

Generalized model for the aggregation rate of colloidal nanoparticles and clusters induced by shear in the presence of repulsive interactions

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ABSTRACT

Aggregation of colloidal nanoparticles in the presence of shear is a key step in processing of many particulate materials, polymeric nanoparticles, food products etc. Predicting the rate of aggregation is important in order to optimize the operating conditions under which coagulation takes place. In this work, we have performed detailed simulations of the aggregation rate of colloidal nanoparticles in the presence of both linear shear flow and repulsive interactions, by numerical solution of the convection-diffusion equation for the pair probability function, from which aggregation rates are computed. Using a simplified model we have interpreted the results of the rigorous calculation and provided a simple criterion to determine the relative importance of all mechanisms involved in the aggregation. The main result is that sufficiently high shear rates can cancel the effect of repulsive interactions and lead to the same aggregation rates found in fully destabilized suspensions.

Keywords: aggregation, colloidal nanoparticles, DLVO, rate constant, pair probability function

1 INTRODUCTION

Coagulation of colloidal nanoparticles in the presence of shear is a key step in processing of many particulate materials, polymeric nanoparticles, food products etc. In the case of charged nanoparticles, coagulation is usually induced out by adding sufficient amount of electrolytes to completely screen all electrostatic interactions. In addition, the suspension is usually sheared to accelerate the coagulation process. However, for certain applications, the addition of large amounts of electrolytes is not beneficial for subsequent processing of the material and removal of electrolytes might be necessary. Therefore, operating with lower amounts of electrolytes, and in particular lower than the critical coagulation concentration, might be desirable. The major obstacle is given by the high sensitivity of the particle stability to the electrolyte concentration, and by the poor understanding of the mechanism of shear induced aggregation in the presence of a repulsive barrier.

For systems that are produced in particulate form, such as polymers and ceramic materials, and then recovered through coagulation, it is well known that quantities such are

the broadness of the cluster mass distribution and the cluster structure obtained during coagulation strongly affect physical and mechanical properties of the final product. Therefore, the determination of the time and in some cases of the space evolution of the entire cluster mass distribution during the coagulation process is often desirable. The kinetic approach based on Population Balance Equations (PBE) is a particularly convenient method to accomplish this task. However, the determination of the aggregation rate constants that appear in the PBEs, and which contain all the physical aspects of the aggregation mechanism, is a very challenging task.

In this work, we have performed detailed simulations of the aggregation rate of both colloidal nanoparticles and fractal clusters in the presence of both shear flow and repulsive interactions, by numerical solution of the convection-diffusion equation for the pair probability function, *i.e.* the probability of finding two particles (respectively two clusters) at a given relative position. The equation has been solved for the most important linear flow fields, *i.e.* simple shear and elongational flow.

In order to gain better physical insight of the interplay between the various mechanisms affecting the aggregation, a simple but effective model is presented and used to interpolate the results of the rigorous calculations. This approach provides a simple expression for the aggregation rate that can be used in population balance equation calculations. Furthermore, the simplified model provides a simple criterion to estimate the relative contributions to the aggregation rate due to shear and to repulsive interactions.

2 DESCRIPTION OF THE MODEL

In order to obtain quantitative information about the aggregation rate of two particles or clusters exposed to a flow field gradient and in the presence of repulsive interactions, we have solved the convection diffusion equation for the pair probability function of finding two particles having a given relative position. This approach is not new, having been used by von Smoluchowski almost a century ago, to derive the famous aggregation rate constant K_{11} for particles in a simple shear flow field [1]:

$$K_{11} = \frac{4}{3} G (R_1 + R_2)^3 \quad (1)$$

where G is the shear rate and R_i is the radius of the i^{th} particle.

More recently, the convection-diffusion equation for the pair probability function has been also used to calculate the rate of aggregation of droplets [2], as well as the rate of aggregation of small colloidal particles [3]. The same approach has been also used to describe the microrheology of stable dispersions of monodisperse spherical particles [4].

The convection diffusion equations accounts for all mechanisms of interactions of particles, *i.e.* convection, diffusion, hydrodynamic interactions and colloidal interactions. The colloidal interactions have been described using classical DLVO theory. Hydrodynamic interactions of particles have been described using the conventional approach described by Kim et al. [5], while hydrodynamic interactions of clusters have been described using the approach described by Baebler et al. [6]. No coupling between hydrodynamic and DLVO interactions should be considered [1].

