Determination of nanoparticle heteroaggregation attachment efficiencies and rates in presence of natural organic matter monomers. Monte Carlo modelling

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Abstract
Understanding the transformation and transport of manufactured nanoparticles (NPs) in aquatic systems remains an important issue due to their potential hazard. Once released in aquatic systems, NPs will interact with natural compounds such as suspended inorganic particles and/or natural organic matter (NOM) and heteroaggregation will control their ultimate fate. Unfortunately, systematic experimental methods to study heteroaggregation are not straightforward and still scarce. In addition, the description of heteroaggregation rate constants and attachment efficiencies is still a matter of debate since no clear definition exists. In this work, an original cluster-cluster Monte Carlo model is developed to get an insight into heteroaggregation process descriptions. A two-component system composed of NPs and NOM fulvic acid monomers is investigated by considering several water models to cover a range of (relevant) conditions from fresh to marine waters. For that purpose, homo- and hetero- individual attachment efficiencies between NPs and NOM units are adjusted (NP-NP, NOM-NOM and NP-NOM). The influence of NP/NOM ratio, […]

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DOI : 10.1016/j.scitotenv.2018.09.017
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In this work, an original cluster-cluster Monte Carlo model is developed to get an insight into heteroaggregation process descriptions. A two-component system composed of NPs and NOM fulvic acid monomers is investigated by considering several water models to cover a range of (relevant) conditions from fresh to marine waters. For that purpose, homo- and hetero- individual attachment efficiencies between NPs and NOM units are adjusted (NP-NP, NOM-NOM and NP-NOM). The influence of NP/NOM ratio, NOM-NOM homoaggregation versus heteroaggregation, and surface coating effects is studied systematically. From a quantitative point of view, aggregation rate constants as well as attachment efficiencies are calculated as a function of physical time so as to characterize the individual influence of each parameter and to allow future comparison with experimental data.

Heteroaggregation processes and global attachment efficiencies corresponding to several mechanisms and depending on the evolution of heteroaggregate structures all along the simulations are defined. The calculation of attachment efficiency values is found dependent on NP/NOM concentration ratios via coating effects, by the initial set of elementary attachment efficiencies and influence of homoaggregation.

Marine water represents a specific case of aggregation where all particle contacts are effective. On the other hand, in “ultrapure” and “fresh waters”, a competition between homo- and heteroaggregation occurs depending on the initial attachment efficiencies therefore indicating that a subtle change in the NP surface properties as well as in the water chemistry have a significant impact on heteroaggregation processes.

Keywords: Heteroaggregation, Nanoparticle, Natural Organic Matter, Attachment efficiency, Surface coating, Monte Carlo simulation
1. Introduction

With the progress of nanomaterials and nanotechnologies (Lahann, 2008; Maynard et al., 2006; Raffa et al., 2010; Sobolev et al., 2009), the production of manufactured nanoparticles (NPs) and consequently their potential impacts in our daily life are continuously increasing (Bhatt and Tripathi, 2011; Carl Englert, 2007; Klaine et al., 2008; Mueller and Nowack, 2008; Schulte et al., 2008). The main interest for nanotechnologies comes from the very large specific surface area and surface properties of NPs, which provide them high chemical reactivity at the nanoscale level. Due to these very specific properties, NPs are used in many different domains such as cosmetics, (nano)medicine, energy, textiles, and (nano)pesticides (Cao and Wang, 2011; Rao et al., 2006; Weir et al., 2012; West and Halas, 2000; Wilkinson, 2003). Unfortunately, many open questions remain with respect to NP release, fate and effects on ecosystems and human health (Auffan et al., 2009; Bhatt and Tripathi, 2011; Gregory, 2005; Ju-Nam and Lead, 2008; Lowry et al., 2012; Moore, 2006; Navarro et al., 2008).

In the environment, determining the fate, transport and NP transformation processes remains challenging and strongly dependent on a wide range of intrinsic and extrinsic parameters (Colvin, 2003; Dale et al., 2015; Fabrega et al., 2011; Moore, 2006; Sani-Kast et al., 2015). In the aquatic environment, the chemical reactivity and transport properties of NPs are expected to be strongly controlled by water properties such as pH, water hardness, ionic composition, temperature (Davis et al., 1978; Ellis et al., 2016; Keller et al., 2010; Koelmans et al., 2015; Nowack et al., 2012; Nowack and Bucheli, 2007), presence of living organisms (Auffan et al., 2009; Braun et al., 2015; Carnal et al., 2015; Ellis et al., 2016; Labib, 1988) and also suspended particulate matter (SPM) (Baalousha, 2009; Cornelis et al., 2013; Garcia et al., 2017; Li et al., 2017; Praetorius et al., 2014; Thio et al., 2011). Subtle changes in water chemistry can profoundly modify NP surface properties, interactions with the surrounding compounds as well as key processes such as NP aggregation and dissolution (Badawy et al., 2010; Ellis et al., 2016; Mukherjee and Weaver, 2010). In particular, the presence of natural organic matter (NOM) at a concentration of few mg/L is expected to have an important impact on the NP surface properties (coating, surface charge modification) and heteroaggregation behavior (Praetorius et al., 2014; Seijo et al., 2009; Thio et al., 2011).

