one, equation (7) predicts an increase of fractal dimension until the maximum value is reached and the process ends. Notably, the rate with which this coalescence process occurs, $v(x, y)$, is inversely proportional to the characteristic time of coalescence τ_c . The characteristic time of coalescence was defined by Frenkel²³ and can be generalized for x -sized clusters as in equation (8):¹⁵

$$\tau_c(x) = x^{1/3} \frac{r_1 \eta_p}{\sigma_p} = x^{1/3} \tau_c(1) \quad (8)$$

where x represents the mass of the cluster considered, r_1 the radius of a primary particle, η_p its viscosity and σ_p its interfacial surface tension. Kinetic laws of coalescence similar to equation (7) have already been reported in the literature.^{18, 24} Notably, if in the colloidal system under investigation a polymerization reaction is occurring (e.g. suspension or emulsion polymerization), the characteristic time of coalescence becomes conversion-dependent and further contributions should be added to equation (8).

3 Numerical solution

The numerical solution of the aforementioned 2-D PBE has been pursued by a previously proposed discretization technique based on Gaussian basis functions (GBF).¹⁹ Before discussing the discretization procedure, whose full details are reported in the Appendix, some manipulations of Equation (1) are required.

3.1 Modified Equations

Employing the notation for coalescence speed $v(x, y)$ as defined by equation (7), the term $\mathcal{I}_A$ reads as:

$$\mathcal{I}_A = \frac{1}{\tau_c(1)} x^{-1/3} \left(\frac{\partial f(x, y, t)}{\partial y} (y_M - y) - f(x, y, t) \right) \quad (9)$$

From the last expression it becomes clear that a boundary condition is necessary to guarantee the solution uniqueness. Thus we enrich the formulation (1) with the boundary condition,

$$\left. \frac{\partial f}{\partial y} \right|_{y=y_m} = 0 \quad (10)$$

that forbids flux of particles beyond the coagulation regime y_m . The coagulation kernel, which defines the reactivity rate for a pair of particles (x_1, y_1) and (x_2, y_2) , can be represented as a sum of separable kernels. In case of DLCA the kernel has the form:

$$\begin{aligned} \beta(x_1, x_2, y_1, y_2) &= \frac{2}{3} \frac{k_B T}{\eta} \left(x_1^{1/y_1} + x_2^{1/y_2} \right) \left(x_1^{-1/y_1} + x_2^{-1/y_2} \right) = \\ &\frac{2}{3} \frac{k_B T}{\eta} \left(2 + \beta_1(x_1, y_1) \beta_2(x_2, y_2) + \beta_2(x_1, y_1) \beta_1(x_2, y_2) \right) \end{aligned} \quad (11)$$

where:

$$\begin{aligned} \beta_1(x, y) &= x^{1/y} \\ \beta_2(x, y) &= x^{-1/y} \end{aligned} \quad (12)$$

In the RLCA case, an analogous separation is made:

$$\begin{aligned}\beta(x_1, x_2, y_1, y_2) &= \frac{2}{3} \frac{k_B T}{\eta} \frac{1}{W} (x_1 x_2)^\gamma (x_1^{1/y_1} + x_2^{1/y_2}) (x_1^{-1/y_1} + x_2^{-1/y_2}) = \\ &\frac{2}{3} \frac{k_B T}{\eta} \frac{1}{W} (2\beta'_0(x_1)\beta'_0(x_2) + \beta'_1(x_1, y_1)\beta'_2(x_2, y_2) + \beta'_2(x_1, y_1)\beta'_1(x_2, y_2)),\end{aligned}\tag{13}$$

where:

$$\begin{aligned}\beta'_0(x) &= x^\gamma \\ \beta'_1(x, y) &= x^{1/y+\gamma} \\ \beta'_2(x, y) &= x^{-1/y+\gamma}\end{aligned}\tag{14}$$

The integration with respect to four variables x_1, x_2, y_1, y_2 that appears in $\mathcal{I}_C$ can be expressed in terms of a double integral, significantly reducing the computational effort required.¹⁸ By substituting $x_2 = x - x_1$ (compare to condition (5)), it is possible to eliminate one integral dimension. A similar, though more elaborated substitution allows a further simplification. In particular, the merging law $g_2(x_1, x_2, y_1, y_2)$, defining all possible combinations of pairs (x_1, y_1) and (x_2, y_2) that aggregate to form a particle (x, y) , is reformulated by narrowing the integration domain in $\mathcal{I}_C$ to all points that satisfy the following constraint:

$$\frac{y_m \ln(x_1 + x_2)}{\ln(x_1^{y_m/y_1} + x_2^{y_m/y_2})} - y = 0\tag{15}$$