The convection-diffusion equation for the pair probability function P has the following form:

$$\nabla \cdot \left(D(r) \nabla P + \frac{D(r) \nabla \Psi}{kT} C - \mathbf{v} C \right) = 0 \quad (2)$$

where D is the diffusion coefficient, which is a function of the separation distance r between the particles due to hydrodynamic interactions, k is Boltzmann constant, T is the absolute temperature, Ψ is the total DLVO interaction potential, given by the sum of the attractive Van der Waal contribution, which for equal size particles can be written as [1]:

$$\Psi_a = -\frac{A}{6} \left(\frac{2R_1^2}{r^2 - 4R_1^2} + \frac{2R_1^2}{r^2} + \log \left(\frac{r^2 - 4R_1^2}{r^2} \right) \right) \quad (3)$$

where A is the Hamaker constant, and a repulsive electrostatic contribution given by:

$$\Psi_r = \frac{4\pi\epsilon}{e_l^2} \left(4e^{\frac{\kappa(r-2R_1)}{2}} \operatorname{arctanh} \left(e^{\frac{\kappa(r-2R_1)}{2}} \tanh \left(\frac{\zeta e_l}{kT} \right) \right) \right)^2 \frac{R_1^2}{r} \log \left(1 + e^{-\kappa(r-2R_1)} \right) \quad (4)$$

where e_l is the electron charge, ϵ is the dielectric permittivity of water, ζ is the surface potential and κ the Debye-Hueckel parameter. The expressions for the velocity profile in the case of elongational flow are reported in reference mmm, while for simple shear they are reported in Van de Venn. The expressions for the hydrodynamic interactions can be also found in the literature, and are omitted here for brevity.

The following boundary conditions are applied:

$$\begin{cases} r = 2R_1 \Rightarrow P = 0 \\ r \rightarrow \infty \Rightarrow P = 1 \end{cases} \quad (5)$$

which express the fact that the pair probability function is zero when two particles (or clusters) touch, while at infinite separation P equals unity.

The solution of the equation has been achieved by using the free Package MUDPACK [7]. After having solved the equation, the rate of aggregation has been calculated by integrating over an arbitrary spherical surface surrounding the reference particle the total flux of particles entering the surface [1]:

$$K_{11} = \iint_S \left(D(r) \nabla P + \frac{D(r) \nabla \Psi}{kT} C - \mathbf{v} C \right) \cdot \mathbf{n} dS \quad (6)$$

3 RESULTS AND DISCUSSION

The values derived from the solution of equation (2) using equation (6) are plotted in Figures 1, 2 and 3.

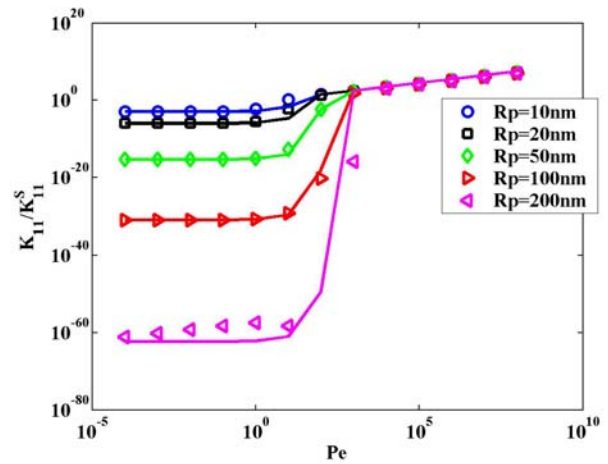


Figure 1: Normalized aggregation rate constant of two particles as a function of Pe number, for various particle sizes.

The quantities on the ordinate are the ratios between the actual rates of aggregation and the Smoluchowski fast diffusion-limited aggregation rate, given by:

$$K_{11}^s = \frac{8kT}{3\eta} \quad (7)$$

where η is the viscosity of the medium.

All the calculations have been performed assuming that the only monovalent symmetric electrolytes are present in the solution, and that the physical properties of particles are those of polystyrene. In Figure 1, for a given electrostatic surface potential of 40mV and a given electrolyte

concentration of 10mM, the normalized aggregation rates are shown as a function of Peclet (Pe) number, defined as:

$$Pe = \frac{3\pi\eta GR_1^3}{kT} \quad (8)$$

are shown for different particle sizes. The Pe number represents the ratio between shear contribution and diffusive contribution. It can be seen that, for low values of the Pe number, the rate of aggregation is independent of shear and dominated by diffusion and by DLVO interactions. In fact, it can be proved that the normalized rate constant equals the inverse Fuchs stability ratio for $Pe=0$. However, as the shear contribution becomes more important, a critical shear rate (*i.e.* a critical Pe number) value is reached where an abrupt increase in the rate of aggregation is obtained. For large enough shear rates, the rate of aggregation becomes equal to the one obtained in the absence of any repulsive barrier. By increasing the particle size, it is observed that the DLVO interactions are more and more important, but the general trend observed above is retained. At high enough shear rates, no repulsive barrier is strong enough to resist the effect of shear, and its contribution is cancelled.

