



# Heteroaggregation of microparticles with nanoparticles changes the chemical reversibility of the microparticles' attachment to planar surfaces



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## ABSTRACT

This study theoretically investigated detachment of homoaggregates and heteroaggregates attached on the planar surfaces at primary minima during transients in solution chemistry. The homoaggregates were represented as small colloidal clusters with well-defined structures or as clusters generated by randomly packing spheres using Monte Carlo method. The heteroaggregates were modeled as microparticles coated with nanoparticles. Surface element integration technique was adopted to calculate Derjaguin–Landau–Verwey–Overbeek (DLVO) interaction energies for the homoaggregates and heteroaggregates at different ionic strengths. Results show that attached homoaggregates on the planar surface at primary minima are irreversible to reduction in solution ionic strength whether the primary spheres of the homoaggregates are nano- or micro-sized. Heteroaggregation of nanoparticles with a microparticle can cause DLVO interaction energy to decrease monotonically with separation distance at low ionic strengths (e.g.,  $\leq 0.01$  M), indicating that the heteroaggregates experience repulsive forces at all separation distances. Therefore, attachment of the heteroaggregates at primary minima can be detached upon reduction in ionic strength. Additionally, we showed that the adhesive forces and torques that the aforementioned heteroaggregates experience can be significantly smaller than those experienced by the microspheres without attaching nanoparticles, thus, the heteroaggregates are readily detached via hydrodynamic drag. Results of study provide plausible explanation for the observations in the literature that attached/aggregated particles can be detached/redispersed from primary minima upon reduction in ionic strength, which challenges the common belief that attachment/aggregation of particles in primary minima is chemically irreversible.

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## 1. Introduction

Aggregation of colloidal particles is widely present in many industrial processes and in the natural environment [24]. For example, engineered nanoparticles, if not protected by steric stabilizing agents, tend to aggregate into clusters up to several microns in aquatic environments ([14,70,31,41]. Colloidal aggregation occurs when colloid collision, motivated by Brownian motion and/or external forces (e.g., gravitational force, hydrodynamic shear), results in particle–particle attachment. The aggregation that occurs in a suspension composed of similar monodisperse colloidal parti-

cles is called homoaggregation [33]. Alternatively, aggregation of dissimilar particles is referred to heteroaggregation [42].

While the process of colloidal aggregation (e.g., colloid stability) has been extensively studied [22,24], fate and transport of the formed aggregates in the aquatic environments have received very limited attention to date. In contrast, the transport of single particles in porous media has received considerable attention. Particularly, a systematical theory [i.e., colloid filtration theory (CFT)] has been developed to describe single particles' attachment, which is one of the primary factors (e.g., detachment and straining) controlling particle transport in porous media [75,49,20,21,54,10,66,58]. The CFT illustrates that particle attachment involves two subsequent steps: (i) transport of particles from bulk fluid to the vicinity of collector surfaces and (ii) chemical–colloidal interactions between particles and surfaces. The transport step is controlled by three individual mechanisms: interception,

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gravitational sedimentation, and Brownian diffusion. The chemical–colloidal interactions include van der Waals attractions, electrical double layer interactions, and short-range repulsions (e.g., hydration forces and steric repulsion). These interaction forces are described by extended Derjaguin–Landau–Verwey–Overbeek (XDLVO) theory [68,44].

Since both CFT and DLVO theory are developed for describing single particles' attachment behavior, the aggregate is commonly treated as an equivalent sphere (e.g., in terms of size, hydrodynamics, or gyration) so that these theoretical models could be used for predictions. Lin and Wiesner [41], however, showed that the colloid interaction energy for the nanoparticle aggregates is on the same order of magnitude as those for the primary particles and is significantly weaker than that for an equivalent sphere defined by the gyration radius of the aggregate. Johnson et al. [37] experimentally showed that fractal aggregates composed of microspheres can settle on average 4–8.3 times faster than predictions by calculations for impermeable or permeable spheres of identical mass, cross-sectional area, or primary particle density. They attributed the differences in settling velocities to the reason that fractal aggregates have large pores, causing smaller overall drags per total cross-sectional area.

Above literature advances understanding about colloidal aggregates' attachment behavior. The detachment of colloidal aggregates, however, has not been investigated to date. Knowledge of the mechanisms controlling colloidal aggregate's detachment is of importance in diverse engineered applications and environmental concerns [6] because detachment of aggregates can cause permeability loss in aquifers, turbidity increase in groundwater withdrawal wells, facilitated transport of contaminants in subsurface environments, etc. Considerable effort has been devoted to the investigation of detachment of single particles from collector surfaces. For example, both microscopic examinations [72] and column experiments [2,56,40] show that single particles attached in the DLVO secondary energy minima can be spontaneously released back to the bulk solution when the secondary energy minima are comparable to the average Brownian kinetic energy ( $1.5kT$ , where  $k$  is Boltzmann constant and  $T$  is absolute temperature). However, the release is commonly minor in a system and, for considerable particle detachment, a hydrodynamic or chemical disturbance to the system (e.g., changing flow velocity and solution chemistry, advancing/receding air–water interfaces) is requisite [5–7,1,13].

