

Simulation of the suspension structure for the improvement of colloidal processes

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ABSTRACT

Colloidal processes are used in many fields of applications to produce multi-material components with specific microstructures. Here, controlling the structure of colloidal suspensions is crucial in order to reliably adapt the suspension rheology to the process and to get the desired microstructure in the final part. We propose to show that numerical simulations, which take into account the discrete nature of the colloidal components, may be of help in this goal. Indeed, we develop and use simulation codes that can be employed to control the suspension stability and the suspension structure: particle ordering, compactness of the aggregate network, percolation properties, etc. We will first explain how a colloidal suspension can be modeled and then illustrate the topic with the specific case of a model alumina-silica system, in which simulation results will be compared to experimental characterizations. We will show that the simulations can well describe the experimental structures of suspensions. Finally, we will present how this kind of computational study can be applied to the complex suspensions of composite electrodes for Li-ion batteries.

Keywords: simulations, colloidal suspensions

1 INTRODUCTION

The colloidal route is commonly used in technological processes. A lot of ceramics shaping processes use suspensions. This is the case for example of the processes of casting, of stereolithography, of inkjet printing... For all these shaping processes, the microstructure of the final shaped materials, which determines the final properties of the body (mechanical, electrical, optical...), depends on the suspension behavior used in the process. It is indeed crucial to understand in details this behavior to improve the process and by consequence the final properties of the shaped materials. To achieve this goal, we develop and use Brownian dynamics simulations, which take into account the discrete nature of colloids. These simulations can be employed to understand and to control the suspension stability and the suspension structure. In the following, this method of simulation will

be described and applications to two different kinds of suspensions will be presented.

2 BROWNIAN DYNAMICS SIMULATIONS

Brownian dynamics simulations are used to simulate the behavior of colloidal suspensions. In these simulations, the fluid is considered as a continuum medium and its effects on the colloids are taken into account through frictional and random forces. The motion of a colloid i is then described by the Langevin equation:

$$m_i \frac{dv_i(t)}{dt} = -\zeta_i v_i(t) + \sum_j F_{ij}(r_{ij}(t)) + \Gamma_i(t) \quad (1)$$

where m_i and v_i are respectively the mass and the velocity of the colloid i . ζ_i is the friction coefficient which depends on the viscosity of the solvent η and the radius of the colloid a_i ($\zeta_i = 6\pi\eta a_i$). $F_{ij}(r_{ij}(t))$ denotes the pair interaction force between the colloids i and j separated by the center-to-center distance r_{ij} . These forces derive generally from pair interaction potentials ($F_{ij}(r_{ij}(t)) = -\nabla U_{ij}(r_{ij}(t))$). $\Gamma_i(t)$ is the random force. Brownian dynamics simulations consist in integrating the Langevin equation numerically and therefore they describe the evolution of the colloid positions as a function of time.

3 APPLICATIONS

3.1 Suspensions of oxide particles for a wet granulation process

We have developed and used Brownian dynamics simulations in the past to study the aggregation process in aqueous suspensions composed of alumina and silica particles, where heteroaggregation occurs. Indeed, the silica is negatively charged and the alumina is positively charged. This study was based on a real system used in a wet granulation shaping process. A more detailed description of this study can be found in Ref. [1, 2, 3]. Here we just focus on one of the important results. In the simulations, the interactions between the particles were modeled by DLVO potentials whose parameters were extracted from experimental measurements. By

comparing simulation results with experimental characterizations, we have shown that the Brownian dynamics simulations can well describe the structure of suspensions in terms of adsorption of small silica particles onto larger alumina particles; aggregation of alumina particles with small silica particles making 'bridges' in between adjacent alumina particles; spatial distribution of the two types of particles as a function of mass and size ratio between the two components. Thus we have shown that the simulations help predicting the structure appearing in such suspensions.

