Effect of repulsive interactions on the rate of doublet formation of colloidal nanoparticles in the presence of convective transport

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ABSTRACT

In this work, we have performed a systematic investigation of the effect of electrostatic repulsive interactions on the aggregation rate of colloidal nanoparticles to from doublets in the presence of a convective transport mechanism. The aggregation rate has been computed by solving numerically the Fuchs–Smoluchowski diffusion–convection equation. Two convective transport mechanisms have been considered: extensional flow field and gravity-induced relative sedimentation. A broad range of conditions commonly encountered in the applications of colloidal dispersions has been analyzed. The relative importance of convective to diffusive contributions has been quantified by using the Peclet number Pe. The simulation results indicate that, in the presence of repulsive interactions, the evolution of the aggregation rate as a function of Pe can always be divided into three distinct regimes, no matter which convective mechanism is considered. At low Pe values the rate of aggregation is independent of convection and is dominated by repulsive interactions. At high Pe values, the rate of aggregation is dominated by convection, and independent of repulsive interactions. At intermediate Pe values, a sharp transition between these two regimes occurs. During this transition, which occurs usually over a 10–100-fold increase in Pe values, the aggregation rate can change by several orders of magnitude. The interval of Pe values where this transition occurs depends upon the nature of the convective transport mechanism, as well as on the height and characteristic lengthscale of the repulsive barrier. A simplified model has been proposed that is capable of quantitatively accounting for the simulations results. The obtained results reveal unexpected features of the effect of ionic strength and particle size on the stability of colloidal suspensions under shear or sedimentation, which have relevant consequences in industrial applications.

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1. Introduction

The quest for a quantitative description of aggregation kinetics of colloidal nanoparticles dates back almost a century [1]. The seminal works of von Smoluchowski [2,3] have opened the way to the understanding of this phenomenon, which plays crucial roles in all fields of science where colloids are present, such as material science, food science, pharmaceutics, waste water treatment [4]. Smoluchowski's works have covered both the case of diffusion-as well as of shear-induced coagulation [2,3]. His approach is based on the solution of a diffusion or convection–diffusion equation for particles moving towards one particle chosen as a reference. The coagulation rate is given by the overall flux of particles impinging on the reference one [2,3]. The work on diffusion-limited aggregation has been extended by Fuchs a few decades later [5], introducing the effect of interparticle interactions. With the combination of Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, the Fuchs–Smoluchowski treatment has been the base for the interpretation of the stability of colloidal aggregation phenomena ever since [1,3,6].

In the last 30 years researchers have tried to investigate the more complex case where a convective aggregation mechanism and DLVO interactions are simultaneously present, with the objective of understanding the complexity of phenomena arising and extending Fuchs–Smoluchowski theory [7–16]. Two main approaches have been devised for this purpose. The first on is based on the solution of the generalized Fuchs–Smoluchowski equation [11–15], either numerical or through perturbation theory, while the second one makes use of trajectory analysis [7–9,17,10,16]. Each method has its own advantages and drawbacks. For example, the use of trajectory analysis, which is probably the most commonly utilized technique, permits the solution of a mathematically simpler problem, *i.e.*, a deterministic system of three ordinary differential equations, where the effect of diffusion is entirely neglected. This approach has led to remarkable discoveries, such as that of stable trajectories for pairs of particles under shear, resulting from a balance between Van der Waals attraction and shear forces [3,7–10,16,17]. Nevertheless, some authors have shown how trajectory analysis, by neglecting the effect of diffusion,

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underestimates the rate of aggregation when the Peclet number Pe, which is defined as the ratio between convection and diffusion transport, takes sufficiently small values [11,12].

Perturbation method has been also used to find asymptotic solutions of the diffusion–convection Fuchs–Smoluchowski equation. This analysis, pioneered by Van de Ven and Mason [7–9] and by Feke and Schowalter [13,14], has led to the discovery of first and second order corrections to account for both the effect of shear on brownian coagulation at low Pe values, and of diffusion on shear coagulation at very high Pe values. Those solutions, which lead to aggregation rates equations expanded as power laws of Pe, provide very useful insights, but fail to give reliable expressions that cover the entire range of Pe values. Additionally, the analysis performed so far does not quantify effectively the transition between the two regimes, especially in the presence of repulsive interactions.