The integration with respect to y_1, y_2 in term $\mathcal{I}_C$ is viewed as a single layer integral,²⁵ and can be reformulated as a line integral on the collection of parametric lines.²⁵

$$L_{x_1, x_2, y}(s) = (y_1(s), y_2(s)), \quad s \in [0, 1]\tag{16}$$

that solve equation (15) for each given set of values $\{x_1, x_2, y\}$. To recover all points from L , equation (15) can be solved numerically for every requested set $\{x_1, x_2, y\}$, or an analytical expression for $(y_1(s), y_2(s))$ can be used. In the latter case, an analytical form can be worked out from (15):

$$\begin{aligned}
y_1 &= g_2^{-1}(x_1, x_2, y_2, y) := \frac{y_m \ln x_1}{\ln((x_1 + x_2)^{y_m/y} - x_2^{y_m/y_2})}; \\
y_2 &= g_2^{-1}(x_1, x_2, y_1, y) := \frac{y_m \ln x_2}{\ln((x_1 + x_2)^{y_m/y} - x_1^{y_m/y_1})}.
\end{aligned} \tag{17}$$

Now, the integration lines (16) can be parameterized as:

$$\begin{cases} y_2(x_1, x_2, s, y) = g_1^{-1}(x_1, x_2, s(b-a) + a, y); \\ y_1(x_1, x_2, s, y) = s(b(x_1, x_2, y) - a(x_1, x_2, y)) + a(x_1, x_2, y). \end{cases} \quad s \in [0, 1]. \tag{18}$$

Here $a(x_1, x_2, y)$ and $b(x_1, x_2, y)$ set bounds on $y_1(x_1, x_2, s, y)$, that is:

$$y_m \leq a(x_1, x_2, y) \leq y_1(x_1, x_2, s, y) \leq b(x_1, x_2, y) \leq y_M \tag{19}$$

By substituting the marginal values $y_{\min}, y_{\max}$ into relations (18) one obtains the expressions

for the bounds a and b . Indeed, assuming $1 < x_1 \leq x_2$, we have:

$$\begin{aligned}
a(x_1, x_2, y) &= \begin{cases} g_1^{-1}(x_1, x_2, y_M, y), & g_2^{-1}(x_1, x_2, y_M, y) > y_M \\ y_m, & g_2^{-1}(x_1, x_2, y_M, y) \leq y_M \end{cases} \\
b(x_1, x_2, y) &= y_M
\end{aligned} \tag{20}$$

As for the case $x_1 > x_2 > 1$, one should note that the symmetry

$g(x_1, x_2, y_1, y_2) = g(x_2, x_1, y_2, y_1)$ enables us to use the collection of lines discussed earlier,

equations (18) and (20).

The ideas described above result in a reduction of the integral dimensionality: only two dimensions are left instead of four present in the initial formulation; explicitly:

$$\begin{aligned}
&\int_1^\infty \int_1^{y_M} \int_{y_m}^{y_M} \int_{y_m}^{y_M} \beta(x_1, x_2, y_1, y_2) f(x_1, y_1, t) f(x_2, y_2, t) \mu dy_1 dy_2 dx_1 dx_2 = \\
&\int_1^\infty \int_{y_m}^{y_M} \int_{y_m}^{y_M} \beta(x_1, x - x_1, y_1, y_2) f(x_1, y_1, t) f(x - x_1, y_2, t) \delta(g(x_1, x - x_1, y_1, y_2) - y) dy_1 dy_2 dx_1 = \\
&\int_1^\infty \int_{L(s)} \beta(x_1, x - x_1, y_1(x_1, x - x_1, s, y), y_2(x_1, x - x_1, s, y)) f(x_1, y_1(x_1, x - x_1, s, y), t) \times \\
&\quad f(x - x_1, y_2(x_1, x - x_1, s, y), t) J(x_1, x - x_1, s, y) ds dy_1
\end{aligned} \tag{21}$$

where

$$J(x_1, x_2, s, y) = \left(\frac{\partial y_1^2}{\partial s}(x_1, x_2, s, y) + \frac{\partial y_2^2}{\partial s}(x_1, x_2, s, y) \right)^{1/2} \times \\ \left(\frac{\partial g_2^2}{\partial y_1}(y_1(x_1, x_2, s, y), y_2(x_1, x_2, s, y)) + \frac{\partial g_2^2}{\partial y_2}(y_1(x_1, x_2, s, y), y_2(x_1, x_2, s, y)) \right)^{-1/2}$$

