Modeling simultaneous deposition and aggregation of colloids

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Abstract

Solid formation and particle deposition in chemical and pharmaceutical processes often leads to heat exchanger or reactor fouling, compromising operability. The aim of this work is to propose a mathematical framework, based on population balance equations, to describe the simultaneous colloid aggregation and deposition. The problem is dealt with by accounting for two distinct cluster mass distributions, the first one describing the free clusters, while the second one the deposited aggregates. Three main events are considered: i) aggregation of two free clusters, ii) deposition of free clusters on the reactor wall (i.e. a free cluster turns into a deposited one), and iii) aggregation of a free cluster with a deposited one. To describe the aggregation of free clusters, three typical aggregation kernels (i.e. diffusion-limited and reaction-limited cluster aggregation as well as simple shear aggregation) have been used. Starting from those kernels, aggregation laws to describe the interaction between a free and a deposited cluster were proposed and a simple cluster-mass dependent deposition law was employed. The simulation results are then discussed in the frame of

one dimensionless parameter, function of the relevant characteristic time of the process (i.e. aggregation and deposition).

Keywords: Deposition, Fouling, Aggregation, Clogging

1 Introduction

The undesired formation and deposition of solid particulate material in industrial processes can hardly be underestimated.¹ The accumulation of such particles on surfaces is also referred to as fouling.² Besides heat exchangers, also reactors can undergo fouling in a great deal of applications, relevant to the chemical and pharmaceutical industries.^{1, 3, 4} In fact, both in established as well as in novel, emerging processes, this is a significant issue, potentially leading to product loss, decreased heat exchange, reactor obstruction (i.e. clogging), and increase in pressure drop.⁵⁻⁸

For instance, in emulsion polymerization reactors, the deposition of polymer particles on the impeller and the reactor walls causes a product loss and increases the need of periodic maintenance of the reactor itself. Moreover, the deposited material acts as seed for further deposition to occur.^{8, 9} In the pharmaceutical industry, reactions such as aminations or carbon-carbon coupling are conducted in organic solvents. Halide salts (e.g. NaCl, KCl), formed as byproducts, are insoluble in these organic solvents and precipitate out of the solution. After nucleation of the first crystals occurs, growth, deposition and agglomeration lead to a pressure drop increase and potentially to the clogging (and shutdown) of the reactor.^{5, 10}

Several strategies have been proposed to deal with the formation of solids. For instance, in flow reactors, the employment of ultrasounds has been shown to induce a size reduction of the solid particles, which prevented reactor clogging in palladium-catalyzed aminations.⁷ Another strategy to reduce fouling is represented by the introduction of inert gas slugs (e.g. of N_2): their “sweeping” action contributes (along with ultrasounds) to maintain the reactor stable as shown in the photodimerization of maleic anhydride.¹¹ In polymerization reactors, cleaning strategies involving the usage of solvents to first swell and then dissolve the deposited material were successfully implemented after the reaction.^{8, 9}

While these practical solutions extend or ease the operability of reactors in the presence of fouling, the need of a fundamental description of solid formation becomes evident, as reliable

mathematical models would improve physico-chemical understanding and provide guidelines for the control and possibly the minimization of solid formation.³

When approaching the fouling problem with deterministic models, different physicochemical phenomena describing the system's stability have to be accounted for besides deposition. When modeling the stability of polymeric colloidal particles for instance, aggregation, coalescence, breakage, and particle resuspension should be considered.^{12, 13} In the frame of a crystallization process, phenomena such as nucleation, growth, agglomeration, breakage, ripening and re-suspension play a relevant role.^{14, 15} Notably, most of the aforementioned processes are affected by reactor parameters, such as temperature and shear.¹⁶⁻¹⁸ The great complexity of the fouling process emerges clearly by this brief analysis. Several authors already dealt with the full problem, especially when considering crystal systems, and proposed models accounting for most of the above mentioned phenomena.^{4, 14} A quite thorough analysis has been made by Kostoglou and Karabels, who developed a population balance equation (PBE) based model to approach the precipitation problem in a turbulent flow reactor.¹⁴ Another interesting model is the one proposed by Majumder and Nagy, who studied the encrust formation in a continuous plug flow crystallizer by means of PBE and accounted for the time-evolution of the encrust layer and its impact on the crystal size distribution.⁴

Typically, in these deterministic descriptions, a 1-dimensional PBE accounting for the time-evolution of the free cluster mass distribution is solved. Free clusters grow and aggregate until they eventually deposit. The deposited material is accounted for by one single equation, describing its progressive accumulation in a "cake".^{4, 14} Considering the deposited material as a non-porous structure is a good assumption in those cases where the particle aggregation, which typically leads to fractal (i.e. porous) structures, is accompanied by a significant growth process, which leads those structures to be compact ones. This is typically the case when dealing with crystallizations at high supersaturations, but at lower supersaturations aggregates with a fractal nature have been observed.¹⁹ Lower supersaturations may become important especially in those cases where

crystallization is undesired, e.g. when crystals are the reaction byproduct.⁷ Also when considering fouling in polymerization reactors, the deposited material cannot be assumed as non-porous, as it is well known that “hard” polymeric particles (e.g. polystyrene) particles aggregate in both stagnant and shear conditions to form fractal clusters.^{20, 21} Even when softer particles are considered, fractal structures are observed, provided that only partial and not full coalescence occurs.¹²

In this frame, the present work aims at shading light on the fate of the depositing fractal clusters and in particular on their role in mediating the subsequent uptake of free clusters. The main idea is to propose a tool which could be employed to rationalize the ongoing phenomena and help designing systematic experiments to study the fouling process. To do so, a deterministic model based on population balance equations, is proposed to account for both the free and the deposited cluster mass distribution. This schematization allows unraveling the interplay between aggregation and deposition and better appreciating the role of these phenomena in the frame of the fouling process. For the sake of simplicity, the schematization is proposed for batch reactors where free clusters can i) aggregate among each other, ii) deposit on the reactor walls, iii) aggregate with already deposited clusters. An extension of this model towards more complicated cases, accounting for further phenomena (e.g. nucleation, growth, breakage, sedimentation, re-suspension) can be readily made thanks to the versatility of the population balance equation approach.²²

2 The Model

Kinetic scheme

Describing the aggregation and deposition phenomena in a batch reactor may be achieved by introducing two different distributions, $F(x, t)$ and $D(x, t)$, where x is the cluster mass of the aggregates (hence the number of primary particles constituting the aggregate) and t is the time.

$F(x, t)dx$ represents the concentration of free clusters consisting of x to $x + \Delta x$ primary particles

at time t . $D(x, t)$ is instead the concentration of deposited clusters consisting of x to $x + \Delta x$ primary particles at time t . Note that the variable y is being used as an alternative to x to distinguish differently sized clusters.

The different clusters interact with one another and with the reactor walls, according to the following kinetic scheme, as shown below and summarized in Figure 1:

Agglomeration of two free clusters

Deposition of a free cluster on the reactor wall

Agglomeration of a free and a deposited cluster

Figure 1 - Kinetic scheme sketch

From the schematic representation of the kinetic steps (Figure 1) it can be seen that the total free clusters concentration decreases, while the total deposited clusters concentration increases only through deposition. In particular, a free cluster is lost when a) it aggregates with another free cluster, b) it deposits on the reactor walls, c) it reacts with a deposited cluster. Conversely, a deposited cluster is formed when a free cluster deposits on the wall, while no mechanism consumes a deposited cluster. Rather, deposited clusters grow in mass by the “uptake” of free clusters, but their total concentration solely depends on the deposition process. Clearly, these processes are all inter-dependent.