Heteroaggregation, which describes the aggregation of dissimilar particles, is a key process having significant consequences on the NP fate, transport, bioavailability, uptake and ecotoxicity in environmental systems such as water, soil and atmosphere (Navarro et al., 2008; Nur et al., 2015; von Moos et al., 2014). Consequently, quantitative information on heteroaggregation such as aggregation rate constants and attachment efficiencies is urgently needed to parameterize NP environmental transport and fate models (Dumont et al., 2015; Praetorius et al., 2012; Quik et al., 2015; Sani-Kast et al., 2015). Attachment efficiencies (α) represent a key parameter in these
processes and illustrate the probability of an efficient collision between identical or different compounds. $\alpha$ values are controlled by the balance between attractive and repulsive forces occurring between compounds and characterize the presence of a potential barrier. In the absence of repulsive forces and barrier, all collisions are efficient and $\alpha$ is equal to unity. Attachment efficiencies can be calculated by estimating the repulsive potential barrier between particles. In simple cases, electrostatic and van der Waals interactions are usually described using the DLVO theory, then the Fuchs stability ratio (R. Wiese and W. Healy, 1970) is determined and related to the attachment efficiency.

Aggregation processes have been largely described and studied using experimental approaches (Albanese and Chan, 2011; Baalousha, 2009; Barton et al., 2014; Loosli et al., 2013; Praetorius et al., 2014) and numerical/theoretical models (Costas et al., 1995; Keller et al., 2010; Markus et al., 2015; Meakin, 1984; Therezien et al., 2014) in various domains such as aerosol formation, flocculation processes for water treatment, blood coagulation and volcanic dust eruption. Most of these studies start from the description made by Marian von Smoluchowski, who developed a mathematical kernel of equations to characterize second-order rate processes of spherical particles under Brownian motion and/or in specific force fields (laminar shear, gravity, …) (Elderfield, 1987; Elimelech et al., 1998; Filbet and Laurenço, 2004; Krivitsky, 1995). In addition to this analytical approach, several aggregation models were also numerically developed in 2D and 3D, such as the Witten and Sander Diffusion Limited Aggregation (Meakin, 1985; Witten and Sander, 1981) and the Cluster-Cluster Aggregation models (Kusaka et al., 2011; Meakin, 1984; Xiong et al., 2010). Furthermore, fractal dimension concepts were introduced to provide a mathematical description of the aggregate structures and to characterize different aggregation regimes (Chakraborti et al., 2003; Kolb and Herrmann, 1987; Kranenburg, 1994).

From an experimental point of view, various methods were developed to determine aggregation rate constants and extract attachment efficiencies (Geitner et al., 2017) and aggregate fractal dimensions (Logan and Kilps, 1995; Puertas et al., 2000). Aggregation rates and attachment efficiency values are generally determined by following the evolution of the particle size as a function of time via Dynamic Light Scattering (DLS) (Afrooz et al., 2014; Gallego-Urrea et al., 2011; Petosa et al., 2010)), laser diffraction (LD) (Labille et al., 2015; Praetorius et al., 2014) or Nanoparticle Tracking Analysis (NTA) (Gallego-Urrea et al., 2011), or by following the differential settling of homo/heteroaggregates in sediments via batch methods (Barton et al., 2014; Geitner et al., 2017). Quantification of heteroaggregation between citrate stabilized gold nanoparticles and hematite colloids was investigated using a novel approach involving time-resolved dynamic light scattering and parallel experiments designed to quantify nanoparticle attachment and heteroaggregate surface charge (Smith et al., 2015). This study, in particular,
underlined the importance of surface coverage in heteroaggregation. However, most of the methods and models were developed and parametrized to investigate aggregation of one type of particles (homoaggregation), especially in the experimental approaches.

When increasing the system heterogeneity, e.g. by considering two types of compounds (NPs and NOM), the system becomes rapidly more complicated to describe, with an increase of the number of possible aggregation scenarios (Figure 1). From numerical and experimental points of views, a more extended description of particle interactions (NPs-NOM; NPs-NPs; NOM-NOM), water and system properties is required to get an insight into different heteroaggregation processes. On the other hand, the type and quality of information obtained from experiments is dependent on the method used. Some techniques will be better designed for the description of fast aggregation rates (LD) while others will be more adapted to slow regimes (DLS, settling batch methods). In most cases, the most reliable information is obtained for early stages of heteroaggregation, whereas a quantitative description of later stages of aggregation is generally limited. In addition, concentration effects and mixing procedures are also expected to play important roles on the heteroaggregation mechanisms, rates and heteroaggregate morphologies. Furthermore, the competition between homo- and heteroaggregation remains complex to distinguish in experiments.