Due to technical aspects related to the numerical implementation, it is convenient to separate the balance of the primary particles from the overall distribution $f(x, y, t)$. Therefore, a specific differential equation for the primary particles, $s(t)$, is written:

$$s'(t) = -s(t) \left(4k_p s(t) + \underbrace{\int_{y_m}^{y_M} \int_2^\infty \beta(x, 1, y, y_M) f(x, y, t) dx dy}_E \right). \quad (22)$$

Here, the term E denotes the total concentration of non-primary particles that can react with a primary one. On another hand, the contribution of primary particles to the overall balance (1) emerges as the following additional term:

$$\mathcal{I}_D = 4s(t)^2 \delta(x-2, y-y_{\min}) \\ + \frac{1}{2} s(t) \beta(1, x-1, m, y) f(x-1, g_2^{-1}(1, x-1, m, y), t) \\ - s(t) \beta(1, x-1, m, y) f(x, y, t). \quad (23)$$

Finally, the complete equation set ready for discretization reads as:

$$\left\{ \begin{aligned}
& \frac{\partial f(x, y, t)}{\partial t} = - \underbrace{\frac{1}{\tau_c(1)} x^{-1/3} \left(\frac{\partial f(x, y, t)}{\partial y} (y_M - y) - f(x, y, t) \right)}_A \\
& \quad - \underbrace{f(x, y, t) \int_1^{y_M} \int_{y_m} \beta(x, x_1, y, y_1) f(x_1, y_1, t) dy_1 dx_1}_B \\
& \quad + 4s(t)^2 \delta(x - 2, y - y_m) - s(t) \beta(1, x - 1, m, y) f(x, y, t) \\
& \quad + \underbrace{\frac{1}{2} s(t) \beta(1, x - 1, m, y) f(x - 1, g_2^{-1}(1, x - 1, m, y), t)}_D \\
& \quad + \frac{1}{2} \int_{L(s)} \beta(x_1, x - x_1, y_1(x_1, x - x_1, s, y), y_2(x_1, x - x_1, s, y)) f(x_1, y_1(x_1, x - x_1, s, y), t) \times \\
& \quad \quad \quad \underbrace{f(x - x_1, y_2(x_1, x - x_1, s, y), t) J(x_1, x - x_1, s, y) ds dx_1}_C \\
& \frac{ds(t)}{dt} = -s(t) \left(4k_p s(t) + \underbrace{\int_{y_m}^{y_M} \int_2^\infty \beta(x, 1, y, y_M) f(x, y, t) dx dy}_E \right)
\end{aligned} \right. \tag{24}$$

3.2 Discretization

According to the chosen discretization technique based on GBF, the distribution $f(x, y, t)$ is approximated by the distribution $\hat{f}(x, y, t)$ that is defined as the following linear combination:

$$\hat{f}(x, y, t) = \sum_{i=1}^N \alpha_i(t) \phi_i(x, y) \tag{25}$$

where the two-dimensional basis functions $\phi_i(x, y)$ are 2-D Gaussian distributions:

$$\phi_i(x, y) = e^{-\frac{(x-x_i)^2}{\sigma_{x,i}}} e^{-\frac{(y-y_i)^2}{\sigma_{y,i}}} . \tag{26}$$

The main advantage of employing GBF for the discretization lies in the convenient properties Gaussian functions have. As already discussed in a previous work, the convolution of two Gaussians is once more a Gaussian, whose mean and standard deviation can be calculated

starting from the means and standard deviations of the Gaussians to be convolved.¹⁹ Exploiting this property, the cumbersome convolution present in equation (24) can be dealt with in a relatively simple way. Notably, in the present case the weighted convolution to be dealt with involve non-integer weights due to the DLCA and RLCA kernels employed. Nevertheless, with some linear transformations it is always possible to reduce the problem to that of a non-weighted convolution, as mentioned already in Kryven et al.¹⁹ Therefore, the implementation of different kernels becomes straightforward and proofs once more the versatility of GBF. A further advantage of using GBF is the possibility to re-write the discretized balance in a quite compact vector form, as detailed in the next paragraph.