Population balance equations (PBE)

Assuming a well-mixed batch reactor and considering the kinetic scheme ((1)-(3)), it is possible to write the population balance equations describing the time evolution of the free and deposited clusters, $F(x, t)$ and $D(x, t)$:

$$\begin{aligned} \frac{\partial F(x, t)}{\partial t} = & -F(x, t) \int_0^\infty \beta(x, y) F(y, t) dy + \frac{1}{2} \int_0^x \beta(x-y, y) F(x-y, t) F(y, t) dy \\ & - k_{dep}(x) A_w(t) F(x, t) - F(x, t) \int_0^\infty \beta^*(x, y) D(y, t) dy \end{aligned} \quad (4)$$

$$\begin{aligned} \frac{\partial D(x, t)}{\partial t} = & k_{dep}(x) A_w(t) F(x, t) - D(x, t) \int_0^\infty \beta^*(y, x) F(y, t) dy \\ & + \int_0^x \beta^*(y, x-y) F(y, t) D(x-y, t) dy \end{aligned} \quad (5)$$

Note that $F(x, t)dx$ and $D(x, t)dx$ are number concentrations $[\# m^{-3}]$, the deposition rate constant $k_{DEP}(x)$ of an x -sized cluster has units $[m^{-2} s^{-1}]$, while $\beta(x, y)$ and $\beta^*(x, y)$ $[m^3 \#^{-1} s^{-1}]$. $\beta(x, y)$ is the aggregation kernel for two free clusters (of sizes x and y), while $\beta^*(x, y)$ describes the aggregation between a free cluster of size x and a deposited cluster of size y .

A complete list of variables is reported in the Symbol List at the end of the paper. "Note that there

is no $\frac{1}{2}$ factor multiplying the convolution integral in equation (5), as $F(x,t)dx$ and $D(x,t)dx$ are two distinct distributions. The deposition rate is proportional to the available wall surface $A_w(t)$ (cf. equation (2), (4) and (5)), i.e. the wall surface which is not yet covered by other clusters. In the limit case, after deposition occurred extensively, $A_w(t) \rightarrow 0$, free clusters will be able to interact only with themselves or with deposited clusters, not anymore with the reactor walls.

To solve the above population balances, it is necessary to write an equation for $A_w(t)$, the available surface of the reactor wall:

$$\frac{dA_w(t)}{dt} = -A_w(t) \int_0^\infty k_{DEP}(x) \pi R_g^2(x) V_{react} F(x,t) dx \quad (6)$$

Where V_{react} is the reactor volume, and $R_g(x)$ is the gyration radius of an x -sized cluster, defined as:

$$R_g(x) = R_p x^{1/d_f} \quad (7)$$

being R_p the radius of the primary particles, d_f the fractal dimension of the cluster population, reflecting clusters' compactness.²³ Note that in equation (6) the area is assumed to decrease proportionally to the area projection of a depositing cluster ($\pi R_g^2(x)$). At the same time, the smaller the available surface area $A_w(t)$, the slower the deposition rate. The initial conditions of the aforementioned equation set (4), (5) and (6) read:

$$F(x, t=0) = \begin{cases} C_{part} & x=1 \\ 0 & x \geq 2 \end{cases} \quad (8)$$

$$D(x, t=0) = 0 \quad x \geq 1 \quad (9)$$

$$A_w(t=0) = A_{w,0} \quad (10)$$

Where C_{part} is the initial primary particle concentration and $A_{w,0}$ is the surface area of the clean reactor. Using a cylindrical reactor with height h_{react} and radius r_{react} one gets:

$$A_{w,0} = 2\pi r_{react}^2 + 2\pi r_{react} h_{react} \quad (11)$$

Kernels

To solve the equation set (4), (5) and (6), the rates of the processes, namely $\beta(x, y)$, $k_{DEP}(x)$, and $\beta^*(x, y)$ have to be defined. According to the mechanisms regulating the interactions among clusters and between clusters and reactor walls, different expressions have to be employed.

As for the aggregation of two free clusters (cf. equation (1)), three cases typically occurring in colloid science are considered,¹⁶ namely diffusion limited cluster aggregation (DLCA), reaction limited cluster aggregation (RLCA) and simple shear aggregation (SSA).^{16, 24} The corresponding aggregation kernels read:

$$\beta_{DLCA}(x, y) = 4\pi(R_g(x) + R_g(y))(D_{iff}(x) + D_{iff}(y)) \quad (12)$$

$$\beta_{RLCA}(x, y) = \frac{1}{W} 4\pi(R_g(x) + R_g(y))(D_{iff}(x) + D_{iff}(y))M(x)M(y) \quad (13)$$

$$\beta_{SSA}(x, y) = \frac{4}{3} \dot{\gamma} (R_g(x) + R_g(y))^3 \quad (14)$$

Where $\dot{\gamma}$ is the shear rate [s^{-1}], $D_{iff}(x)$ is the diffusivity of a cluster of size x , $R_g(x)$ is the gyration radius (cf. equation (7)) and W is the Fuchs stability factor, accounting for the interparticle repulsive interaction.²⁵ $M(x)$ reflects the experimental observation that in RLCA conditions the aggregate reactivity scales with its mass.²⁶ $D_{iff}(x)$ and $M(x)$ are defined as:^{16, 20}

$$D_{iff}(x) = \frac{k_B T}{6\pi\eta_c R_g(x)} \quad (15)$$

$$M(x) = x^\lambda \quad (16)$$

Where λ is considered as a fitting parameter, (typically $\lambda \cong 0.5$)²⁰, k_B is the Boltzmann constant, T is the temperature and η_c is the viscosity of the continuous phase.

Different mechanisms will result in different free cluster mass distributions. This is particularly important in the deposition process. Free clusters can undergo deposition, and stick to the reactor walls (cf. equation (2)). As a matter of fact, deposition is a very complex phenomenon and depends on a great number of parameters (e.g. flow rate, particle interaction potential, temperature, cluster mass).²⁷ For the sake of simplicity, the following expression is employed in the present work:

$$k_{DEP}(x) = k_{DEP,0} g(x) = k_{DEP,0} x^{(d_f-1)/d_f} \quad (17)$$

Note that $k_{DEP}(x)$ is written as a function of a deposition rate constant $k_{DEP,0}$ and a cluster mass-related function $g(x) = x^{(d_f-1)/d_f}$. The deposition rate constant $k_{DEP,0}$ reflects the interactions between clusters and wall, and varies according to the particles type (e.g. polymeric or crystalline in nature), the wall material (e.g. metallic, polymeric), their mutual interaction potential, and the environmental conditions (e.g. temperature, shear). The function $g(x)$ quantifies the number of primary particles present on the clusters' outer surface,²⁴ which are those effectively regulating the interaction between clusters and reactor walls. In other terms, at fixed d_f , larger clusters will deposit faster than smaller ones as they possess more particles on their outer surface which can interact with the reactor walls. At the same time, equally sized clusters have a larger probability of interacting with the walls, the larger their d_f (i.e. the less porous they are). The two latter concepts can be appreciated in Figure 2 where $k_{DEP}(x)/k_{DEP,0}$ vs x is reported for clusters with different fractal dimensions.

