SHEAR-INDUCED AGGREGATION OF COLLOIDAL PARTICLES
A comparison between two different approaches to the modelling of colloidal interactions

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INTRODUCTION

Suspensions of colloidal particles are relevant to a wide variety of industrial processes, including materials and food processing, production of pharmaceuticals, waste water treatment and others. In most of these applications the control over the aggregation phenomena plays a key role, since many properties of the suspensions are dependent upon the size, the morphologies and their distribution over the population of suspended clusters.
Population Balance Equations (PBEs), sometimes solved in a stochastic way [1] (Monte Carlo method), are frequently used to study the dynamics of destabilized colloidal systems interested by aggregation phenomena. This approach dates back to the analysis of fast coagulation by Von Smoluchowski, who drawn a simple model to describe the rate of aggregation of spherical particles [2]. However, in colloidal suspension particles aggregate to form clusters with structures that can only rarely be assimilated to a spherical shape.
On the contrary, Discrete Element Methods (DEMs) [3] offer a fully predictive approach for the study of the aggregation phenomena occurring in colloidal suspensions; by modelling all the relevant forces acting on each primary particle composing the aggregates, DEMs are able to track their trajectory independently from their shape.
The present work aims to study the aggregation behaviour of an aqueous dilute suspension of colloidal particles under the effect of a uniform shear flow. To this purpose we developed a mixed deterministic-stochastic method, which, combining a Monte Carlo algorithm with a DEM model, allowed us to study in detail the dynamical evolution of a large sample of a population of colloidal aggregates. Two different models were used to describe the colloidal interaction between primary particles and their effect on the aggregation behaviour was analysed.

1 NUMERICAL METHOD

Population Balance Equations (PBEs) are useful to investigate the dynamical evolution of a population of colloidal particles. For a purely aggregating system the rate of variation of the number concentration of aggregates of class *i* (i.e., made of *i* primary particles) reads as

$$\frac{dn_i}{dt} = \frac{1}{2}\sum_{j=1}^{i-1} \alpha_{j,i-j} K_{j,i-j} n_j n_{i-j} - n_i \sum_{j=1}^{\infty} \alpha_{i,j} K_{i,j} n_j \qquad i = 1,2,....,\ \infty \qquad (1)$$

where the first term on the r.h.s. expresses the rate of birth of aggregates of class *i*, as a consequence of the aggregation of two smaller aggregates, whereas the second term represents the rate of death of aggregates *i* because of their aggregation with other aggregates. In *Eq. (1)*, the term $K\alpha$ corresponds to the aggregation kernel, given by the product of *K*, an encounter rate, dependent on the mechanism that triggers the collisions, with the aggregation efficiency α, which represents the probability for a certain pair of aggregates to coagulate once they are one next to each other. We resorted to the well-established model formulated by Von Smoluchowski [2] to describe the two-body encounter kinetics *K* in a shear flow as

$$K_{i,j} = \tfrac{4}{3}\dot{\gamma}\left(R_{out,i} + R_{out,j}\right)^3 \qquad (2)$$

with $R_{out,i}$ and $R_{out,j}$ being the outer radii of a pair of aggregates i,j and with γ being the shear rate intensity. We used the information of *Eq. (2)* to setup a Monte Carlo algorithm.
Unfortunately, simple models for the aggregation efficiency α of colloidal aggregates have not been developed yet. The aggregation efficiency is, in fact, the result of an interplay of several factors, such as Van der Waals attraction, cluster morphologies, long-ranged hydrodynamic interactions and lubrication effects. Therefore, we developed a DEM model which is able to address all these factors and to ascertain in a fully predictive way if an aggregation will or not occur.

1.1 Monte Carlo algorithm

The method we adopted for the stochastic solution of *Eq. (1)* is an event-driven, rejection-free Monte Carlo algorithm. We based our algorithm on the concept of the interval of quiescence i.e, we assumed that the time interval elapsing between two subsequent encounter events is a random variable which obeys an exponential distribution [1]. On the basis of the encounter frequencies, the Monte Carlo algorithm was used to sample a statistically expected sequence of encounter events i.e., the algorithm was in charge to sample the aggregates involved and their initial coordinates in the shear flow field. *Fig. 1a* represents the initial setup of a typical encounter event.

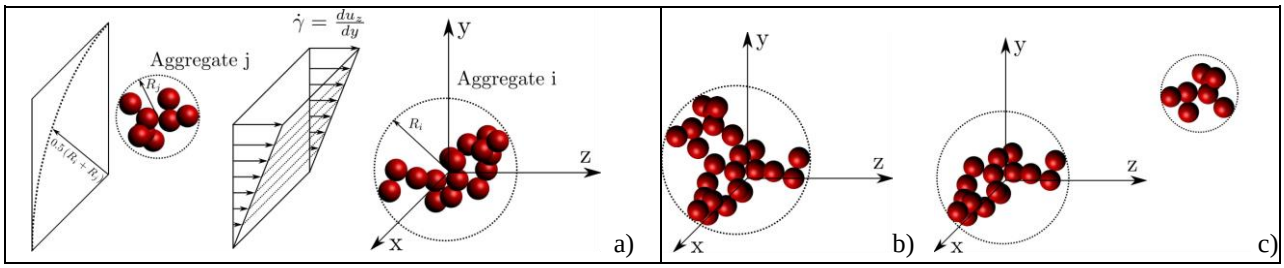

Fig. 1. a) Initial setup of an encounter event; b) An aggregation; c) A missed aggregation