In light of these experimental challenges, computer simulations represent a powerful approach to investigate in details heteroaggregation processes between NPs and NOM and get an insight into the impact of specific parameters such as the concentration ratio between NOM and NPs or processes such as NOM coating (and evolution with time) and impact on heteroaggregation. In this study, a cluster-cluster aggregation model is developed to investigate heteroaggregation mechanisms of a NP and NOM mixtures and by adjusting individual attachment efficiencies. Different relevant environmental scenarios such as: (i) heteroaggregation in marine waters (high ionic strength promoting homoaggregation) (ii) fresh waters (low ionic strength promoting heteroaggregation over homoaggregation) and (iii) ultrapure waters (resulting in heteroaggregation only) are considered via the adjustment of the individual attachment efficiencies. In this study, we are assuming a strong interaction between NPs and NOM in a situation representative of a system composed of positively charged NPs in presence of negatively charged NOM units. The low expected concentrations of NPs in natural systems compared to the high NOM concentrations is taken into account by adjusting the relative concentrations between both types of particles. Monte Carlo modelling provides the opportunity to get an insight into heteroaggregation mechanisms and to follow the evolution of the attachment efficiency parameter from primary heteroaggregation
to global attachment values. Moreover, computer simulations allow to cover a wide range of different parameters
and environmental scenarios.

In the first part of this paper, theoretical concepts and the heteroaggregation model are presented. Then, the model
is validated based on homoaggregation simulations. Surface and solution properties (attachment efficiencies,
NOM/NP concentrations) are then adjusted to investigate some specific environmental processes such as surface
coating and saturation, and heteroaggregation in presence of NOM homoaggregation. Finally, kinetic aggregation
rates are calculated for different water models as well as the corresponding heteroaggregation attachment
efficiencies.

2. Theory and model description

2.1 Aggregation theory

The individual aggregation rate constant between two particles of sizes $i$ and $j$ is usually defined by:

$$k_{ij}^{agg} = \alpha_{ij} k_{ij}^{coll}$$  \hspace{1cm} (1.1)

where, on the one hand, $k_{ij}^{coll}$ represents the collision rate constant, which is generally dependent on particle sizes
and densities as well as corresponding transport model (Brownian motion, orthokinetic or differential
sedimentation) (Elimelech et al., 1998). On the other hand, the sticking probability or attachment efficiency $\alpha_{ij}$ is
dependent of the sum of the interaction forces between the two particles. This attachment efficiency is usually
comprised between zero and unity. Zero corresponds to a stable suspension without aggregation (predominance
of repulsive forces) whereas $\alpha_{ij} = 1$ corresponds to a system where each contact between particles is efficient
regarding the formation of irreversible bonds.

In the Smoluchowski theory (Smoluchowski, 1916), a kernel of equations is used to describe each possible reaction
between particles. Then the formation rate of aggregates of size $k$ is defined by:

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{i=k-1} \alpha_{ij} k_{ij}^{coll} n_i n_j - n_k \sum_{i=1}^{\infty} \alpha_{ik} k_{ik}^{coll} n_i$$  \hspace{1cm} (1.2)

where $n_{i,j,k}$ is the number concentration of particles of sizes $i,j,k$ at time $t$. The first part of the equation represents
the formation rate of aggregates $k$ resulting from the collision of particles of size $i$ and $j$, respectively, while the
second part describes the removal of these aggregates resulting from collisions with particles of size $i$.

For small identical particles (below 1 $\mu$m), the perikinetic case with Brownian motion is the most relevant and
equation (1.2) can be rewritten for the very early stage of the aggregation process as:

$$\left( \frac{dn_1}{dt} \right)_{t \to 0} = - \frac{k_{homo}}{2} n_1^2$$  \hspace{1cm} (1.3)
where $k_{homo}^{\text{particle}}$ represents the aggregation rate constant for primary particles, defined as particle removal rate constant equal to $k_{homo}^{\text{particle}} = \frac{8k_BT}{3\mu}$, $k_b$ the Boltzmann constant, $T$ the temperature and $\mu$ the viscosity. For an aqueous dispersion, at $T = 293$ K and $\mu = 1.00 \times 10^{-3}$ m$^2$ s$^{-1}$, the rate constant is equal to $1.09 \times 10^{-17}$ m$^3$ s$^{-1}$.

Another parameter, which is derived from this equation, is the aggregation rate constant $k_{homo}^{\text{agg}}$ which describes the evolution of the object concentration (total number of particles and aggregates). This parameter, also referred to as heteroaggregation rate constant in the case of more than one compound present in the solution, is directly related to the particle removal rate constant and is equal to $k_{homo}^{\text{agg}} = \frac{k_{homo}^{\text{particle}}}{2}$, i.e. $5.47 \times 10^{-18}$ m$^3$ s$^{-1}$.

