Particle-based Model for Prediction of Dynamic Behavior and Rheological Properties of Colloidal Dispersions

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Highlights

- Advanced particle-based modeling of concentrated particulate dispersions
- Addressing complicated issues relevant for industrial reactors in many areas
- Predicting dynamics of coagulation and fouling
- Modeling of rheological properties – non-Newtonian viscosity, viscoelasticity

1. Introduction

Colloidal dispersions are common in a large variety of applications, such as food, pharmaceutical products, personal care or polymer latexes. Many of these involve a colloidal dispersion during the reaction phase of the production and phenomena related to the colloidal nature of the system are therefore central to their description and control. The current understanding of colloidal dispersions subjected to a shear is restricted to the limit of diluted or moderately concentrated dispersions in the bulk. However, in real applications (e.g., emulsion polymerization) volume fractions of particles up to 50 % are commonly encountered. Moreover, typical industrial systems suffer not only from coagulation, i.e., bulk loss of stability, but also from fouling, i.e., the attachment of particles onto walls and clogging of the apparatus. There is therefore a large need to broaden the theoretical understanding of these systems in terms of their rheology and overall stability to the region of large concentrations and to exploit this knowledge in control of chemical processes.

2. Methods

Mathematical modeling can be a useful tool to achieve this goal. We use two different approaches to the modeling of concentrated dispersions. First, to gain a deep understanding of the mechanisms that take place in these systems, we use a model based on the Discrete Element Method that resolves individual particles. The spatially 3D model accounts for several categories of forces occurring in the system. First, the interaction of the particles with the fluid is captured through the two-way coupling of the movement of the particles and the fluid together with the description of lubrication forces. Second, we model the interaction between the particles that are stabilized, adhesive and elastic and this is achieved by using a connection of two well-established models often used in literature. The DLVO theory describes forces originating from the electric double layer together with van der Waals forces; i.e., both non-contact forces. On the other hand, the JKR theory describes the simultaneous action of elastic and adhesive forces for particles in contact. Finally, tangential interactions and interactions between the particle and the wall are implemented in the model. With all these components, the model enables us to capture the dynamics of coagulation and fouling in terms of their characteristic time. An important output of the model is the size and structure of the produced clusters and the extent of their attachment to walls. The implementation of force balance at the boundary of the considered domain enables us to predict both the suspension viscosity and the viscoelastic properties in terms of the storage and loss moduli.

The second approach is based on the computation of the flow-field between an isolated pair of particles. It is therefore much less computationally demanding and allows us to obtain simplified correlations between viscosity and particle properties. Both these approaches are used to model the dynamic behavior of a waterborne colloidal suspension subjected to shear.

3. Results and discussion

With the 3D model, we successfully model the autocatalytic coagulation in stabilized colloidal suspensions. [1] We also propose a scaling for the steady-state cluster size that is given by the competition between coagulation and breakage of clusters. [2] We determined that the dynamics of fouling is much slower than in the case of coagulation. This is a consequence of the fouling mechanism that we revealed. Our simulations show that the fouling of walls occurs only after the coagulation has taken place in the bulk.

Using the combined modeling approach, we show that the validity of the no-slip boundary condition on the surface of particles is highly questionable in sheared concentrated dispersions. [3] This finding has principally important consequences for a large variety of dispersed systems. In non-Brownian hard-sphere suspensions, the presence of slip on particle surface explains the experimentally observed shear thinning, i.e., the decrease of viscosity with shear rate. [4] In colloidal latexes, this approach allows us to model the processes of coagulation and fouling and explain the observed changes in viscosity.

The viscoelastic properties are shown to be significant not only for adhesive and stabilized particles, but also for hard spheres. In the small-amplitude limit, both storage and loss moduli followed power-law scaling with the frequency of the oscillatory motion. In addition, the storage modulus is quickly growing with the increasing particle volume fraction.

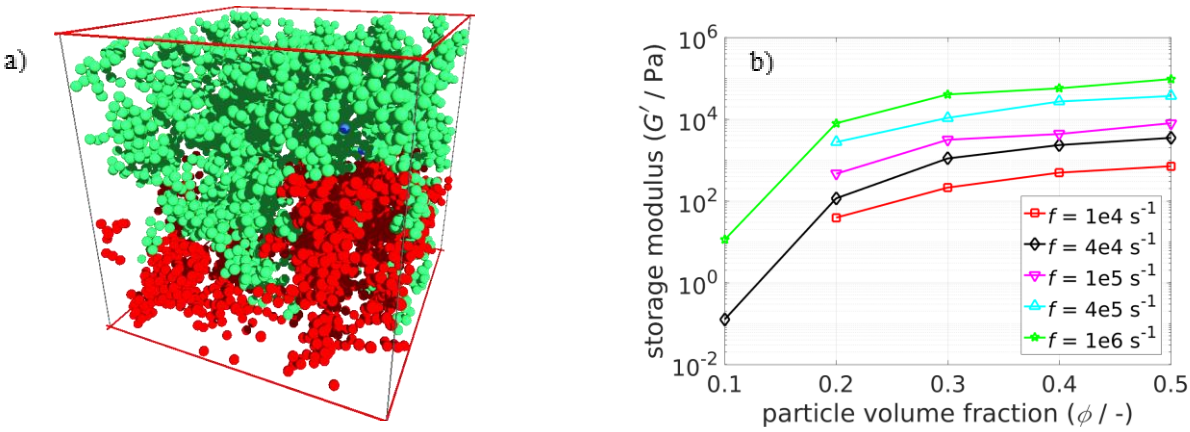

Figure 1. (a) A snapshot from a fouling simulation with particles in clusters (green) and attached to the wall (red). (b) Storage modulus as a function of particle volume fraction for different values of frequency as predicted by the 3D model.

4. Conclusions

The developed particle-based models allow to predict the properties of concentrated dispersions in chemical processes. Furthermore, we aim at making these properties observable in real systems by the correct interpretation of rheological measurements and by relating the observed changes in macroscopic quantities to the changes of the dispersion characteristics. We are thus able to address many issues relevant to operability of various processes involving colloidal dispersions.

References

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Keywords

Particle-based modeling; Coagulation; Rheology; Dispersion reactors.