Figure 2 - Normalized deposition rate $k_{DEP}(x)/k_{DEP,0}$ vs x at $d_f = \{1.8, 2.1, 2.4, 2.7\}$

Note that the selected fractal dimensions are values typically reported for DLCA ($d_f = 1.8$), RLCA ($d_f = 2.1$) and SSA ($d_f = 2.4 - 2.7$).^{21, 28, 29}

As soon as free and deposited clusters co-exist, they can also “react” with one another (cf. equation (3)), increasing the mass (but not the number) of deposited clusters. To define the aggregation between a free cluster and a deposited one in the frame of the above-mentioned mechanisms (DLCA, RLCA, SSA), the expressions (12)-(14) have been modified. In particular, assuming that the x -sized cluster is the free (diffusing) cluster and that the y -sized cluster is the deposited (non-diffusing) one, the following kernels have been selected:

$$\beta_{DLCA}^*(x, y) = 2\pi(R_g(x) + R_g(y))D_{iff}(x) \quad (18)$$

$$\beta_{RLCA}^*(x, y) = \frac{1}{W} 2\pi(R_g(x) + R_g(y))D_{iff}(x)M(x)M(y) \quad (19)$$

$$\beta_{SSA}^*(x, y) = \frac{2}{3}\dot{\gamma}(R_g(x) + R_g(y))^3 \quad (20)$$

Note that $\beta_{DLCA}^*(x, y)$ and $\beta_{RLCA}^*(x, y)$ differ from the corresponding $\beta_{DLCA}(x, y)$ and $\beta_{RLCA}(x, y)$ ones for the fact that i) the diffusivity of the deposited cluster (here the y -sized cluster) has been put equal to zero and ii) the prefactor is 2 and not 4. The latter change in prefactor can be rationalized recalling that the aggregation kernels between two free clusters have been originally derived by computing the particles flux colliding, from all possible directions, with a given particle.¹⁶ Therefore, in the aggregation of a free and a deposited cluster, the particle flux of free aggregates colliding with the deposited one has to be divided by two, as the incoming flux of free particles can arrive only from one side (the fluid side) and not the wall (cf. Figure 1). The same reasoning has been applied when modifying the SSA kernel, resulting in having also in this case in a smaller prefactor (by a factor 2).

Substituting the definitions of $R_g(x)$, $D_{iff}(x)$ and $M(x)$ (equation (7), (15) and (16)) in the kernel expressions (equation (12)-(14) and (18)-(20)), one obtains the following expressions as a function of the cluster masses (cf. Table 1):

Table 1 - Overview of the employed kernels

	$\beta(x, y)$	$\beta^*(x, y)^{(a)}$	$k_{DEP}(x)$
DLCA	$\frac{2}{3} \frac{k_B T}{\eta_c} (x^{1/d_f} + y^{1/d_f}) (x^{-1/d_f} + y^{-1/d_f})$	$\frac{1}{3} \frac{k_B T}{\eta_c} (x^{1/d_f} + y^{1/d_f}) (x^{-1/d_f})$	$k_{DEP,0} x^{(d_f-1)/d_f}$
RLCA	$\frac{2}{3} \frac{k_B T}{\eta_c} \frac{1}{W} (x^{1/d_f} + y^{1/d_f}) (x^{-1/d_f} + y^{-1/d_f}) (xy)^\lambda$	$\frac{1}{3} \frac{k_B T}{\eta_c} \frac{1}{W} (x^{1/d_f} + y^{1/d_f}) (x^{-1/d_f}) (xy)^\lambda$	$k_{DEP,0} x^{(d_f-1)/d_f}$
SSA	$\frac{4}{3} \dot{\gamma} R_p^3 (x^{1/d_f} + y^{1/d_f})^3$	$\frac{2}{3} \dot{\gamma} R_p^3 (x^{1/d_f} + y^{1/d_f})^3$	$k_{DEP,0} x^{(d_f-1)/d_f}$

^(a) Note that for $\beta^*(x, y)$ it has been assumed that x is the free cluster and y the deposited one

Comparing the expressions for $\beta(x, y)$ and $\beta^*(x, y)$ (cf. Table 1), it is possible to appreciate that the aggregation event between two free clusters is always faster than the one between a free and a deposited one. In the SSA case, this is evident as the two expressions differ only by a factor 2. As

for the DLCA and RLCA cases, it is convenient to compute the ratio of $\beta(x, y)$ over $\beta^*(x, y)$.

Given the expressions (cf. Table 1), their ratio, $r_\beta(x, y)$, is going to be the same for both cases:

$$r_\beta(x, y) = \frac{\beta_{DLCA}(x, y)}{\beta_{DLCA}^*(x, y)} = \frac{\beta_{RLCA}(x, y)}{\beta_{RLCA}^*(x, y)} = \frac{2(x^{-1/d_f} + y^{-1/d_f})}{(x^{-1/d_f})} = 2 + 2x^{1/d_f} y^{-1/d_f} \quad (21)$$

It is clear from equation (21) that $r_\beta(x, y)$ is equal to at least 2, given that the term $2x^{1/d_f} y^{-1/d_f} \rightarrow 0$ for $y \rightarrow \infty$. In other words, aggregation between two free clusters occurs at least two times faster than aggregation between a free and a deposited cluster. Notably, even though the same expression can be used for both the DLCA and RLCA regimes (cf. equation (21)), $r_\beta(x, y)$ has different absolute values as different fractal dimensions characterize the two mechanisms.²⁹ To better visualize the kernels employed in the present work as well as the ratio $r_\beta(x, y)$, these are reported in Figure 3.

Figure 3 - Employed aggregation kernels against cluster masses x and y . a), b), c) aggregation kernels for two free clusters in DLCA, RLCA and SSA regimes, respectively. d), e) aggregation kernels for a free and a deposited cluster in DLCA and RLCA, respectively. e) ratio $r_\beta(x, y)$ (cf. equation (23)). Aggregation kernels a)-e) are normalized by the aggregation rate (in the corresponding regime) of two primary particles $\beta(1,1)$. $d_f = 1.8, 2.1, 2.4$ in DLCA, RLCA and SSA respectively, and $\lambda = 0.5$ for the RLCA kernel.

Figure 3 clarifies how cluster masses affect aggregation rates in the different cases. Note that the kernels are scaled on their $\beta(1,1)$ value. Focusing on the aggregation between free clusters (Figure 3a)-3c)) it can be seen that for $\beta_{DLCA}(x,y)$, the aggregation between large and small clusters is the fastest one (Figure 3a)), while for $\beta_{RLCA}(x,y)$ and $\beta_{SSA}(x,y)$ the aggregation between two large clusters is the fastest event (Figure 3b) and 3c)). Note that the aforementioned kernels (Figure 3a)-3c)) are symmetric with respect to x and y . These latter considerations are widely accepted in the literature¹⁶ and have been reported in order to emphasize the different nature of the selected kernels describing the interaction between free and deposited clusters. Figure 3d) shows that $\beta_{DLCA}^*(x,y)$ has quite a different shape when compared with the kernel it stems from, $\beta_{DLCA}(x,y)$ (Figure 3a)). Besides a difference in absolute values, there is no symmetry with respect to x and y . This is due to the fact that in $\beta_{DLCA}^*(x,y)$, the y -sized clusters are deposited (non-diffusing) and the x -sized clusters are the free (diffusing) clusters (cf. equation (18)). Therefore, the most favorable event remains (as for the standard $\beta_{DLCA}(x,y)$) the aggregation between a large and a small cluster, but only if the large cluster is deposited and the small cluster is free. This implies that in the frame of the aggregation between a free and deposited cluster, the most favorable cluster to grow is a large deposited one (towards which a small free cluster can diffuse). Smaller deposited clusters are less likely to react as they represent a small “target” for freely diffusing clusters. Large free clusters can also react with deposited clusters (both small and large) but they do so to a lesser extent (as compared to free small clusters) because their larger size reduces their mobility (cf. equation (15)). The same concept can be visualized in Figure 3e)), where $r_\beta(x,y)$ is reported using $d_f = 1.8$. $r_\beta(x,y)$ represents the likelihood of a free x -sized cluster to react with a free y -sized one, as compared to a free x -sized cluster to react with a deposited y -sized one. It is seen that large free clusters are particularly more prone to react with small free clusters than with small deposited ones. This is once more due to the low diffusivity of larger clusters, which can be targeted by small