Simulations also allowed us to understand the final structure of the granules obtained from different suspensions. It is indeed observed that when granulation is performed with suspensions where silica and alumina particles have similar sizes, after drying and sintering steps, the granules have a hollow core [3]. However, when silica and alumina particles have a high size ratio, the granules are full and compact. According to the simulation results, this behavior is attributed to the difference of porosity in the aggregates. When silica and alumina particles have similar sizes, the aggregates are made of an intercalation between alumina and silica particles, because similar particles are repelling each other. This guarantees highly porous structures. However, when silica particles are much smaller than the alumina ones, they are responsible of the aggregation of the alumina particles by bridging, but there is much less porosity inside the aggregates. Brownian dynamics simulations appear as a useful tool to understand and predict the qualitative porosity of the granules obtained by this granulation process.

Because of the sphericity of colloids and the well known interactions between the components used in this study, the system can be considered as model. In the following, we will present how Brownian dynamics simulations can be used in much complex suspensions of electrodes for Li-ion batteries.

3.2 Suspensions of electrodes for Li-ion batteries

Electrodes of Li-ion batteries are composite materials generally obtained by tape-casting or extrusion. They are often composed of active materials, conductive additives and polymers. During the last years, it has been shown that the electrochemical performances of Lithium batteries are intimately linked to the structure of the electrodes which depends on the behavior of the suspensions used during the shaping process [4]. It is thus crucial to well understand this behavior to better control the process and the structure of electrodes in order to improve the efficiency of the battery. To achieve good electrochemical performances, different conditions on the structure of electrodes have to be fulfilled:

- a percolating network of the conductive additives has

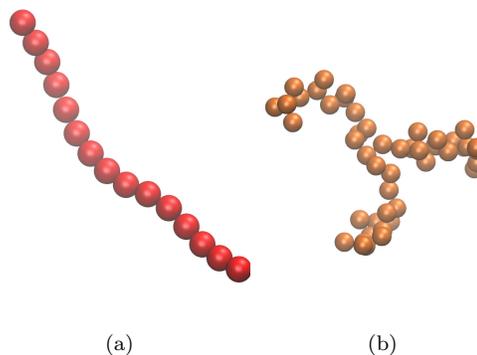


Figure 1: (a) Example of one carbon fiber used in the simulations and (b) example of one non-deformable carbon black aggregate used in simulations. For visibility the images are not represented at the same scale.

to be built up in order to ensure the transport of the electrons within the electrodes if the active material is not conductive. If the active material is conductive, the percolating network is not mandatory however it remains generally helpful to facilitate the electronic conductivity.

- a high number of contacts between the active material and the conductive network is generally preferable to better ensure the transfer of electrons between the active mass and the conductive additives.

A lot of parameters can influence the structure of suspensions for electrodes (pH, size of components, temperature, additives...) and by consequence on the structure of the final electrodes. Simulations that take into account the discrete nature of particles in suspensions, appear in this case as a very useful tool to understand the role of each parameter. However, these simulations are actually few developed for these systems because of the complexity of the suspension modeling. In the following, we will present how simple Brownian dynamics simulations can help to understand the role of the conductive additive shape on the structure of the suspension.

Description of the simulations: Simulations are performed for suspensions composed of lithium titanate particles (LTO) of 500 nm ($\rho_L = 4000 \text{ kg m}^{-3}$) and carbon conductive additives ($\rho_c = 2000 \text{ kg m}^{-3}$). Two kinds of non spherical additives are considered : carbon black aggregates (CB) and carbon fibers (CF). Carbon fibers are elongated entities and carbon blacks are fractal aggregates composed of fused elementary particles. In the simulations, LTO particles will be represented as spherical particles. Carbon fibers will be modeled as a chain of 15 spherical particles of 100 nm linked together by an elastic potential (see Figure 1a). In order to avoid large deformations of the fibers which would not be realistic, a linear repulsive potential is added between non-

adjacent spheres when the angle between adjacent pairs of spheres exceeds 10° . Carbon blacks are modeled as non-deformable fractal aggregates composed of elementary particles of 20 nm, which do not interact together (see Figure 1b). The carbon aggregates are moved as a whole. For that, the Langevin equation is modified to introduce the diffusion coefficient of the global aggregate. Because of its non-deformable shape, rotation is also introduced for carbon black aggregates. More details on this modeling can be found in Ref [5, 6]. The polymeric components are implicitly included in the solvent and in the interaction forces. In this study, all the interactions between the components are considered as attractive and are modeled by a generalized short-range Lennard-Jones potential:

$$U_{ij} = 4\epsilon_{ij}k_B T \left[\left(\frac{a_i + a_j}{r_{ij}} \right)^{36} - \left(\frac{a_i + a_j}{r_{ij}} \right)^{18} \right] \quad (2)$$

where k_B is the constant of Boltzmann, T the temperature and ϵ_{ij} is the potential well depth in units of $k_B T$. ϵ_{ij} is fixed at 7 for the interactions between two LTO particles and for the interactions between two carbon components (fibers or carbon blacks). ϵ_{ij} is fixed at 14, for the interactions between LTO and a carbon component. Simulations are performed at 298 K for a solvent of viscosity $\eta = 10^{-3}$ Pas. A cubic box with periodic boundary conditions is used. The box size depends on the solid volume fraction ϕ present in the system (here $\phi = 0.2$). The time step is fixed at $\delta t = 5.10^{-9}$ s. All the simulations are performed with 14 LTO particles. Results are analyzed at $t = 0.05$ s.

Results and discussion: First, simulations are performed without carbon fibers. Two compositions are considered: one with 5w% of CB and a second with 10w% of CB. For each composition, 10 independent simulations are carried out and in the following the results are averaged over all the independent simulations. A snapshot of simulation for 5w% of carbon black is shown in Figure 2. At the end of simulations, all the components are mixed in the simulation box and aggregated. As already mentioned, two structural properties appear as primordial for the application. First, the carbon network must percolate and then the number of contacts between the carbon network and the active materials must be high. Since the Brownian dynamics simulations give the positions of the components in the box, they allow to study these properties. For each simulation, the number of contacts between the carbon network and the LTO particles is computed and the dimensionality of percolation of carbon network is determined as described in Ref. [7]. The dimensionality of percolation determines how the carbon network spans in the simulation box. A dimensionality of percolation equal to 1 means that the carbon network spans in the box from end to end in 1 dimension and a dimensionality of

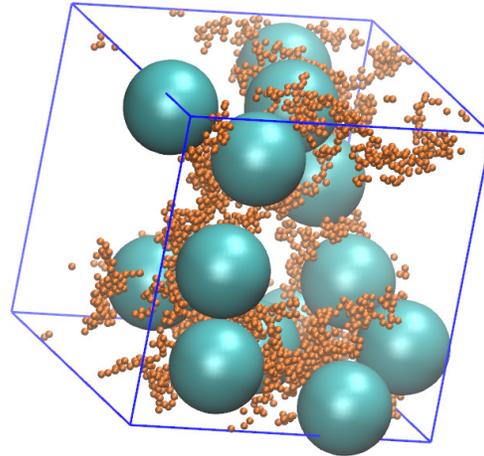


Figure 2: Simulation snapshot at $t = 0.05$ s for a suspension composed of 14 LTO particles and 5w% of carbon black aggregates ($\phi = 0.2$). CB is represented in orange and LTO in cyan.

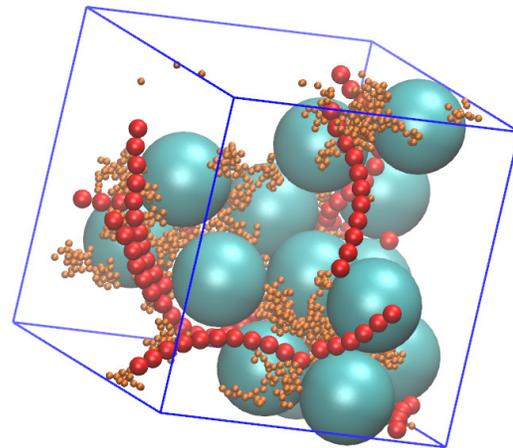


Figure 3: Simulation snapshot at $t = 0.05$ s for a suspension composed of 14 LTO particles, 2.5w% of carbon black aggregates and 2.5w% of carbon fibers ($\phi = 0.2$). CB is represented in orange, CF in red and LTO in cyan.