The time dependent expansion coefficients $\alpha_i(t)$, organized as the column vector $\boldsymbol{\alpha}(t)$, are obtained from the following system of non-linear differential equations:

$$\begin{cases} \dot{\boldsymbol{\alpha}}(t) = \hat{\mathcal{I}}_A \boldsymbol{\alpha}(t) + \hat{\mathcal{I}}_B \boldsymbol{\alpha}(t) + \hat{\mathcal{I}}_C \boldsymbol{\alpha}(t) + \hat{\mathcal{I}}_D \boldsymbol{\alpha}(t) \\ s'(t) = -s(t)(4s(t) + \hat{\mathcal{I}}_E \boldsymbol{\alpha}(t)) \end{cases} \quad (27)$$

where $\mathcal{I}_A, \dots, \mathcal{I}_E$, defined in Appendix 1, represent approximations of the corresponding terms in the equation system (24). Time integration of Equation (27) with the initial condition:

$$s(0) = M \quad (28)$$

yields an approximation of the unknown two dimensional density distribution $f(x, y, t)$. Note that the primary particle conversion is readily obtained as:

$$\chi(t) = \frac{M - s(t)}{M} \quad (29)$$

The success of the discretization approach is strongly dependent on the system of basis function centers x_i, y_i and on their parameters $\sigma_{x,i}, \sigma_{y,i}$. While the geometric grid has been widely used to discretize the classical aggregation problem,²⁶ a strategy for the fractal dimension is less obvious, as it depends on the interplay of the coalescence and aggregation

rates. Therefore, the ratio of the two process rates, $p(x, y)$ (defined in equation (30)), is introduced and employed to identify a proper grid.

$$p(x, y) = \frac{v_{COAL}(x, y)}{v_{AGG}(x, y)}$$

where:

$$\begin{aligned} v_{AGG}(x, y) &= \frac{8}{3} \frac{k_B T}{\eta} M \frac{P(x, x)}{W} \quad \text{with} \quad \begin{cases} W = 10^0 \text{ and } P(x, x) = 10^0 & DLCA \\ W = 10^5 \text{ and } P(x, x) = x^{2\lambda} & RLCA \end{cases} \quad (30) \\ v_{COAL}(x, y) &= \tau_C^{-1}(1) x^{-1/3} (3 - y) \quad \text{with} \quad \begin{cases} \tau_C(1) = 10^{-1} \text{ s} & DLCA \\ \tau_C(1) = 10^4 \text{ s} & RLCA \end{cases} \end{aligned}$$

For sake of simplicity, v_{AGG} , representing the aggregation rate, has been estimated assuming aggregation between equally-sized clusters, which in the DLCA regime results in a size-independent rate, whereas in the RLCA case it is proportional to $x^{2\lambda}$. Despite this limitation, the evaluation of $p(x, y)$ allows one to understand which is the dominant mechanism, coagulation or coalescence. This is shown in Figure 1, where the plane cluster size vs. fractal dimension is divided in different domains characterized by the value of $p(x, y)$. Such values span through several orders of magnitude in both the DLCA and RLCA cases when using the selected set of parameter values. This indicates that the interplay of the two mechanisms dramatically changes with size and fractal dimension of the cluster considered. Therefore, to reduce numerical instabilities, we require the distance between two adjacent basis function centers (y_a, y_b) to be proportional to $p(x, y)^{-1}$, i.e.:

$$y_a - y_b \propto p(x, y)^{-1} \quad (31)$$

FIGURE 1

On the other hand, the connectivity parameters $\sigma_{x,i}, \sigma_{y,i}$ are chosen as a function of the distance between adjustment basis centers, as suggested previously.²⁷ Finally, assuming the

system of basis functions is given, the time independent components of the discretized equation (27) are computed only once and before the ODE integration. This principle allows major economy of computational time and is of great use especially when repeating the simulation for different parameter sets (e.g. for parameter estimation).

The cpu-time spent to build constant matrices from Appendix 1 was 13 hours, whereas integration times were in the order of 20-30 min running a Matlab v7.14 script on a personal computer with a 2.8 GHz processor. Considerable reductions in process times can be achieved by employing low-level programming languages (e.g. Fortran or C++ code) instead. In particular, 881 two-dimensional basis functions for discretizing have been employed, i.e. 881 ODE have been solved.

4 Results

Implementing the aforementioned discretization technique, a series of parametric simulations could be carried out to explore the dynamic behavior of the 2-D distribution under different conditions. The set of parameter values employed in the simulations is detailed in Table 1.

TABLE 1

The values employed refer to water as a continuous phase as this is a typical solvent employed for colloidal particles in a great deal of application. $W = 10^5$ has been chosen as Fuchs stability ratios of the same order of magnitude have already been reported in the literature for water-based systems.²⁸ The choice of the characteristic times of coalescence will be discussed in the next sections.

Notably, given the primary particle radius of 50 nm and their concentration of $10^{17} \text{ \#/m}^3$ the system has an occupied volume fraction of $5.2 \cdot 10^{-5}$; hence, the aggregation-coalescence process is studied in fairly diluted conditions, where the mean-field approximation underlying the PBE approach has practically no impact. First the results employing the DLCA kernel are discussed; afterwards the RLCA case is dealt with and a comparison between the two conditions is attempted.