clusters only if these are free. When comparing $\beta_{RLCA}^*(x, y)$ (Figure 3e)) with $\beta_{RLCA}(x, y)$ (Figure 3b)), smaller differences in the shapes are observed, as compared to the ones previously discussed ($\beta_{DLCA}^*(x, y)$ vs. $\beta_{DLCA}(x, y)$). This is due to the term accounting for the cluster masses $(xy)^\lambda$. Nevertheless, a significant difference is present, as already anticipated by the computation of the ratio $r_\beta(x, y)$, (cf. equation (21)). Notably, in Figure 3, β_{SSA}^* has not been reported, as it differs from β_{SSA} merely by a factor 2 (cf. Table 1), meaning that the most favorable aggregation event between a deposited and a free cluster involves two large clusters, both when two free clusters or one free and one deposited cluster aggregate.

3 Numerical resolution

The distributions $F(x, t)$ and $D(x, t)$ are approximated to a sum of Gaussian functions in order to reduce the size of the problem, given that the cluster mass x typically reaches values up to $10^4 - 10^6$, implying a corresponding large number of equations have to be solved. The employed approximations read:

$$F(x, t) \cong \sum_{i=1}^{N_G} \alpha_i e^{-s_i(x-x_i)^2} \quad (22)$$

$$D(x, t) \cong \sum_{i=1}^{N_G} \beta_i e^{-s_i(x-x_i)^2} \quad (23)$$

Note that the N_G are the number of Gaussians used for the approximation. The Gaussians are placed in the positions x_i and have heights α_i and β_i , according to the distribution function they are describing, namely $F(x, t)$ or $D(x, t)$. The parameter s_i describes the overlapping degree of the Gaussians and is fixed once the Gaussian centers are defined:

$$s_i = \frac{1}{(x_{i+1} - x_i)^2} \quad (24)$$

This discretization technique has been proven successful in a number of cases, ranging from polymerization modeling to colloid-related applications.^{12, 30, 31} For the sake of brevity, the discretized balances for the different cases are reported in the Electronic Supplementary Information.

4 Results and discussion

4.1 Useful quantities and characteristic times

Solving the two PBE (equation (4) and (5)) with the ODE equation (6) allows to follow the deposition/aggregation process, by computing quantities such as the free and deposited cluster mass fractions (ω_F, ω_D) and their corresponding occupied volume fractions (ϕ_F, ϕ_D):

$$\omega_F = \frac{\int_0^{\infty} x F(x, t) dx}{\int_0^{\infty} x F(x, t) dx + \int_0^{\infty} x D(x, t) dx} \quad (25)$$

$$\omega_D = 1 - \omega_F \quad (26)$$

$$\phi_F = \frac{4}{3} \pi \int_0^{\infty} R_g^3(x) F(x, t) dx \quad (27)$$

$$\phi_D = \frac{4}{3} \pi \int_0^{\infty} R_g^3(x) D(x, t) dx \quad (28)$$

Further quantities to be extracted from the free and the deposited cluster mass distributions are their normalized k -th order moments ($\mu_{F,N}^k, \mu_{D,N}^k$), and their polydispersities (PD_F, PD_D):

$$\mu_{F,N}^k = \frac{\int_0^{\infty} x^k F(x, t) dx}{C_{part}} \quad (29)$$

$$\mu_{D,N}^k = \frac{\int_0^\infty x^k D(x,t) dx}{C_{part}} \quad (30)$$

$$PD_F = \frac{\mu_{F,N}^0 \mu_{F,N}^2}{\left[\mu_{F,N}^1\right]^2} \quad (31)$$

$$PD_D = \frac{\mu_{D,N}^0 \mu_{D,N}^2}{\left[\mu_{D,N}^1\right]^2} \quad (32)$$

To properly compare the different case studies, characterized by quite different kinetics and time scales, the following non-dimensional time, τ_N , has been introduced: ²⁰

$$\tau_N = \frac{t}{\tau_A} \quad (33)$$

Where τ_A is the characteristic time of aggregation of two free primary particles, defined as:

$$\tau_A = \frac{1}{\beta(1,1)C_{part}} \quad (34)$$

Note that $\beta(1,1)$ changes according to the aggregation regime considered (cf. Table 1):

$$\beta_{DLCA}(1,1) = \frac{8}{3} \frac{k_B T}{\eta_C} \quad (35)$$

$$\beta_{RLCA}(1,1) = \frac{8}{3} \frac{k_B T}{\eta_C} \frac{1}{W} \quad (36)$$

$$\beta_{SSA}(1,1) = \frac{32}{3} \dot{\gamma} R_p^3 \quad (37)$$

Another useful quantity to discuss the simulation results is τ_{DEP} , the characteristic time of primary particles deposition. Starting from equation (6), describing the time-evolution of the available reactor wall area as a first-order process, the following characteristic time can be defined:

$$\frac{dA_w(t)}{dt} = -A_w(t) \underbrace{\int_0^\infty k_{DEP}(x) \pi R_g^2(x) V_{react} F(x,t) dx}_{\tau_{DEP}^{-1}} \quad (38)$$

$$\tau_{DEP} = \frac{1}{\int_0^\infty k_{DEP}(x) \pi R_g^2(x) V_{react} F(x,t) dx}$$

Writing τ_{DEP} assuming that only primary particles are present, and recalling definitions (7) and (17), one gets then:

$$\tau_{DEP} = \frac{1}{k_{DEP,0} \pi R_p^2 V_{react} C_{part}} \quad (39)$$

It is then possible to discuss the various aggregation regimes for different values of the ratio between the deposition and the free clusters aggregation characteristic time:

$$r_\tau = \frac{\tau_{DEP}}{\tau_A} \quad (40)$$

Despite the characteristic times ratio is only representative of primary particles, it provides interesting insights into the features of the simultaneously occurring processes of aggregation and deposition. Three cases can be distinguished:

- i) $r_\tau \approx 1$: the time required for deposition and aggregation to occur are comparable and deposited material will be available from the very beginning of the aggregation process, taking up free clusters and affecting their distribution.
- ii) $r_\tau < 1$: the same reasoning as in case i) holds, as deposition will be even faster than aggregation, quickly saturating the available reactor walls area, therefore affecting the free cluster distribution as deposited clusters are available to interact with the free ones
- iii) $r_\tau > 1$: the time required for deposition to occur is larger than the one for aggregation. In other words, despite some clusters may deposit, the free cluster distribution will be less impacted by deposited material. In particular, the larger r_τ , the less free clusters will be affected by deposited ones. This latter concept does not hold if the process time

$\tau_P \ll \tau_{DEP}$: deposition will occur within the process time and free clusters will eventually interact with the deposited material.

Note that the characteristic time of aggregation between a free and a deposited cluster is not being considered as it would be strongly dependent on the aggregation between two free clusters, as discussed in section 2.

The parameter values employed in the different simulations (DLCA, RLCA, SSA) can be divided in two groups: those physical and reactor parameters which were kept constant for all aggregation regimes (cf. Table 2) and those which were different case by case (cf. Table 3).

