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

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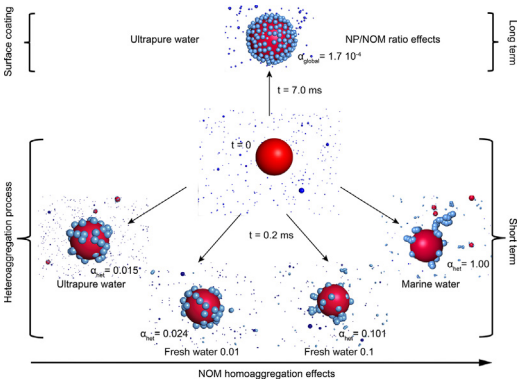
HIGHLIGHTS

- A novel and original approach is developed to study heteroaggregation between NPs and NOM molecules.
- Heteroaggregation rates and attachment efficiencies are calculated in contrasting conditions.
- NPs and NOM interactions are playing key roles in controlling the balance between homo and heteroaggregation.
- A clear distinction should be made between individual, primary and global heteroaggregation rates.

GRAPHICAL ABSTRACT



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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, 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

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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.

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. α 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 α 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 (Wiese and 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 Laurençot, 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 (Fig. 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