4.1. DLCA Kernel

When employing the DLCA Kernel for the simulation, it is assumed that every collision between clusters leads to the formation of a larger cluster, having size equal to the sum of the two colliding aggregates. In particular it should be noted that the DLCA Kernel favors the aggregation of large-small clusters, whereas equally sized clusters react with one another with the same rate, disregarding of their size, as can be easily seen from equation (3). The

shape of the distribution employing the DLCA Kernel can be appreciated in Figure 2 **Error!**
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FIGURE 2

Figure 2 shows the distribution for the DLCA regime at a primary particle conversion $\chi = 0.87$ using a characteristic time of coalescence $\tau_c(1) = 10^{-1} s$. The distribution develops towards two asymptotic directions, one at low and one at high clusters masses. In other words, the clusters exhibit a distribution of fractal dimensions which ranges from 1.8 to 2.5 approximately. Notably, 1.8 represents the minimum fractal dimension which can be obtained in the present case due to the DLCA aggregation regime. A fractal dimension of 2.5 instead could be theoretically overcome if enough time for a higher extent of coalescence was given. Notably, smaller clusters exhibit a broader distribution of fractal dimensions than larger ones. Actually, starting from a certain cluster size (x about 50), the fractal dimension distribution narrows significantly and reaches values of about 1.9. This reflects the physics of the system: clusters have a rate of coalescence which is inversely proportional to the characteristic time of coalescence (equation (8)), hence their rate of coalescence reads $\nu(x, y) \propto x^{-1/3}$, x being the cluster mass. The latter relationship indicates that coalescence progressively slows down with increasing cluster mass. The aforementioned reasoning indicates clearly the necessity of employing a time-dependent fractal dimension in an aggregating-coalescing colloidal system, as this would otherwise lead to a wrong kernel estimation eventually resulting in incorrect predictions. In fact, in such a system, the shape of the distribution is dependent on the ratio of coalescence and aggregation extents. These two quantities are dependent from one another: coalescence can occur only after aggregation takes place, whereas cluster aggregation

depends on the cluster diffusivity and size, quantities which are both dependent on the fractal dimension and hence on the coalescence extent.

To get insights on the role of coalescence in the different stages of the aggregation process, simulations were performed employing two different characteristic times of coalescence, namely a) $\tau_c(1) = 10^0 s$ and b) $\tau_c(1) = 10^{-1} s$. The results are shown in Figure 3 where the cluster size is plotted against primary particle conversion (defined as in equation (29)) and fractal dimension, whereas the greyscale (color on line) reflects the cluster concentration. The coalescence rate affects the distribution shape in time: in the case of slower coalescence (case a), the clusters fractal dimension does not increase significantly upon primary particle conversion, ranging between 1.8 and 2.4. This happens only after 90% of the primary particle aggregated, indicating that several aggregation steps had to occur, before coalescence could affect significantly the fractal dimension of the clusters. Moreover, only smaller clusters reach such fractal dimensions, whereas larger clusters maintain a fractal dimension very close to 2. On the other hand, when coalescence is faster (case b) the fractal dimension range of the clusters is much broader, from 1.8 to 3.0, a broadness reached already before 90% conversion of primary particles. Once again, it's rather the small clusters which exhibit such fractal dimension, although the larger clusters have in this case an average fractal dimension of about 2.2, significantly larger when compared to the case a).

FIGURE 3

To further elucidate the role of coalescence during the aggregation process, the contour lines of the 2-D distribution have been plotted in Figure 4 at two different conversions ($\chi = 0.87, \chi = 0.99$) and coalescence times ($\tau_c(1) = 10^0 s, \tau_c(1) = 10^{-1} s$). Comparing the

lines at conversion $\chi = 0.87$ at two different coalescence rates (panels *a* and *c*), it is clear that when coalescence is faster (panel *a*) the fractal dimension distribution is broader and spans between 2 and 2.6 (compared to the much smaller range 1.8-2.1 for slower coalescence at the same conversion, panel *c*). This difference results in a higher reactivity of the more open clusters, which leads to a slightly larger maximum cluster size. The main difference between these clusters though, lies in their spatial organization as fractal dimensions of 1.8 indicate very open clusters, while 2.6 quite compact ones. The same result holds when comparing the two distributions at almost complete primary particle conversion, $\chi = 0.999$: when coalescence is faster (panel *b*) fractal dimensions are broader (values range from 2 to 3), whereas for slower coalescence (panel *d*) the fractal dimensions are confined between 1.9 and 2.6. Clearly both ranges are extended when compared to the case at $\chi = 0.87$, as more time for coalescence to restructure the cluster passed. Once more, clusters with a smaller fractal dimension, hence obtained with slower coalescence, tend to react faster and produce slightly larger cluster size ($x = 850$ vs. 750).