Table 2 – Physical and reactor parameter values employed all simulations

Parameter	Value	Units
T	298.15 K	K
k_B	1.38×10^{-23}	$J K^{-1}$
η_C	8.9×10^{-4}	$Pa s$
R_p	50×10^{-9}	m
ϕ_0	10^{-4}	–
h_{react}	2×10^{-1}	m
r_{react}	1×10^{-1}	m

Table 3 Parameter values specific to the different aggregation regimes

	$d_f [-]$	$W [-]$	$\dot{\gamma} [s^{-1}]$	$\lambda [-]$	$\tau_P [s]$	$k_{DEP,0} [m^{-2}s^{-1}]$
DLCA	1.8	-	-	-	4.2×10^3	$2.5 \times \{10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}\}$
RLCA	2.1	10^3	–	0.4	4.2×10^4	$2.5 \times \{10^{-8}, 10^{-7}, 10^{-6}, 10^{-5}, 10^{-4}\}$
SSA	2.7	-	9.25	-	2.1×10^3	$2.5 \times \{10^{-8}, 10^{-7}, 10^{-6}, 10^{-5}, 10^{-4}\}$

The regime-specific parameter values in Table 3 correspond to typically reported literature ones.^{16,}

^{28, 29} Moreover, these set of parameters were chosen in order to allow studying the aggregation/deposition problem in the same range of the parameter value r_t throughout the different aggregation regimes. The process characteristic time has been chosen in order to have

situations where the deposition process of primary particles is shorter, comparable or longer than the entire process.

Note that the chosen kernels are only representative ones and were selected to explore the model's potential. While different choices in this sense would clearly affect the simulations result, the general approach of i) accounting for both the free and the deposited cluster mass distributions and ii) discussing the results in terms of the characteristic times ratio, r_τ holds.

4.2 Diffusion limited cluster aggregation (DLCA)

Before showing simulation results in the DLCA case to exemplify the model's potential, it is useful to evaluate the ratio of the characteristic times of deposition and aggregation in the DLCA regime, $r_{\tau,DLCA}$ (combining equation (40), (39), (35),(34)):

$$r_{\tau,DLCA} = \frac{\tau_{DEP}}{\tau_{A,DLCA}} = \frac{\beta(1,1) \cancel{C_{part}}}{k_{DEP,0} \pi R_p^2 V_T \cancel{C_{part}}} = \frac{8k_B T}{3\eta_C k_{DEP,0} \pi R_p^2 V_T} \quad (41)$$

Equation (41) shows the parameters playing a key role in the DLCA case, allowing to explore the features of the present model.

Using the parameter values reported in Table 2 and Table 3 allows to span over a range of $r_{\tau,DLCA}$ comprised between $10^0 - 10^4$. The simulation results are shown in Figure 4.

Figure 4 - Average properties in the DLCA case – a) Normalized reactor area $A_W / A_{W,0}$ vs τ_N ; b) Polydispersities PD_F, PD_D vs τ_N ; c) free clusters mass fraction ω_F vs τ_N ; d) deposited clusters mass fraction ω_D vs τ_N ; e) free clusters occupied volume fraction ϕ_F vs τ_N ; f) deposited clusters occupied volume fractions ϕ_D vs τ_N ; g) Normalized, free clusters 0th order moment, $\mu_{F,N}^0$ vs τ_N ; h) Normalized, deposited clusters 0th order moment $\mu_{D,N}^0$ vs τ_N . Dashed lines represent deposited clusters properties, while continuous lines indicate free cluster properties. The color code reads: violet, $r_\tau = 10^0$; blue $r_\tau = 10^1$; green $r_\tau = 10^2$; yellow $r_\tau = 10^3$; red; $r_\tau = 10^4$

In Figure 4 several average properties of the free and the deposited cluster mass distributions are shown as a function of the normalized time τ_N for different values of the parameter r_τ . The larger r_τ , the slower the deposition process (cf. equation (40)) and the smaller the relevance of the deposited clusters. For instance, for larger r_τ values, a longer time is necessary for the saturation of the normalized reactor wall area, $A_w / A_{w,0}$ (cf. Figure 4a). Notably, even for $r_\tau = 10^4$ (red curve in Figure 4a)), a complete saturation of the reactor walls is observed. This might look surprising given that the process time is comparable to the characteristic time for deposition, i.e. $\tau_p \approx \tau_{DEP} \approx 4000s$ (equation (39), Table 2 and 3). On the other hand, in the present kinetic scheme, the rate of deposition is faster for larger clusters than for smaller ones (cf. Figure 2), and the τ_{DEP} represents only primary particles deposition. In other words, both larger and smaller clusters contribute to the deposition process resulting in the saturation of the available surface area. Notably, although such saturation occurs at very low τ_N values (Figure 4a), a significant formation of the deposited cluster mass fraction ω_d (and corresponding loss of free clusters mass fraction, ω_f) is observed only at later stages of the aggregation process. (Figure 4c) and 4d)). This consideration holds for all values of r_τ considered. For instance, focusing on the case $r_\tau = 1$ (violet curves), it can be seen that the normalized area is fully saturated at $\tau_N = 10^1$, while $\omega_f > 0.9$ (and $\omega_d < 0.1$) at that time point. This can be explained considering that with the selected reactor size (cf. Table 2), the initial occupied volume fraction ($\phi_0 = 10^{-4}$) and particle size ($R_p = 50 \times 10^{-9} m$), one has an available surface area at time zero of $0.1885 m^2$, and 1.2×10^{15} particles. Assuming that only primary particles deposit and that each particle occupies an area equal to its projected one (i.e. πR_p^2), 2.4×10^{13} particles (i.e. 2% of the initially available particles) suffice to cover the entire reactor surface. Given that this calculation neglects larger clusters (which occupy larger areas), it is clear that a full deposition of the reactor walls occurs at very low values of the deposited mass fraction ω_d . At the

same time it is worth noting that the deposited clusters distribution at saturation will be very different according to the r_τ value. For low r_τ values, deposition occurs at comparable time scales as aggregation, therefore most of the clusters depositing on the reactor walls will be small. Conversely, for larger values of r_τ , the free cluster mass distribution will grow first, leading the deposited clusters to be on average larger than in the case of smaller r_τ . These different distributions at full saturation (caused by different r_τ values) will affect the subsequent aggregation process between free and deposited clusters.

This can be appreciated, for instance, when considering the time evolution of the cluster mass polydispersity of the free (PD_F) and deposited (PD_D) clusters (cf. Figure 4b). Larger r_τ values imply a slower deposition and therefore a delayed full saturation of the reactor surfaces. As a result, aggregation between free clusters is favored (as compared to the free-deposited aggregation, as the concentration of deposited clusters is small). This means that at very large r_τ values, the free cluster distribution will behave almost as if the deposited clusters were not present. As a matter of fact, for $r_\tau = 10^4$, the free clusters polydispersity, (PD_F), remains constant throughout the aggregation process (cf. continuous red curve in Figure 4b), as expected in the classical DLCA regime.¹⁶ Smaller values of r_τ , where deposited clusters are present from the very beginning of the aggregation process, show instead a progressively decreasing PD_F (cf. continuous curves in Figure 4b). This suggests that the interaction between free and deposited clusters is size-specific, as already pointed out in section 2. For this reason, the polydispersity of deposited clusters, PD_D , increases abruptly towards values of about 4 (cf. dashed lines in Figure 4b). In some cases, at low r_τ values, the PD_D reaches a steady state (cf. violet and blue dashed curves in Figure 4b). Such a steady state is observed when most of the clusters are deposited, i.e. when $\omega_F \rightarrow 0$ (and $\omega_D \rightarrow 1$), as shown for the blue and violet curves in Figure 4c) and 4d), respectively.