### 2.2 Heteroaggregation model

Our model is based on a Monte Carlo (MC) cluster-cluster aggregation model (CCA). MC modelling is a common approach used to simulate the Brownian motion of small particles (Labbez and Jönsson, 2009; Liu et al., 2011; Seijo et al., 2006). In this study, simulations are performed to reproduce this random displacement, to consider the interaction between particles via a set of attachment efficiencies and to get an insight into the primary stage of heteroaggregation. Simulations are carried out in a canonical ensemble of volume $V$ and temperature $T$ fixed. NPs and NOM are described by an off-lattice three-dimensional coarse-grained model. The particles are modelled using spherical units (nanoparticles and NOM monomers). Therefore, particles refer to isolated NPs and NOM. With time, particles are forming aggregates with complex morphologies. The designation “objects” refers to aggregates and particles (i.e. isolated NPs and NOM units). NOM is modelled as fulvic acids (FA) monomers, which are one of the major components of humic substances. FA are represented at the coarse grained level with a radius of 1 nm (Seijo et al., 2009) whereas NP radius is arbitrarily set to 10 nm. Of course, the model allows adjustment of different NP sizes. An infinitely diluted aqueous solution with a continuum representation of the solvent and a fixed temperature of 298K are considered. The modelling cell is cubic and the minimum image convention is used to take into account the periodicity of the system. The size of the simulation box can vary and be adjusted, depending on the particle volume occupied. The size of the cell ranges between 874 to 3176 nm according to the system under investigation and to keep a constant volume fraction. To create the initial system configuration, particles are inserted randomly inside the simulation cell and an excluded volume test is made to avoid any direct contact. For each simulation step, all particles (and aggregates) are randomly moved one by one according to their sizes (equivalent volume). All the resulting contacts are tested after each displacement. If the center-to-center distance between two particles is lower than the sum of the respective particle radii, then a MC attachment test is
performed by comparing a random number chosen between 0 and 1 to the attachment efficiency corresponding to
the type of contact. Then, the movement is accepted or not according to the initial set of attachment values.
To consider realistic displacements all the particles (NPs and NOM) and aggregates are not moving with the same
velocity. All the movements as well as the physical time are based on the displacement of the NPs. This
displacement is arbitrarily fixed to 1 nm (10%) of the NP radius. The displacement of the rest of the objects is
based on the cubic root of the equivalent volume ratio, \( r_{\text{dis}} = \sqrt[3]{\frac{V_{\text{FreeNP}}}{V_{\text{object}}}} \). This formula allows taking into account
the equivalent volume of each object. When this ratio is higher than 1, the object is translated \( x \) times where \( x \)
represents the integer of \( r_{\text{dis}} \). Otherwise, in the case of \( r_{\text{dis}} < 1 \), the object is moved once by the factor \( r_{\text{dis}} \times 1 \text{nm} \).
Finally, at each MC step of the simulation, all the positions and status are recorded and stored so as to perform
post data treatment and calculation of mean values and variables such as the number of particles and objects
variation with time on which calculations of kinetic rate constants are based. For each system studied, ten replicates
are considered to improve data interpretation from a statistical point of view.

2.3 Physical time vs Monte Carlo time

All our simulations are performed using a Monte Carlo procedure (Frenkel, 2004; Frenkel and Smit, 2001) which
results in the formation of aggregates as a function of the MC steps. One of the most important parameters in our
model analysis is the physical time \( t \). To establish a link between the particle displacement and physical time, we
have developed and validated a procedure which calculates the correspondence between MC steps and physical
time. This model is based on the mean free path calculation due to Brownian motion and on the Einstein-Stokes
equation for spherical particles. In three dimensions, the mean square displacement of a Brownian particle can be
written as:

\[
< r^2 > = 6Dt
\]  

(1.4)

where \( D \) is the Stokes-Einstein diffusion coefficient defined as:

\[
D = \frac{k_BT}{6\pi\mu R}
\]  

(1.5)

where \( R \) represents the particle radius. By combining equations (1.4) and (1.5), a link is established between the
particle size, displacement, temperature, solution viscosity, and physical time. In our heteroaggregation model,
displacement is based on the isolated NP displacement and on the ratio of the equivalent volumes. To further
validate our procedure, one thousand NPs, with a radius \( R \) equal to 10 nm, were introduced in an infinite simulation
box and randomly moved by a radius of 1 nm during 100000 MC steps. Each \( 10^5 \) MC steps, the average mean free
path of all the nanoparticles was calculated as a function of $t$. After performing a set of ten different simulations, the correspondence between one MC step and the physical time was determined and found equal to 7.45 ns/ MC step for a temperature and a viscosity equal to 293 K and 0.001 m$^2$.s$^{-1}$, respectively.