FIGURE 4

The previous results (Figure 2-Figure 4) prove that coalescence plays a significant role in DLCA aggregation and it has to be accounted for to ensure accurate model predictions. On the other hand it is worth to remember that DLCA aggregation occurs in quite small time frames, as its characteristic time, $\tau_{AGGR}^{DLCA} \approx W / (M_0 \beta_{11})$, is less than $10^0 s$ in the present system. Therefore, coalescence has to be quite fast to actually affect the cluster mass distribution while aggregation occurs: this was the reason for the choice of the specific values $\tau_c(1) = 10^{-1} s$ and $\tau_c(1) = 10^0 s$.

4.2 RLCA Kernel

Another interesting Kernel to be employed to appreciate the competition between aggregation and coalescence is the RLCA Kernel (equation (4)), as it represents the coagulation rates of a typical colloidal system in the presence of stabilizers (emulsifiers, block-copolymers). In the parametric studies carried out in this frame, $W = 10^5$ and characteristic times of coalescence of 10^4 s and 10^5 s have been used.

Notably, the minimum fractal dimension considered in this case is 2.1, whereas in the DLCA case it was 1.8, being these two values typically accepted in the literature as representative of the respective aggregation regimes.² To ensure a fair comparison between simulations employing such different kernels, a constant value of the ratio of the aggregation rate to coalescence rate has been chosen. In other words, to keep the ratio $p(x, y)$ (equation (30)) constant, the ratio $W / \tau_{c,1}$ was adjusted in the RLCA cases to be equal to the DLCA ones. In this case $\tau_{AGGR}^{RLCA} \approx W / (\beta_{11}M) \approx 8 \times 10^4 s$, and the chosen coalescence characteristic times were $\tau_c(1) = 10^4 s$ and $\tau_c(1) = 10^5 s$, whereas $\tau_{AGGR}^{DLCA} \approx W / (\beta_{11}M) \approx 8 \times 10^{-1} s$ and the coalescence characteristic times were $\tau_c(1) = 10^{-1} s$ and $\tau_c(1) = 10^0 s$, respectively.

A typical 2-D distribution at $\chi = 0.87$ for the RLCA Kernel can be seen in Figure 5. As in the case of the DLCA Kernel (**Error! Reference source not found.**Figure 2), the distribution surface develops towards two main, asymptotic directions: smaller clusters tend to have a wide fractal dimension distribution, whereas larger cluster ($x > 50$) a narrower one, with average value around 2.2. The physics underlying this different behavior is clearly the same: smaller cluster tend to coalesce faster than larger ones. In the RLCA case under examination, the maximum cluster sizes reached are quite larger when compared to the DLCA case at the same conversion (**Figure 2**)

This is due to the fact that large-large cluster interaction is favored in RLCA (due to the $(x_1 x_2)^\gamma$ proportionality in the Kernel, equation (4)), which leads to the formation of larger cluster at constant primary particle conversion.

FIGURE 5

When comparing the contour lines in the RLCA case at two different primary particle conversions, $\chi = 0.70$ and $\chi = 0.87$, and two different coalescence times, $\tau_c(1) = 10^4 s$ and $\tau_c(1) = 10^5 s$, as shown in Figure 6, it is confirmed that a faster coalescence implies a slower aggregation rate. This can be best seen when comparing panel *b* and *d* (comparing hence the contour lines at the same conversion $\chi = 0.87$ for $\tau_c(1) = 10^4 s$ and $\tau_c(1) = 10^5 s$, respectively). In the case of slower coalescence (panel *d*), clusters made of up to 1000 primary particles are found, whereas the maximum sized aggregates in panel *b*, are of about 250. With the RLCA aggregation Kernel this difference becomes

more evident than in the DLCA case (panel *b* and *d* of Figure 5

Figure 5

), where the difference between the maximum sized clusters was smaller, once again due to the specific Kernel type. Moreover, the faster the coalescence, the wider the distribution of fractal dimensions (panels *a* and *b*): d_f reaches values up to 2.6, whereas with a slower coalescence, fractal dimension values smaller than 2.3 are found (panels *c* and *d*).