The last technique that has been used to tackle the problem is the full numerical solution of Fuchs–Smoluchowski convection–diffusion equation. Different numerical methods have been used to accomplished this task. Zinchenko and Davis [11,12] have utilized Galerkin-finite-difference approximations coupled to analytical continuation, being able to solve the equation in the case of fluid droplets for arbitrary Pe number values. Their investigations have covered both cases of simple shear motion and of gravity induced coagulation, but in the presence only of attractive interactions. Melis et al. [15] have solved Fuchs–Smoluchowski equation for the case of extensional flow including all interactions. The method used was based on transforming the elliptic convection–diffusion equation into a parabolic equation by neglecting diffusion in tangential direction, and by discretizing the final equation first in the radial direction, then along the angular variable. This work represents to the best of our knowledge the first case where the transition from DLVO controlled aggregation to shear controlled aggregation is explicitly shown, even though under a few limiting conditions, mostly due to numerical difficulties arising from the stiffness of the equations to be solved. Nevertheless, these calculations have hinted that, while in the absence of a repulsive barrier the transition between diffusion-limited and shear controlled aggregation is smooth, in the presence of repulsive interactions the transition between the two regimes is quite sharp and occurs over a narrow range of Pe values. Similar observations can be drawn from data published by Baldyga et al. [18], who extended the work of Melis et al. to the case of unequal particles. A work by Wilson et al. [19] has instead addressed the problem of aggregation of nanoparticles induced either by either gravity or electrophoresis, in the presence of attractive and repulsive interactions. The method used was again the transformation of elliptic Fuchs–Smoluchowski equation into a parabolic equation. Their results on both gravity and electrophoresis-induced aggregation show the same qualitative trend observed by Melis et al.: a sharp transition between diffusion-controlled and convection-controlled regimes.

The investigation of shear-induced coagulation of particles in the presence of repulsive interactions is not only a problem of intrinsic fundamental interest, but has also strong practical relevance. Many coagulation processes performed on industrial scale often require the addition of massive amount of electrolytes, which are often undesired in the final product. Therefore, being able to perform coagulation processes with limited amounts-or even in the absence-of electrolytes is advantageous. This has motivated our effort to propose simplified models capable of capturing the essential physics of the process. In two recently published papers [20,21], two analytical expressions for the rate of aggregation of particles have been proposed, accounting for the presence of both shear and DLVO interactions. Both models start by solving a simplified form of the convection–diffusion equation, which is amenable to a simple (analytical [20] or numerical [21]) solution.

The first model utilizes an unrealistic velocity profile that is nevertheless capable of providing a simple expression valid for all Pe values [20]. Instead, in Ref. [21] a boundary layer approximation has been introduced, the thickness of which is a function of Pe and of ionic strength [21]. Inside the boundary layer the relative velocity profile and the hydrodynamic interactions are accounted for in a more rigorous manner, allowing one to obtain a more accurate estimate of the rate of aggregation. This second expression is however often not accurate in the regime of very high Peclet values, i.e., $Pe > 100$.

The objective of this work is twofold. First of all, a series of accurate calculations of aggregation rate of colloidal nanoparticles in the simultaneous presence of a convective transport mechanism and of repulsive interactions have been performed, in order to better clarify the effect of various physical parameters on the transition between the regime controlled by repulsive interactions and the one controlled by convection. The results have been obtained by numerically solving the full Fuchs–Smoluchowski equation. The convection mechanisms selected are axisymmetrical extensional flow and relative sedimentation, since in both cases the mathematical problem has a cylindrical symmetry. The first case is relevant for coagulation under turbulent conditions, since it has been argued that turbulent flow below the Kolmogorov scale can be effectively represented by an axisymmetrical extensional flow [15]. Sedimentation, on the other hand, is one of the chief mechanisms of aggregation in environmental applications and in waste water treatment [4,22–24]. Due to the robustness of the code used, more realistic values of the physical parameters have been investigated as compared to what published in the literature thus far. The second objective of the work is to quantitatively interpret the simulations results in terms of a simplified model, obtained by combining the two aforementioned models proposed in the literature in one unique framework. In this manner, an expression capable of providing quantitative results over the entire spectrum of conditions investigated is obtained.

2. Theoretical background

2.1. Model formulation

The rate of aggregation of colloidal particles has been computed by Smoluchowski by solving a diffusion equation, describing the diffusion of colloidal particles towards one spherical particle that is chosen as a reference, and further imposing an absorbing boundary condition at the point where the reference and diffusing particles touch, i.e., at a distance equal to the sum of their radii [1,3]. This means that the concentration profile is set to zero at this collision boundary, to account for the fact that upon collision particles are consumed by the coagulation event. The second boundary condition assumes that at infinite distance from the reference particle the concentration reaches the bulk value, implying that the perturbation induced by the reference particle is vanished. Smoluchowski considered also the case of shear aggregation [3], in which case the diffusion equation becomes a diffusion–convection equation, but he neglected completely the effect of diffusion and computed only the overall flux of particles carried by the fluid towards the reference particle. Fuchs, on the other hand, considered explicitly the effect of interparticle interactions between the particles, and modified the the diffusion equation by adding a convective contribution accounting for them [5]. Work performed in the last 40 years has clarified the role played by hydrodynamic interactions between pairs of particles [25–27]. When all these effects are considered together, the generalized Fuchs–Smoluchowski's diffusion–convection equation takes the form [1]:

$$\nabla \cdot (\mathbf{D} \cdot \nabla c - (\mathbf{v}_{int} + \mathbf{v}_{conv})c) = 0 \tag{1}$$