Another quantity which is affected in the presence of a significant deposition process (i.e. for small r_τ values), is the occupied volume fraction of the free clusters, $\phi_F(t)$ (cf. Figure 4e)). Instead of steadily increasing in time, it exhibits a maximum and then decreases in favor of the deposited occupied volume fraction $\phi_D(t)$ (cf. Figure 4e)). Eventually, after most of the clusters are captured by the deposited phase, $\phi_F(t) \rightarrow 0$ and $\phi_D(t)$ grows very slowly, as less free clusters are available for reaction with deposited ones. In some cases where basically no free clusters are available, $\phi_D(t)$ reaches a steady state (violet and blue dashed curves in Figure 4f)).

The role of deposition and more specifically of the deposited cluster mass distribution can be appreciated when inspecting Figure 4g), where the normalized 0th order moments of the free clusters mass distribution, $\mu_{F,N}^0$, are shown vs τ_N . When deposition occurs slowly (large r_τ), the free cluster concentration decreases only because of the binary aggregation process: two clusters aggregate, forming only one larger cluster, hence one cluster is “lost”. In the case where deposition occurs, two further mechanisms consume free clusters: i) the deposition of a free cluster on the walls, and ii) the aggregation between a free and a deposited cluster. As a result, the normalized concentration of free clusters ($\mu_{F,N}^0$), decreases more rapidly in the case where deposition occurs (cf. Figure 4g)). Conversely, the normalized deposited clusters concentration, $\mu_{D,N}^0$, quickly reaches a steady state and remains constant throughout the process (cf. Figure 4h)). This can be explained recalling that once the reactor walls are saturated and a number of clusters are deposited, these clusters may only grow in size due to aggregation with free clusters. Deposited clusters cannot interact with one another (cf. kinetic scheme in Figure 1), and their concentrations remains therefore constant. Also in this case, the steady state is reached at times τ_N when the reactor walls area are completely saturated (cf. Figure 4a).

The present model allows to obtain interesting information also on the normalized free and deposited cluster mass distributions, which are reported for 3 different values of r_τ (namely $10^0, 10^2, 10^4$) at different time points τ_N , in Figure 5.

Figure 5 - a),c),e) $F_N(x,t)$ vs x at different non dimensional times τ_N , with $r_\tau = 10^0$, $r_\tau = 10^2$ and $r_\tau = 10^4$, respectively; b), d), f) $D_N(x,t)$ vs x at different non dimensional times τ_N , with $r_\tau = 10^0$, $r_\tau = 10^2$ and $r_\tau = 10^4$, respectively; Continuous lines indicate free clusters, dashed lines deposited clusters. Color codes for τ_N : violet $\tau_N = 250$; blue $\tau_N = 500$; green $\tau_N = 750$; yellow $\tau_N = 1000$; red $\tau_N = 1250$.

Comparing the free and the deposited cluster mass distributions (Figure 5 a), c) e) vs Figure 5 b), d), f), a very different shape is immediately observed. Such difference in distribution shape is related to the different kernels regulating the aggregation of two free clusters and a free with a deposited one (cf. Table 1). In the DLCA case, when considering the aggregation between two free clusters, the fastest reaction event occurs between a small and a large cluster, as discussed in section 2. When a free cluster interacts with a deposited one the small-large combination is once more the fastest event, but under the condition that the large cluster is the deposited one and the free one is the smaller one (cf. Figure 3a) and 3d)). In fact, as the deposited clusters cannot diffuse, their aggregation likelihood is linked merely to their extension, which is in turn related to their mass. As a result, the deposited cluster distribution will develop mostly through the “uptake” of free small clusters, while promoting the growth of its largest aggregates. Smaller deposited cluster will have a tendency to accumulate whereas larger ones to grow, shifting the distribution to the right. Such shift occurs progressively slower in time (cf. Figure 5b), d), f)) given that the free clusters concentration progressively decreases in time (cf. Figure 4g)). This general behavior of $D_N(x, t)$ is observed for any r_τ considered (cf. Figure 5b), d), f)) and explains the shape of its distributions. While at larger time points τ_N the distributions $D_N(x, t)$ progressively shift to the right in all cases, the absolute concentrations decrease at increasing r_τ (cf. y-axis in Figure 5b), d) and f)). This trend confirms the already observed normalized 0th order moment $\mu_{D,N}^0$ vs τ_N reported in Figure 4h).

As for $F_N(x, t)$ in time, the behavior changes significantly according to the value of r_τ . For large values of r_τ ($10^2, 10^4$) both the left and right tail and of $F_N(x, t)$ advance in time, as expected for DLCA distributions (cf. Figure 5c) and 5e)).¹⁶ Conversely, for $r_\tau = 1$ (cf. Figure 5a)), the left tail of $F_N(x, t)$ shifts to the right, while the right tail shifts first to the right (for $\tau_N > 250$), and then stops moving, actually slightly moving to the left (note that the red curve in Figure 5a) corresponds

to the largest τ_N considered). This shift of the left tail to the right and of the right tail to the left implies a decrease in the polydispersity, as already observed for small values of r_τ in Figure 4b). Such a decrease in polydispersity is linked to the reactivity of free clusters with the deposited ones. As soon as a free cluster aggregates with a deposited one, the free cluster becomes part of the deposited aggregate. The latter reaction is the fastest when a free small cluster aggregates with a large deposited one (cf. section 2 and Figure 3d)). Therefore, the free cluster distribution $F_N(x, t)$ will mostly lose small clusters and hence its left tail will shift to the right. Moreover, this loss of free small clusters reduces the reaction rate between a small free and a large free cluster, which is the key responsible for the growth of larger clusters. As a result, the right tail of the distribution will “move less” to the right. On top of this, the small (but non-zero!) reactivity of large free clusters aggregating with deposited ones, will push the right tail towards the left, mildly contributing in decreasing the polydispersity as well.

This first simulation set highlights the importance of accounting for both the deposited and free cluster mass distribution. In particular, through the ratio of characteristic times of deposition and aggregation, r_τ , it is seen how some well-accepted features of the DLCA aggregation mechanism (e.g. the polydispersity) are significantly affected in the presence of deposited material.

4.3 Reaction limited cluster aggregation (RLCA)

The model has been further tested by using the RLCA kernel to model the aggregation and deposition process (cf. section 2 and parameters from Table 2 and 3). The results are reported in Figure 6 (averaged properties) and Figure 7 (distributed properties) for different r_τ values. Note that while the r_τ range explored is the same as for the DLCA case (10^0 - 10^4), the process time (τ_p) considered is much larger in the RLCA case (4.2×10^4 vs 4.2×10^3 s).

Figure 6 - Average properties in the RLCA case – a) Normalized reactor area $A_W / A_{W,0}$ vs τ_N ; b) Polydispersities PD_F, PD_D vs τ_N ; c) free clusters mass fraction ω_F vs τ_N ; d) deposited clusters mass fraction ω_D vs τ_N ; e) free clusters occupied volume fraction ϕ_F vs τ_N ; f) deposited clusters occupied volume fractions ϕ_D vs τ_N ; g) Normalized, free clusters 0th order moment, $\mu_{F,N}^0$ vs τ_N ; h) Normalized, deposited clusters 0th order moment $\mu_{D,N}^0$ vs τ_N . Dashed lines represent deposited clusters properties, while continuous lines indicate free cluster properties. The color code reads: violet, $r_\tau = 10^0$; blue $r_\tau = 10^1$; green $r_\tau = 10^2$; yellow $r_\tau = 10^3$; red; $r_\tau = 10^4$

Figure 7 - a),c),e) $F(x,t)$ vs x at different non dimensional times τ_N , with $r_\tau = 10^0$, $r_\tau = 10^2$ and $r_\tau = 10^4$, respectively; b), d), f) $D(x,t)$ vs x at different non dimensional times τ_N , with $r_\tau = 10^0$, $r_\tau = 10^2$ and $r_\tau = 10^4$, respectively; Continuous lines indicate free clusters, dashed lines deposited clusters. Color codes for τ_N : violet $\tau_N = 15$; blue $\tau_N = 20$; green $\tau_N = 25$; yellow $\tau_N = 30$; red $\tau_N = 40$.