Table 1: Results of simulations at $t = 0.05$ s. ns is the averaged number of contacts between LTO and carbon additives and D_{perc} is the averaged dimensionality of percolation. (Averages obtained on 10 simulations)

Compositions	D_{perc}	ns
5w% of CB	0.6	1067
10w% of CB	2.9	1187
2.5w% of CB + 2.5%w of CF	1.6	689

percolation of 2 or 3 means that the network spans in 2 or 3 dimensions in the box respectively. Results obtained for the simulations at $t = 0.05$ s are reported in Table 1. An increase of the carbon content in the suspension increases the dimensionality of percolation and also the number of contacts between the LTO particles and the carbon network, which shows that increasing the content of CB can improve the structural properties. Nevertheless, it is noteworthy that the mass of additives must remain low in order to not decrease too much the mass loading of the electrodes.

Actually, formulation of electrodes for Lithium battery use carbon additives with a higher shape anisotropy than CB (carbon nanotubes, carbon fibers...) [8]. In a second part of the numerical study, carbon fibers are thus added in Brownian dynamics simulations. Simulations are performed with a total amount of 5w% of carbon, with half of the carbon blacks replaced by carbon fibers (2.5w% of CB + 2.5w% of CF). A snapshot of simulation at $t = 0.05$ s is shown in Figure 3. As previously, all the components are aggregated. The number of contacts between the LTO particles and the carbon network (ie network composed of CF and CB) are reported in Table 1 as well as the dimensionality of percolation of the carbon network. The presence of CF increases the dimensionality of percolation, which should result in a better electronic wiring in the suspension. However the number of contacts between LTO particles and the carbon network decreases. These results are in agreement with previous experimental observations, which have shown that introduction of fibers in the formulation of a carbon coated Li-FePO₄ based composite electrodes leads to a better electronic wiring when the porosity is not optimized (case of electrodes before calendaring step) [8].

This example shows that even if the Brownian dynamics simulations used here are quite simple, they can be used to understand the role of the shape of conductive additives on the suspension structure. They highlight that the introduction of fibers in the suspensions enhanced the dimensionality of percolation of the carbon network.

4 CONCLUSION

Brownian dynamics simulations have been developed and applied to two different kinds of suspensions. First

simulations have been applied to a model suspension composed of oxide spherical particles and then to more complex suspensions of electrodes for Li-ion batteries where some colloids are not spherical. They have shown that even if they are simple, they can be helpful to understand the structure of the suspensions used during the shaping process and therefore to understand the microstructure of the final object (granules or electrodes respectively). To conclude, such simulations appear as a very interesting tool to improve the colloidal processes.

Acknowledgements

The authors thank CALI and its team for computing facility. Figures 1, 2 and 3 have been obtained by VMD, a molecular graphics program developed by the Theoretical Biophysics Group in the Beckman Institute for Advanced Science and Technology at the University of Illinois at Urbana-Champaign [9].

REFERENCES

- [1] M. Cerbelaud, A. Videcoq, P. Abélard, C. Pagnoux, F. Rossignol and R. Ferrando, *Langmuir*, 24, 3001, 2008.
- [2] M. Cerbelaud, A. Videcoq, P. Abélard and R. Ferrando, *J. Colloid Interface Sci.*, 332, 360, 2009.
- [3] M. Cerbelaud, A. Videcoq, P. Abélard, C. Pagnoux, F. Rossignol and R. Ferrando, *Soft Matter*, 6, 370, 2010.
- [4] D. Guy, B. Lestriez and D. Guyomard, *Advanced Materials* 2004, 16, 554-557
- [5] M. Cerbelaud, B. Lestriez, R. Ferrando, A. Videcoq, M. Richard-Plouet, M.T. Caldes and D. Guyomard, *Langmuir*, 30, 2660, 2014
- [6] M. Cerbelaud, B. Lestriez, A. Videcoq, R. Ferrando and D. Guyomard, 'Understanding the structure of electrodes suspensions for Li-ion batteries: a numerical study', submitted.
- [7] M. Piechowiak, A. Videcoq, R. Ferrando, D. Bochicchio, C. Pagnoux and F. Rossignol, *Phys. Chem. Chem. Phys.*, 14, 1431, 2012
- [8] C. Fongy, S. Jouanneau, D. Guyomard and B. Lestriez, *J. Power Sources*, 196, 8494, 2011
- [9] W. Humphrey, A. Dalke and K. Schulten, *J. Mol. Graphics*, 14, 33, 1996.