FIGURE 6

Finally, some interesting conclusions can be drawn when comparing the DLCA and RLCA fractal dimension distributions as a function of conversion at the same **conversion** ($\chi=0.87$) and different $\tau_c(1)$ (Figure 7). It turns out that both aggregation regimes lead to a

bimodality when coalescence is fast enough (compare panels *a* and *c* of Figure 7

Figure 7

). On the other hand, such bimodality is not observed when coalescence is slow (panels *b* and *d*) and only a drift from the starting fractal dimension to a slightly larger one is observed. When coalescence is occurring fast enough, smaller clusters will actually coalesce, leading to larger fractal dimension values. Larger cluster will also coalesce, but to a minor extent, as the coalescence rate is inversely proportional to the coalescence characteristic time (equation (8)), resulting thus in $v(x,y) \propto x^{-1/3}$. Therefore, a smaller fractal dimension will be found for such larger clusters, explaining the bimodality observed in Figure 7.

FIGURE 7

5 Conclusions

In the present paper, the 2-D population balance for a stagnant aggregating-coalescing colloidal system has been solved employing cluster mass and fractal dimension as internal coordinates. In particular, DLCA and RLCA kernels have been used, even though any other type of Kernel could have been considered without affecting the solution strategy. The Gaussian basis functions method has been employed for discretization and revealed its power in dealing with convolutions.

It was confirmed that coalescence significantly influences the shape and the aggregation rate of clusters, by affecting their fractal dimension. This is valid especially for smaller sized cluster, rather than for larger sized ones, on which coalescence has a smaller impact. As a matter of fact this distinction between smaller and larger clusters leads to the presence of two asymptotic behaviors in terms of cluster masses: smaller cluster will exhibit a larger fractal dimension distribution (up to values of 3), whereas larger clusters maintain the fractal dimension characteristic of the aggregation regime assumed (1.8 for DLCA and 2.1 for RLCA).

This 2-D formulation, having cluster mass and fractal dimension as internal coordinates, allows not only to account for coalescence, but in general for any other phenomena affecting the fractal dimension of the aggregating clusters, such as breakage or restructuring. Notably, also modeling of heterogeneous polymerization benefits of such a model where all the aforementioned phenomena occur. In other words, this same modeling and the corresponding solution can be easily extended to include other important phenomena occurring in colloidal system and could become a valuable tool to elucidate their complex interplay.

Appendix 1

The discretized differential operator $\mathcal{I}_A$ has the form:

$$\mathcal{I}_A \mathbf{a}(t) = \mathbf{A}^{-1} \mathbf{D} \mathbf{a}(t) \quad (32)$$

where:

$$\begin{aligned} (\mathbf{D})_{i,j} &= - \left(\frac{\partial v(x, y)}{\partial y} \phi_j(x, y) + \frac{\partial \phi_j(x, y)}{\partial y} v(x, y) [y_i \neq y_{\min}] \right) \Bigg|_{x=x_i, y=y_i} \\ &= \tau_{c,l}^{-1} x_i^{-1/3} (1 - 2\sigma_j(x_i - x_j)(y_{\max} - y_i)[y_i \neq y_{\min}]) \phi_j(x_i, y_i) \end{aligned} \quad (33)$$

$$(\mathbf{A})_{i,j} = \phi_j(x_i, y_i)$$

where the Iverson bracket $[y_i \neq y_{\min}]$ equals one if the conjunction is true and zero otherwise. The bracket implements the boundary condition (10).

The approximation of the consumption term $\mathcal{I}_B$ is implemented as:

$$(\mathcal{I}_B \mathbf{a}(t))_l = \sum_{k=1}^n a_{l,k} \mathbf{a}(t) \mathbf{C}_k^- \mathbf{a}(t), \quad (34)$$

where:

$$(\mathbf{C}_k^-)_{i,j} = -\phi_i(x_k, y_k) \int_0^\infty \int_{y_{\min}}^{y_{\min}} \beta(x_k, x, y_k, y) \phi_j(x, y) dx dy, \quad (35)$$

and $a_{i,j}$ are the coefficients of the inverse interpolation matrix (33):

$$a_{i,j} = (\mathbf{A}^{-1})_{i,j}. \quad (36)$$

The nonlinear transformation $\mathcal{I}_C$ is used to approximate the convolution integral $\mathcal{I}_C$:

$$\mathcal{I}_C \mathbf{a}(t) = \sum_{k=1}^n a_{l,k} \mathbf{a}(t) \mathbf{C}_k^+ \mathbf{a}(t). \quad (37)$$

where $\mathbf{C}_k^+$ is a collection of $n \times n$ matrices whose generic element is:

$$\begin{aligned} (\mathbf{C}_k^+)_{i,j} = & \frac{1}{2} \int_0^{x_k} \int_{L(s)} \beta(x, x_k - x, y_1(x, x_k - x, s, y_k), y_2(x, x_k - x, s, y_k)) \\ & \times \phi_i(x, y_1(x, x_k - x, s, y_k)) \phi_j(x_k - x, y_2(x, x_k - x, s, y_k)) \\ & \times J(x, x_k - x, s, y_k) ds dx \end{aligned} \quad (38)$$