### 2.4 Attachment Efficiency

Experimentally, the attachment efficiency (Lyklema, 2005) is generally defined as the ratio between the aggregation rate and the aggregation rate when all the collisions are expected to be efficient, for example at high ionic strength. In our model, the individual attachment efficiency is not computed but constitutes an input parameter which is representative of individual NP and NOM surface properties, solution chemistry, and resulting interaction forces. As shown in Figure 1, several attachment efficiencies can describe heteroaggregation at different time scales of the process. At the very early stages, during the formation of dimers and trimers, $\alpha'_{\text{hetero}}$ is usually considered, then $\alpha''_{\text{hetero}}$ corresponding to the heteroaggregation of dimers and trimers is taken into account while at long stages a more system-specific, $\alpha_{\text{global}}$ must be defined. Therefore, $\alpha_{\text{hetero}}$, which is the contribution of $\alpha'_{\text{hetero}}$ and $\alpha''_{\text{hetero}}$ is commonly representative of the formation of small heteroaggregates. Since the heteroaggregate sizes and morphologies evolve all along the heteroaggregation process, the effective attachment efficiency values are expected to change from primary to secondary heteroaggregation, and heteroaggregation to global attachment efficiencies as shown in Figure 1. This is a crucial issue with important consequences on the parametrization of long time scale NP fate transport model. Indeed, in some cases, NP surfaces can be rapidly coated with NOM with $\alpha'_{\text{hetero}}$ close to 1, resulting in surface saturation, then leading to system stabilization with an $\alpha_{\text{global}}$ value close to zero.

To characterize NP coating process with NOM in our model, the number of NOM particles attached on the NP surface $n_{\text{att}}$ is recorded and the fraction of surface saturation $f_s$ is calculated as the ratio of the sum of NOM projected surfaces over NP surface according to:

$$f_s = \frac{\sum_{i=1}^{n_{\text{att}}} \pi R_i}{4\pi R_{\text{NP}}^2}$$

where $R_i$ represents the radius of the NOM particle which is adsorbed.

In this study, different attachment efficiency values for homo/heteroaggregation are given in Table 1 so as to explore different environmentally contrasting conditions, from marine to fresh waters. NOM-NOM homoaggregation is permitted with different individual attachment efficiencies. These individual attachment efficiency values are arbitrarily selected so as to simulate aquatic media with low (fresh water 0.01 and 0.1) and
high ionic strength (marine water). All along this work, $\alpha_{NP-NOM}$ is considered equal to 1. Once again, it should be noted that these values can be adjusted to explore different scenarios.

3. Results

3.1 Model Validation

Before investigating the influence of NP and NOM concentrations as well as the effect of various individual attachment efficiencies on the relative importance of heteroaggregation, validation of the numerical model developed here is required and, more particularly, the procedure used for the calculation of the physical time. For that purpose, homoaggregation simulations were carried out with 15000 MC steps with a simulation box of 4000 nm in length containing 1000 NPs and with $\alpha_{NP-NP} = 1.0$. The numbers of particles and objects were systematically calculated as a function of the physical time so as to estimate aggregation rate constants via the variation with time of the number of particles and objects according to equation 1.3. As shown in Figure 2a, for homoaggregation, the number of objects and particles continuously decreases with physical time $t$. The loss of NPs is more efficient (faster) than the removal of objects all along the simulation time. This is due to the correlation between formation and removal of particles during the aggregation process. Indeed, when a dimer is formed, two particles disappear in the counting of particles. Furthermore, as shown in Figure 2b, the concentration of objects and particles is correlated to the physical time. At the very early stages of the aggregation process, i.e., when dimers and trimers are formed, linear curves are observed and aggregation and particle removal rate constants can be extrapolated with values equal respectively to $5.81 \times 10^{-18}$ and $1.18 \times 10^{-17} \text{m}^3 \text{s}^{-1}$. These values are in good agreement if comparison is made with the values calculated from the Smoluchowski theory (section 2.1). A factor of two is obtained between $k_{homo}^{\text{particle}}$ and $k_{homo}^{\text{agg}}$ ($k_{homo}^{\text{particle}} / k_{homo}^{\text{agg}} = 2.03$) indicating that the physical time calculated by our diffusion model fits well.