This study theoretically examined detachment of colloidal aggregates attached on the planar surfaces at DLVO energy primary minima. The colloidal aggregates were represented by packing identical spheres or by coating microparticles with nanoparticles. The surface element integration (SEI) technique was employed to calculate DLVO interaction energies/forces for the aggregates at different solution ionic strengths [8,9,41]. We showed that the aggregates of identical spheres are irreversible to reduction in solution ionic strength. The attached microspheres coated by nanoparticles can be detached from planar surfaces by decreasing ionic strengths. The coated nanoparticles also significantly decrease the adhesive forces between the microparticles and the planar surface, thus, the attached heteroaggregates are much more favored to be detached by applied forces compared to single microparticles. Additionally, we theoretically explain why viruses exhibit conservative transport behavior in the environments although small particles have low energy barriers and are readily to be attached in primary minima.

## 2. Theory

### 2.1. Generation of colloidal aggregates

Fig. 1 presents examples of colloidal aggregates generated by clustering of a number of spheres. The clusters I and II result in tet-

rahedral and octahedral coordination configurations, respectively. A number of studies [43,76–78,16,71,55] have developed methods to prepare aforementioned small clusters using engineered particles (e.g., gold nanoparticle and silica particle). These small colloidal clusters with well-defined structures have drawn considerable attention in recent years in colloidal self-assembly. Yi et al. [76] demonstrated that these small aggregates possess lower symmetry than the spheres from which they are made and offer the possibility of forming more complex colloidal phases and structures. The cluster III was created as an aggregate of 20 spheres obtained by randomly placing them in the lattice sites of a simple cubic lattice by the Monte Carlo method [18]. Specifically, the first sphere was placed at the origin of the rectangular coordinate system. The position of the second sphere was randomly selected out of six possibilities. To place the third and any further spheres, a sphere that was already placed in the lattice was randomly chosen. Then the position of the new sphere was selected out of six possibilities in respect of the sphere chosen. Through occupancy test, the new sphere was placed if the position selected was free. Otherwise, the search for a suitable site was repeated. The cluster IV was created by placing 18 small spheres of equal sizes on a large sphere surface. The coordinates of the sphere centers for cluster III and the coordinates of the contacts between each small sphere and the large sphere for cluster IV are given in Table 1.

### 2.2. Calculation of DLVO interaction energies

The SEI technique was used to calculate DLVO interaction energies between aforementioned aggregates and the planar surface. The SEI technique, developed by Bhattacharjee and Elimelech [8], can give exact evaluation of DLVO interaction energy between a single particle of any shape and a flat surface [59]. Lin and Wiesner [41] showed that, based on the principle of the SEI, it is mathematically equivalent to calculate the interaction energy between an aggregate and a flat surface by simply summing the interaction energy between each primary particle and the flat surface. Details about using SEI to calculate the interaction energy between a primary sphere and a flat surface can be found in previous studies [8,59]. Briefly, the Cartesian coordinate system was employed (see Fig. 1). The coordinate system originates from the center of the primary particle, with the  $z$  axis pointing toward the planar surface. The  $xy$  plane of the coordinate system is oriented parallel to the planar surface.

The primary sphere surface was discretized into small area elements. The total interaction energy ( $U$ ) was calculated as the sum of the differential interaction energy ( $E$ ) between each area element  $dS$  and the planar surface:

$$\begin{aligned} U(H) &= \sum_S E(h) \mathbf{n} \cdot \mathbf{k} dS \\ &= \sum_A \left( E\left(H+R-\sqrt{R^2-(x^2+y^2)}\right) - E\left(H+R+\sqrt{R^2-(x^2+y^2)}\right) \right) dA \end{aligned} \quad (1)$$

where  $H$  is minimum separation distance between the primary particle and the planar surface,  $h$  is local separation distance between the element  $dS$  and the planar surface,  $\mathbf{n}$  is unit outward normal to the primary particle surface,  $\mathbf{k}$  is unit vector along the positive  $z$ -direction,  $S$  is total surface area of the primary particle,  $A$  is total projected area of the primary particle on the planar surface,  $R$  is radius of the primary particle, and  $dA$  is the projected area of  $dS$  on the planar surface.

The interaction energy between  $dS$  and the planar surface [i.e.,  $E(h)$ ] is calculated by adding van der Waals (VDW) attraction and the constant potential double layer (DL) interaction:

$$E(h) = E^{\text{VDW}}(h) + E^{\text{DL}}(h) \quad (2)$$

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