Two major differences distinguish the RLCA regime from the DLCA one: i) not every collision between clusters results in the formation of a larger aggregate and ii) clusters reactivity increases with their mass.²⁶ Due to the reduced reactivity of the clusters (accounted for by the Fuchs stability ratio W), a larger process time τ_p was selected for the RLCA case. At the same time, the employed parameters imply that the τ_{DEP} results, in some cases, larger than the process time. Nevertheless, as τ_{DEP} represents only the deposition rate of primary particles and larger clusters deposit faster than smaller ones (cf. Figure 2), deposition still occurs to a significant extent. This can be appreciated in Figure 6a), where the normalized reactor wall surface is reported against τ_N for different r_τ values. Note that here r_τ is defined in the RLCA case using the corresponding aggregation characteristic time:

$$r_{\tau,RLCA} = \frac{\tau_{DEP}}{\tau_{A,RLCA}} = \frac{\beta(1,1) \cancel{C_{part}}}{Wk_{DEP,0} \pi R_p^2 V_T \cancel{C_{part}}} = \frac{8k_B T}{3W\eta_C k_{DEP,0} \pi R_p^2 V_T} \quad (42)$$

Only for the largest r_τ considered, the normalized reactor wall surface is not completely covered (cf. red curve in Figure 6a)). As already discussed in section 4.2 in the DLCA case, the full coverage is reached without a significant mass loss of free clusters (and corresponding gain in deposited clusters), as shown in Figure 6c) and 6d), where ω_F and ω_D are reported against the nondimensional time τ_N . At the same time, the presence of a deposited cluster mass distribution with which the free clusters interact, induces a significant change in properties such as the polydispersity (cf. Figure 6b)). For lower values of r_τ (cf. violet and blue curves in Figure 6b)), the polydispersity of the free clusters (PD_F), reaches a maximum and then decreases, indicating that also in the RLCA case aggregation between free and deposited clusters is size specific. Note that for larger values of r_τ , i.e. when the deposition takes longer (yellow and red curves) and a lower deposited mass fraction is observed (cf. Figure 6d), the PD_F steadily increases, indicating

that the aggregation process of free clusters is not significantly affected by the deposited cluster mass distribution. As for the deposited cluster polydispersity, PD_D , it increases steadily for the cases where r_τ is large whereas it reaches a steady state for lower r_τ values (violet and blue curve in Figure 6b₂). As already discussed in the DLCA case, such plateau occurs at τ_N at which almost no free clusters are available ($\omega_F \rightarrow 0$), as can be observed for the violet and blue curves in Figure 6c). The free and deposited occupied volume fractions (ϕ_F, ϕ_D) have similar trends as in the DLCA case. ϕ_F increases, reaches a maximum and then decreases when deposited clusters start to significantly uptake free clusters. Conversely, ϕ_D increases in time, until it reaches a plateau in those cases where $\omega_F \rightarrow 0$ and no free clusters are available for increasing the deposited material. Note that a significant difference in terms of ϕ_F is observed for the different r_τ employed, indicating once more the impact of the distributed cluster distribution on the free ones. At the same time, the deposited clusters do not affect all the properties of the free clusters. For instance, their normalized 0th order moment, $\mu_{F,N}^0$ is basically constant for all the r_τ values considered. This is because in the RLCA case, the fastest reactive event is the aggregation between two large clusters (cf. Table 1). Starting from primary particles at time zero, after few aggregation events, the first clusters arise. Before deposition occurs significantly, the cluster-cluster interaction will promote the aggregation of large clusters, hence the largest clusters will be free clusters rather than deposited ones. As a result, even though deposition is present to a significant extent, it does not significantly affect $\mu_{F,N}^0$. As for the normalized concentration of deposited clusters, $\mu_{D,N}^0$, it steadily increases (the more the smaller r_τ), as can be seen in Figure 6h). In certain cases (for smaller r_τ), a plateau is reached at times τ_N where the reactor surface is saturated (cf. violet, blue, green and yellow curves in Figure 6h)).

The distributed properties reported in Figure 7 show how the normalized free cluster distributions (Figure 7 a), c), e)) and the normalized distributed ones (Figure 7b), d) f)) have comparable shapes, both with a long right tail. Some differences still arise. Focusing on the cases where $r_\tau = 10^2, 10^4$, it can be seen how the front of $F_N(x, t)$ shifts (in time) to the right at the expenses of the less concentrated smaller clusters (i.e. the distribution tail). This trend reflects the classically discussed RLCA case.¹⁶ Conversely, while the front of $D_N(x, t)$ shifts to the right, this does not impact the concentration of smaller clusters, which remain constant. Such shift in $D_N(x, t)$ is therefore due to the uptake of free clusters, which preferentially interact with larger deposited clusters as these offer a larger “surface” to react with, as opposed to smaller clusters. While the same reasoning holds also for $D_N(x, t)$ with $r_\tau = 10^0$, $F_N(x, t)$ initially shifts to the right, but eventually shifts to the left when the aggregation between free and deposited clusters becomes significant. This is consistent with the polydispersity trend of the free clusters already observed in Figure 6b₁), which eventually decreases as more and more free clusters are reacting with deposited material.

4.4 Simple shear aggregation (SSA)

For the last simulation set performed, the simple shear aggregation (SSA) has been considered. Once again the same ratio of r_τ has been explored ($10^0 - 10^4$), adjusting the process time τ_p to shorter times ($2.1 \times 10^3 s$ in SSA vs. $4.2 \times 10^3 s$ in DLCA and $4.2 \times 10^4 s$ in RLCA), to avoid the formation of excessively large clusters, which are particularly reactive in this regime (cf. Table 1).

In the present case, r_τ has the following definition:

$$r_{\tau, SSA} = \frac{\tau_{DEP}}{\tau_{A, SSA}} = \frac{\beta(1,1) \cancel{C_{part}}}{k_{DEP,0} \pi R_p^2 V_T \cancel{C_{part}}} = \frac{32 R_p^\beta \dot{\gamma}}{3 k_{DEP,0} \pi R_p^2 V_T} = \frac{32 R_p \dot{\gamma}}{3 k_{DEP,0} \pi V_T} \quad (43)$$

Interestingly, as opposed to the previous cases (cf. equation (41) and (42)), an increase in the primary particle radius R_p increases r_τ . At the same time, in the SSA regime the interaction of large - large clusters is the most likely aggregation event. As a result, the trends are very similar when compared to the ones already discussed in the frame of the RLCA case and are reported in the ESI for the sake of brevity (cf. Figure S1 and S2). Even though in the SSA case parameters such as the shear rate $\dot{\gamma}$ and R_p play a different role than in the DLCA or RLCA case, the use of the non-dimensional parameter r_τ allows to readily assess their impact.