3.2 Surface coating and heteroaggregation rates at constant natural organic matter concentration

To get an insight into the influence of the relative NP/NOM concentration ratio on NP surface coating process, and impact on heteroaggregation, simulations were performed over $10^6$ MC steps in ultrapure water with $\alpha_{NP-NOM} = 1.0$ and $\alpha_{NP-NP} = \alpha_{NOM-NOM} = 0.0$ (Table 1). The number of NOM particles was kept constant for all the simulations and equal to 1000 whereas the number of NPs was varied. The NP number was adjusted from 1 to 100 which, considering the size of the simulation box, is equivalent to a variation between $1.6 \times 10^{16}$ and $157.10^{16}$ particles.L$^{-1}$. As shown in Figure 3a, in which the percentage of surface saturation and the average number of
adsorbed NOM per NPs are plotted as a function of the physical time, two different behaviors are observed at short and long-time scales for each NP concentration. At the early stages of the simulation, the fraction of surface saturation and the number of absorbed NOM increase rapidly until reaching a plateau value at longer time. Efficient collisions are predominant at the beginning of the simulation due to NP surface availability for the NOM particles. Fraction of surface saturation reaches a maximum value for a ratio of 1 NP and 1000 NOM and is equal to 85%, which corresponds to 340 adsorbed particles (full surface saturation would correspond to 400). This maximum value is not found to change (increase) by considering more than 1000 NOM monomers. With increasing NP concentration, coverage decreases as well as the number of NOM particles in the solution (Figure 3b) and saturation has a lowest impact promoting heteroaggregation instead of saturation. Such saturation effect is the result of the balance between the number of NOM in the simulation box and the accessible surface of the NP which is a function of the number of NOM already adsorbed on the NPs as shown in Figure 4. As shown by Smith et al (Smith et al., 2015), surface coverage is limited by the geometry of the particles and by the number of objects already deposited on the surface and very similar conclusions compared to our results were obtained. At high NP/NOM ratio, the number of NOM particles in the simulation box moves to zero quite rapidly. It should be noted that the NP surface available is also reduced by the formation of heteroaggregates as shown in Figure 4. Indeed, NOM particles, once adsorbed at the NP surface, can act as bridging units between NPs and reduce the possibility of NOM particles to be adsorbed in the bridging zone.

Furthermore, saturation effects are playing a key role at different periods of the heteroaggregation process and, in particular, on the heteroaggregation rate constants. As shown in Figure 3c, the heteroaggregation rate constant can be extrapolated from the temporal evolution of the object concentration and comparison can be made between the aggregation rate progress at short (heteroaggregation rate) and long time (global heteroaggregation rate) at low NP/NOM ratios. At the early stages, NP free surface is available and the heteroaggregation process takes place with a continuous decrease of the number of objects whereas, with time, the capacity of adsorbing NOM particles becomes more and more limited. As a result, the number of objects is slowly decreasing with time and, very interestingly, two distinct values of \( k \) corresponding respectively to heteroaggregation at short time and, in presence of surface saturation effect at “long” time can be calculated. Equilibrium effects are therefore expected to reduce the heteroaggregation rate constants.
3.3 Heteroaggregation rates at variable NOM concentration.

Heteroaggregation is now discussed by considering a fixed NP number and variable NOM concentration. Different scenarios regarding the initial attachment efficiencies are investigated and the corresponding heteroaggregation rate constants and attachment efficiencies \( \alpha_{\text{hetero}} \) are determined. The heteroaggregation process is studied by considering different number ratios of NPs and NOM (\( 2.10^{-3} \) to \( 2.10^{-2} \)), corresponding to 10 NPs and 500 to 5000 NOM particles present in the simulation box at the initial time. Four different models of waters: marine, ultrapure, and fresh waters “0.1” and “0.01” are considered (where 0.1 and 0.01 are corresponding to the NOM-NOM individual attachment efficiencies). The main difference between the fresh waters conditions is related to the importance of homoaggregation, between NOM particles. The case of marine water is a favorable and “reference” case where all the collisions are efficient (i.e. all attachment efficiencies are equal to 1). 30000 MC steps are carried out for each NPs/NOM ratio and for each water model we concentrate on the very first stages of the heteroaggregation. Our analysis is once again based on the variation with time of the total number of objects.

As shown in Figure 5, in which the time variation of the inverse of the object concentration is given for the different water models, at a fixed ratio (10 NPs and 1000 NOM), distinct behaviors are observed. For the marine water, homoaggregation between NOM as well as NPs plays a key role in the overall aggregation process. Indeed, the object number is rapidly decreasing as a function of time indicating a fast aggregation process. For freshwaters and ultrapure water, the object removal rate is found to be lower and progressively shifted to low values with the decrease of \( \alpha_{\text{NOM-NOM}} \). The ultrapure water condition is found to be very similar to fresh water when NOM homoaggregation is weak. To make the analysis more quantitative, aggregation rate constants have been determined by linear regression at the first simulation stages (30-40 \( \mu \)s) at different NOM concentrations. They are given in Table 2.

In Figure 6, the heteroaggregation rate constants are explicitly represented as a function of NOM concentration. It is found that for marine water, the heteroaggregation rate constant is continuously increasing with of the number of NOM. Particles rapidly disappear and form a significant number of aggregates (as shown in Figure 8). On the other hand, in ultrapure and fresh water 0.1 and 0.01, heteroaggregation rate constants are slightly decreasing with the increase of NOM concentration to reach plateau values. \( k_{\text{hetero}}^{\text{agg}} \) decreases to low values at high NOM concentration compared to marine waters in which homoaggregation is the dominant mechanism. Indeed, in the case of marine waters, the heteroaggregation rate constant is close to the theoretical value obtained for
homoaggregation especially for high NOM concentration, as expected, because except for the slightly different size of NP and NOM they almost behave as a homoaggregating system due to the same individual attachment efficiencies. It should be noted that the kinetic rate constant is smaller than the theoretical value owing to the fact that two processes are involved here i.e. homoaggregation but also NOM adsorption (which is also heteroaggregation) at the NP surface which reduces the heteroaggregation rates compared to homoaggregation.