The discretization for the term $\mathcal{I}_D$ has the form:

$$\mathcal{I}_D \mathbf{a}(t) = 2 s(t)^2 \mathbf{a}_{2,m} + \frac{1}{2} s(t) \mathbf{A}^{-1} \mathbf{C}^1 \mathbf{a}(t), \quad (39)$$

$$\begin{aligned} (\mathbf{C}^1)_{i,j} = & \beta(1, x-1, m, y_2(1, m, x_i-1, y_i)) \\ & \times \phi_j(x_i-1, y_2(1, x_i-1, m, y_i)) - \beta(1, m, x_i, y_i) \phi_j(x_i, y_i). \end{aligned} \quad (40)$$

Here $\mathbf{a}_{2,m}$ resembles the expansion of the type (25) for distribution of doublets $(2, m)$:

$$\begin{aligned} \mathbf{a}_{2,m} = & \mathbf{A}^{-1} (s_1, s_2, \dots, s_n)^T; \\ s_i = & \begin{cases} 1, & x_i = 2, y_i = m; \\ 0, & \text{otherwise.} \end{cases} \end{aligned} \quad (41)$$

The discretization for the term $\mathcal{I}_E$ reads as:

$$\mathcal{I}_E \mathbf{a}(t) = \sum_j \mathbf{a}_j(t) \int_0^\infty \int_{y_{\min}}^{y_{\max}} \beta(x, 1, y, y_{\max}) \phi_j(x, y) dx dy \quad (42)$$

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Keywords: Aggregation, Coalescence, Population Balance equation, Modeling

Table 1
Parameter values employed for the simulations

Parameter	value	Units
T	298.15	K
k_B	1.38×10^{-23}	J/K
$\tau_{C,1}$	$10^{-1}, 10^0$ (DLCA), $10^4, 10^5$ (RLCA)	s
r_l	50×10^{-9}	m
η_C	8.9×10^{-4}	Pa s
M	10^{17}	$\#/\text{m}^3$
y_{min}	1.8	-
y_{max}	3	-
W	10^5	-
γ	0.5	-

Figure 1

Ratio between coagulation and coalescence rate as a function of cluster size x and fractal dimension y

Figure 2

Three-dimensional representation of the density distribution $f(x, y, t_{end})$ where $t_{end} = 9.29 \times 10^{-1} s$, i.e. at a primary particle conversion $\chi = 0.87$ and coalescence $\tau_c(1) = 10^{-1} s$. DLCA kernel was considered

Figure 3

Time evolution of the density distributions, obtained for different coalescence times, a:
 $\tau_c(1) = 10^0 s$, **b:** $\tau_c(1) = 10^{-1} s$

Figure 4

Contour lines of the two-dimensional density distribution $f(x, y, t)$ at primary particle conversion $\chi = 0.87$ (a,c) and $\chi = 0.999$ (b,d) employing two values for the characteristic time of coalescence $\tau_c(1) = 10^{-1} s$ (a,b) and $\tau_c(1) = 10^0 s$ (c,d)

Figure 5

Three-dimensional representation of the density distribution $f(x, y, t_{end})$ where $t_{end} = 9.95 \times 10^4 s$, i.e. at a primary particle conversion $\chi = 0.87$ and coalescence $\tau_{c,1} = 10^4 s$ using the RLCA Kernel

Figure 6

Contour lines of the two-dimensional density distribution $f(x, y, t)$ obtained for RLCA at primary particle conversions $\chi = 0.7$ (a,c) and $\chi = 0.87$ (b,d) employing two values for the characteristic time of coalescence, $\tau_c(1) = 10^4 s$ (a,b) and $\tau_c(1) = 10^5 s$ (c,d).

Figure 7

Time evolution of fractal dimension distribution obtained for a. DLCA, $\tau_c(1) = 10^{-1}s$, b. DLCA $\tau_c(1) = 10^0s$, c. RLCA $\tau_c(1) = 10^4s$, d. RLCA $\tau_c(1) = 10^5s$.

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Table of contents

The particle size distribution of a stagnant colloidal system undergoing aggregation and coalescence is deepened by solving a 2-D population balance equation. It turns out that a fast coalescence leads primary particles to organizing in rather compact and small clusters, whereas for slow coalescence larger, open cluster are being formed. The latter conclusion holds for both the DLCA and the RLCA regimes.