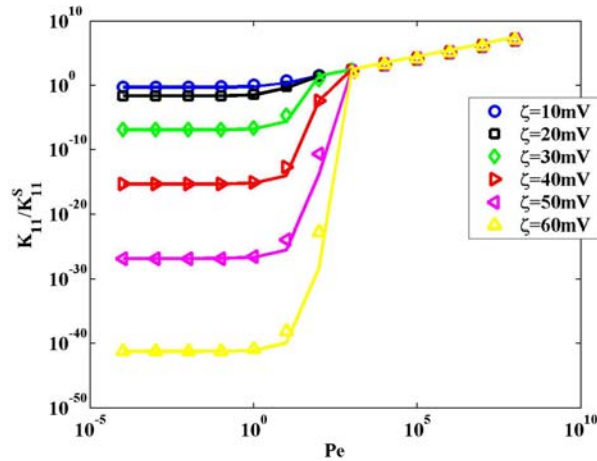


Figure 2: Normalized aggregation rate constant of two particles as a function of Pe number, for various electrostatic potentials.

In Figure 2, the same trend is observed when for a given particle size (50nm), the surface potential is changed. An increase in the surface potential just requires an increase in the critical Pe number necessary to overcome the energy barrier. An identical trend is observed in Figure 3, where the salt concentration is changed, and keeping constant all other parameters. At higher salt concentrations the electrostatic barrier is progressively lowered due to the screening of the electrostatic interaction, reducing the value of shear required to induce fast aggregation.

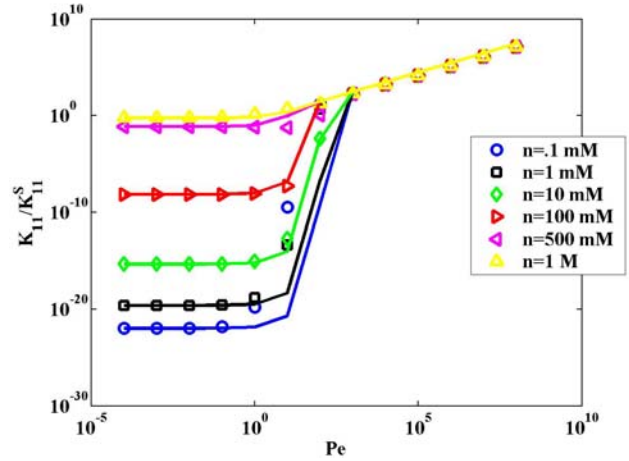


Figure 3: Normalized aggregation rate constant of two particles as a function of Pe number, for various electrolyte concentrations.

In order to rationalize these results, and condense them in a simple equation, a semi-empirical kernel is proposed. This model assumes that the effect of hydrodynamic interactions can be described, within a prefactor, by assuming that there is a flow field converging towards the reference particle. The advantage of using this unrealistic flow field is that the convection-diffusion equation (2) can be solved analytically, and the following expression for the rate of aggregation can be derived:

$$K_{11} = \frac{8\pi DR_1}{2R_1 \int_{2R_p}^{\infty} e^{-\alpha Pe \frac{R_1}{r} + \frac{\Psi(r)}{kT}} \frac{dr}{r^2}} \quad (9)$$

The above equation, when the value of the parameter α is equal to 0.3, can fit very well the results of the rigorous simulations, as shown by the continuous lines in all of the three figures. What equation (9) shows in an amazingly simple manner is the fact that the contribution of shear forces directly competes with DLVO interactions. For high enough Pe numbers, where Pe dominates over the maximum of the repulsive barrier, the effect of electrostatic interactions becomes negligible. The other interesting consequence of equation (9) is that it can be applied even in the case of more complex interparticle interactions. Similar conclusions can be drawn in the case of fractal clusters, which are treated at the level of porous particles.

4 CONCLUSIONS

The calculations performed in this work have demonstrated a general feature of aggregation rate constants in the presence of shear and repulsive interactions between

particles. At low Peclet numbers, i.e. at low shear rate, the aggregation rate of two particles (or clusters) is controlled by repulsive interactions and not affected by shear. However, as Peclet number is increased, a critical value is reached after which nanoparticles (or clusters) aggregation rate becomes quickly shear controlled. For large enough Peclet number values the aggregation rate becomes the same as if no repulsive barrier was present. This behavior can be rationalized by using the proposed simplified kernel (equation (9)), which clearly shows how the rate of aggregation is determined direct by the competition between shear (expressed by the Peclet number) and the height of the repulsive barrier.

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