In ultrapure and fresh waters, $k_{hetero}^{agg}$ is found to be significantly smaller and it decreases with the NOM concentration. The heteroaggregation process is controlled by the balance between the available free space at the NP surface and the probability of collision between NPs and NOM. At low concentration, surface coverage is less important hence promoting heteroaggregation and consequently the increase of $k_{hetero}^{agg}$.

In Figure 7, the heteroaggregation attachment efficiencies of each water model and different relative concentration ratio are calculated by considering marine water as the reference values (highest possible aggregation rate). $\alpha_{hetero}^{agg}$ values, derived from heteroaggregation rate constant, are plotted as a function of the NP/NOM ratio and reported in Table 3.

At high NOM concentration, the attachment efficiencies are close to zero due to surface saturation effects and reduced collision probability. In the case of fresh water “0.01”, these values are a little bit higher due to limited homoaggregation which takes place (for fresh water 0.01 $\alpha_{hetero}^{agg} \approx 0.01$). At low $\alpha_{\text{NOM-NOM}}$, the attachment efficiencies of ultrapure and fresh water 0.01 have similar behavior due to the weak impact of homoaggregation on the heteroaggregation process. The more available free NP surface as well as a decrease of saturation effects contribute to more effective heteroaggregation between NOM and NPs. This increase of $\alpha_{hetero}^{agg}$ with NOM concentration decrease is also observed in fresh water 0.1. However, in this case, the homoaggregation has a strong impact on the hetero attachment efficiencies with a more significant increase of heteroaggregation rate constant (for fresh water 0.1 $\alpha_{hetero}^{agg} = 0.45$). As shown here, a subtle change in the input parameters, or environmental conditions, such as the individual attachment efficiencies can have a strong impact on the heteroaggregation process and related attachment efficiency values. To help in data interpretation and observations, simulation snapshots are given in Figure 8. Saturation effects are illustrated if one considers the ultrapure water case and by increasing the NOM concentration. On the other hand, the presence of NOM homoaggregates is clearly shown for fresh water 0.1 and marine waters for which the surface saturation effects are respectively reduced or absent, resulting in an increase of $\alpha_{hetero}^{agg}$ values.
4. Conclusions

In this study, various environmental scenarios from fresh to marine waters as well as mechanisms such as homo- and heteroaggregation have been investigated via the development of an original and novel Monte Carlo cluster-cluster aggregation approach. We have shown that Monte Carlo calculations when linked with physical time can constitute a powerful approach to get an insight into heteroaggregation process between NPs and NOM and to obtain a better description of heteroaggregation in different water models. Complex processes such as surface saturation, homoaggregation and heteroaggregation, which are expected to control aggregation kinetics of NPs, can be investigated in details. Concentration ratios of NPs and NOM have been found to play a key role in the heteroaggregation processes. From a mechanistic point of view, NOM can act as bridging units to create large heteroaggregates or stabilize NPs. Marine water model here represents a specific and favorable case of aggregation where all contacts are effective and as a reference situation for the calculation of attachment efficiencies. On the other hand, in ultrapure and fresh waters, a competition between homo- and heteroaggregation occurs depending on the initial attachment efficiencies and concentration ratios.

The simulations and results described in this paper constitute a preliminary step towards the description of more complex processes and systems, which could involve more than two components i.e. by including inorganic colloids or by considering NOM as small aggregates already present in the dispersing medium. One could also think to consider weak NP-NOM interactions instead of strong affinity individual attachment values or to compute them via calculation of Fuchs stability ratio via DLVO theory or to simply use experimental values.

5. Acknowledgement

The authors are grateful to the financial support received from the European Commission within the Horizon 2020 Program (NanoFase 15.0183-2, 646002).


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Table 1: Individual attachment efficiencies used in the ultra-pure water, marine and fresh water scenarios.

<table>
<thead>
<tr>
<th>Type of water</th>
<th>Type of contact</th>
<th>$\alpha_{NP-NOM}$</th>
<th>$\alpha_{NOM-NOM}$</th>
<th>$\alpha_{NP-NP}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrapure</td>
<td></td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Fresh 0.01</td>
<td></td>
<td>1.0</td>
<td>0.01</td>
<td>0.0</td>
</tr>
<tr>
<td>Fresh 0.1</td>
<td></td>
<td>1.0</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Marine</td>
<td></td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 2. Heteroaggregation rate constants, $k_{hetero}^{agg}$ ($10^{-18}$ m$^3$ s$^{-1}$) for ultrapure, marine and fresh water models at different NOM concentrations. NPs = 10.