5 Conclusions

In the present paper a deterministic model based on population balance equations has been developed to describe the simultaneous aggregation and deposition of colloids. In particular, by distinguishing between the free and the deposited cluster mass distribution, three kinetic events were accounted for: i) the aggregation between two free clusters, ii) the deposition of a free cluster on the reactor walls and iii) the aggregation between a free and a deposited cluster.

Three different aggregation regimes were explored to describe the aggregation between free clusters, namely diffusion-limited and reaction-limited cluster aggregation, as well as simple shear aggregation. Variations of such aggregation kernels were proposed to describe the aggregation between free and deposited clusters while a simple size-dependent kinetics for the deposition of a free cluster on the reactor walls has been employed.

By introducing the dimensionless parameter r_τ , i.e. the ratio of the deposition and the aggregation characteristic times (cf. equation (40)), it was possible to distinguish among three different cases. In particular:

i) $r_\tau \approx 1$, where the comparable deposition and aggregation times cause the uptake of free clusters by deposited ones from the very beginning of the aggregation process;

ii) $r_t < 1$, where the same reasoning as case i) holds, but deposition is even faster than aggregation;

iii) $r_t > 1$, where the time required for deposition to occur is larger than the one for aggregation and relatively larger aggregates will be formed before being incorporated by deposited material. Moreover, the role of the process time τ_p arises: longer process times allow an even very slow deposition to occur.

Several simulations of the three aggregation regimes have been performed at different values of the parameter r_t . By studying averaged and distributed properties of the free and deposited cluster mass distributions, the impact of the deposited material emerged. It was shown that time evolutions of key properties of the free cluster mass distribution, such as the polydispersity or the occupied volume fraction, were significantly changed across the three aggregation regimes considered.

This model could be a useful tool in better understanding fouling problems, e.g in emulsion polymerization reactors, or clogging, e.g. when undesired crystals (i.e. byproducts) form and accumulate in reactors. Despite the model's simplicity, two main directions could be explored:

- i) comparing the model with experimental data to propose and validate kinetic expressions accounting for the deposition and the aggregation between free and deposited clusters;
- ii) extending the model framework to account for other key phenomena occurring in these situations, such as nucleation, growth, re-suspension and breakage and deepen the relevance of the ongoing phenomena.

In general, the model is useful when the fractal nature of the deposited clusters plays a key role in the subsequent uptake of free clusters.

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Symbol List

Symbol	Meaning	Units
$A_{w,0}$	Free reactor wall surface at time zero	$[m^2]$
$A_w(t)$	Free reactor wall surface	$[m^2]$
$\underline{\underline{C}}$	Change of base matrix	$[-]$
C_{part}	Primary particle concentration	$[# m^{-3}]$
d_f	Fractal dimension of the clusters	$[-]$
$D(x,t)dx$	Concentration of deposited clusters with sizes comprised between x and $x + \Delta x$	$[# m^{-3}]$
$D_{iff}(x)$	Diffusivity of an x -sized cluster	$[m^2 s^{-1}]$
$D_N(x,t)dx$	Normalized (over C_{part}) deposited cluster distribution with sizes comprised between x and $x + \Delta x$	$[-]$
$F(x,t)dx$	Concentration of free clusters with sizes comprised between x and $x + \Delta x$	$[# m^{-3}]$
$F_N(x,t)dx$	Normalized (over C_{part}) free cluster distribution with sizes comprised between x and $x + \Delta x$	$[-]$
$g(x)$	Function accounting for size-dependent deposition	$[-]$
$g_k(x), G_k(x,t)$	Auxiliary functions for treating the population balance equations	$[-]$
$h_k(x), H_k(x,t)$	Auxiliary functions for treating the population balance equations	$[-]$
h_{react}	Reactor height	$[m]$
k_B	Boltzmann constant	$[J K^{-1}]$
$k_{DEP,0}$	Deposition rate constant	$[m^{-2} s^{-1}]$
$k_{DEP}(x)$	Deposition rate of an x -sized cluster	$[m^{-2} s^{-1}]$
$l_k(x), L_{D,k}(x,t), L_{F,k}(x,t)$	Auxiliary functions for treating the population balance equations	$[-]$
$m_k(y), M_{D,k}(x,t), M_{F,k}(x,t)$		

$M(x)$	Function accounting for the cluster mass-dependent reactivity of an x -sized cluster	$[-]$
$n_k(x), N_k(x, t)$	Auxiliary functions for treating the population balance equations	$[-]$
PD_F, PD_D	Polydispersities of the free and the deposited cluster distributions	$[-]$
r_{react}	Reactor radius	$[m]$
$r_\beta(x, y)$	ratio of $\beta(x, y)$ over $\beta^*(x, y)$	$[-]$
r_τ	Ratio of the deposition and aggregation characteristic times	$[-]$
$r_{\tau, DLCA}$	r_τ in the three different regimes, DLCA, RLCA; SSA	$[-]$
$r_{\tau, RLCA}$		
$r_{\tau, SSA}$		
R_p	Primary particle radius	$[m]$
s_i	Parameter accounting for the Gaussian function overlapping	$[-]$
t	time	$[s]$
T	Temperature	$[K]$
V_{react}	Reactor volume	$[m^3]$
W	Fuchs stability ratio	$[-]$
$\underline{\underline{W_x}}$	Weighting matrixes used in the discretization method	$[-]$
x, y	Number of particles constituting a cluster	$[-]$

Greek Letters

$\alpha_i(t)$	Height of the Gaussians approximating the free cluster mass distribution	$[-]$
$\beta_i(t)$	Height of the Gaussians approximating the deposited cluster mass distribution	$[-]$
$\beta(x, y)$	Aggregation rate between two free clusters of size x and y	$[m^3 s^{-1} \#^{-1}]$
$\beta_{DLCA}(x, y)$	$\beta(x, y)$ in the DLCA, RLCA, and SSA regimes	$[m^3 s^{-1} \#^{-1}]$
$\beta_{RLCA}(x, y)$		
$\beta_{SSA}(x, y)$		
$\beta^*(x, y)$	Aggregation rate between a free cluster of size x and a deposited cluster of size y	$[m^3 s^{-1} \#^{-1}]$
$\beta_{DLCA}^*(x, y)$	$\beta^*(x, y)$ in the DLCA, RLCA, and SSA regimes	$[m^3 s^{-1} \#^{-1}]$
$\beta_{RLCA}^*(x, y)$		
$\beta_{SSA}^*(x, y)$		

$\underline{\gamma}, \underline{\gamma}^w$	Vectors employed in discretization of the PBE	$[-]$
$\dot{\gamma}$	Shear rate	$[s^{-1}]$
η_C	Viscosity of the continuous phase	$[Pa\ s]$
$\kappa_{FF}, \kappa_{FW}, \kappa_{FD}$	Prefactor accounting for the interaction between: free clusters (F), deposited clusters (D), and walls (W)	$[m^3 s^{-1} \#^{-1}]$
λ	Exponent in the function $M(x)$	$[-]$
$\mu_{F,N}^k, \mu_{D,N}^k$	Normalized k -th moment of the free and deposited clusters	$[-]$
τ_N	Non dimensional time	$[-]$
τ_A	Characteristic time of aggregation	$[s]$
τ_{DEP}	Characteristic time of deposition	$[s]$
τ_P	Process characteristic time	$[s]$
ϕ_F, ϕ_D	Occupied volume fractions of the free and the deposited cluster mass distributions	$[-]$
$\underline{\underline{\psi}}$	Matrix used in the discretization of the PBE	$[-]$
ω_F, ω_D	Free and deposited mass fractions	$[-]$

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