<table>
<thead>
<tr>
<th>Total number of NOM particles</th>
<th>500</th>
<th>1000</th>
<th>2000</th>
<th>3000</th>
<th>4000</th>
<th>5000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrapure</td>
<td>0.65</td>
<td>0.30</td>
<td>0.16</td>
<td>0.10</td>
<td>0.08</td>
<td>0.06</td>
</tr>
<tr>
<td>Fresh 0.01</td>
<td>0.71</td>
<td>0.36</td>
<td>0.20</td>
<td>0.14</td>
<td>0.12</td>
<td>0.10</td>
</tr>
<tr>
<td>Fresh 0.1</td>
<td>1.36</td>
<td>0.65</td>
<td>0.52</td>
<td>0.46</td>
<td>0.45</td>
<td>0.44</td>
</tr>
<tr>
<td>Marine</td>
<td>3.00</td>
<td>3.08</td>
<td>3.18</td>
<td>3.59</td>
<td>3.84</td>
<td>4.16</td>
</tr>
</tbody>
</table>

Table 3. Heteroaggregation attachment efficiencies for ultrapure and fresh water at different NOM concentrations.

<table>
<thead>
<tr>
<th>Number of NOM particles</th>
<th>Ultrapure water (0.0)</th>
<th>Fresh water (0.01)</th>
<th>Fresh water (0.1)</th>
<th>$\alpha_{hetero}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.216</td>
<td>0.238</td>
<td>0.454</td>
<td>&gt; 0.2</td>
</tr>
<tr>
<td>1000</td>
<td>0.103</td>
<td>0.118</td>
<td>0.211</td>
<td>0.1-0.2</td>
</tr>
<tr>
<td>2000</td>
<td>0.051</td>
<td>0.063</td>
<td>0.163</td>
<td>0.02-0.1</td>
</tr>
<tr>
<td>3000</td>
<td>0.029</td>
<td>0.040</td>
<td>0.129</td>
<td>&lt; 0.02</td>
</tr>
<tr>
<td>4000</td>
<td>0.020</td>
<td>0.030</td>
<td>0.116</td>
<td></td>
</tr>
<tr>
<td>5000</td>
<td>0.015</td>
<td>0.024</td>
<td>0.101</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. Description of homo- and heteroaggregation processes and corresponding attachment efficiencies.
Figure 2. Homoaggregation process with $\alpha_{NP-NP} = 1$. a) Variation versus physical time of the number of particles and objects (particles and aggregates). b) Variation of $\frac{1}{[N]}$ as a function of physical time where $[N]$ represents the particle and object number concentration allowing the calculation of the kinetic rate constants $k_{\text{homo}}^{\text{particle}}$ and $k_{\text{homo}}^{\text{agg}}$ respectively.
Figure 3. Heteroaggregation in presence of NOM and NPs. a) Surface saturation variation as a function of NPs and physical time and average number of NOM attached to the NP surface. b) Variation of the number of NOM particles (not attached) as a function of physical time. c) Determination of the heteroaggregation rate constant in presence of one \( k_{\text{hetero}}^{\text{1NP}} \) and two NPs \( k_{\text{hetero}}^{\text{2NP}} \) based on the variation of the number of objects. \( \alpha_{\text{NOM-NOM}} = \alpha_{\text{NP-NP}} = 0 \) and \( \alpha_{\text{NP-NOM}} = 1 \). \( k_{\text{hetero}} \) and \( k_{\text{global}} \) refer respectively to heteroaggregation and global aggregation rate constant.
Figure 4. Simulation pictures of the NP surface coating in presence of 1000 NOM units and for three different NP concentrations (a) 1, (b) 25 and (c) 100 NPs. NPs are in red ($R = 10$ nm), NOM adsorbed and desorbed are respectively in clear blue and dark blue ($R = 1$ nm). Formation of heteroaggregates is promoted by decreasing the NOM/NP ratio so as to reduce surface saturation effects and promote bridging aggregation between nanoparticles by NOM monomers. Attached NOM is represented by larger spheres for a better visualization.
Figure 5. Variation of the inverse of the object concentration for the different water models with $\alpha_{NP-NOM} = 1$ and for 10 NPs and 1000 NOM particles. Heteroaggregation rate is found the most important in marine water in which both homoaggregation and heteroaggregation occur. Heteroaggregation rate is further reduced due to the decrease of $\alpha_{NOM-NOM}$ values.
Figure 6. Evolution of the heteroaggregation rate constant for each water models as a function of the number of NOM. A decrease of the heteroaggregation rate is observed with increasing NOM concentration due to surface saturation effects, excepted for marine water in which homoaggregation is playing a more important role.
Figure 7. Variation of the heteroaggregation attachment efficiencies for each water model as a function of the NP/NOM ratios. $\alpha_{hetero}^{agg}$ values are strongly dependent on the relative NOM concentrations as well as NOM-NOM homoaggregation.
Figure 8. Snapshots of heteroaggregates and homoaggregates at different NOM concentrations, for the different water models and at the same physical time (220 μs). Snapshots clearly indicate an effect of surface coating and NOM homoaggregation on heteroaggregation. $a^{agg}_{hetero}$ values are indicated for each situation excepted for marine water case where is equal to one (most favorable conditions).