1.2 DEM model

A Discrete Element Method was used to ascertain the outcome of each encounter sampled by the Monte Carlo algorithm. Two outcomes are possible: an aggregation (*Fig. 1b*) occurs whenever a larger aggregate is formed as a consequence of the birth of a new irreversible mechanical contact between the two involved aggregates. A missed collision (*Fig. 1c*) corresponds to the case in which aggregates pass close to each other, without colliding.
The basic idea behind a DEM model is that aggregates are composed by monomeric units (spherical primary particles in the present work), which coagulate as a consequence of the interplay between the colloidal interaction and the convective transport operated by the flow field. Based on the assumption that the inertia of particles is negligibly small, the Newton equations of motion of each primary particle can be approximated by a force and torque balance of the following kind

$$\boldsymbol{F}_{coll} + \boldsymbol{F}_{H} \approx 0, \qquad \boldsymbol{T}_{coll} + \boldsymbol{T}_{H} \approx 0 \tag{3}$$

where $\boldsymbol{F}_H$ and $\boldsymbol{T}_H$ represent respectively the hydrodynamic force and torque exerted by the fluid on the particles, whereas $\boldsymbol{F}_{coll}$ and $\boldsymbol{T}_{coll}$ are the force and torque which originate from the colloidal interactions. Under the assumption of large Péclet number the thermal motion of particles was considered to be negligible compared to the convective transport mechanism.
To model the hydrodynamic interactions, we resorted to Stokesian Dynamics [4], a well-established technique which allowed us to model in detail the complete spectrum of the hydrodynamic interaction between primary particles, from the far-field to the near-field (i.e. lubrication) part. Regarding the colloidal interaction between primary particles two different models were used. The first one (model A) employs a model solely for the normal interaction i.e, it assumes that particles interact exclusively along the line connecting their centres. Van der Waals attractive forces [5] and a model for the contact interaction, developed starting from the JKR theory of contact mechanics

[6], were introduced. Model B also contemplates a model for the tangential interaction; it has been shown that colloidal particles, once they are in mechanical contact, offer a certain resistance to the relative displacement along the contact plane [7]. For this reason, a spring-like force model was introduced to confer a torsional, rolling and sliding resistance to every bond between two primary particles [8].

2 RESULTS AND DISCUSSION

We simulated the shear-induced aggregation process occurring in a sample of a dilute colloidal suspension (volume solid fraction = 10^{-4}) adopting the previously mentioned models to describe the colloidal interaction between primary particles. In both cases we started from a monodisperse population composed by 200 spherical polystyrene particles (with radius a = 500 nm) dispersed in water and subject to a uniform shear flow with an intensity equal to 10 s^{-1}.
The first obvious consequence of the aggregation phenomena consists in the variation of the concentration of aggregates in the sample volume. Independently from the model adopted for the colloidal interactions, we observed an almost linear reduction in the number of suspended aggregates, as apparent in *Fig. 2a*.

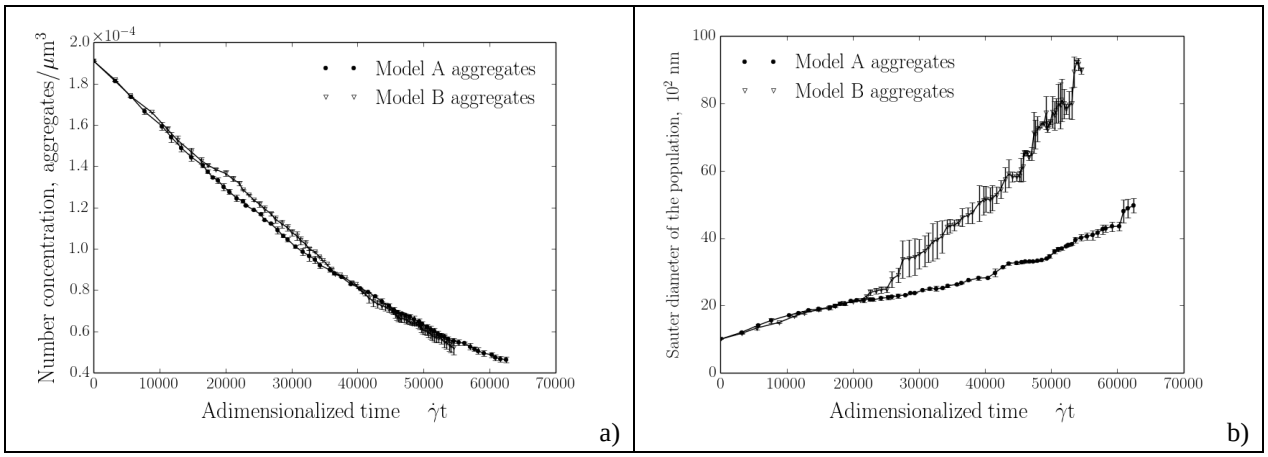

Fig.2. a) Temporal evolution of the number concentration of aggregates for the two different models adopted for the colloidal interaction; b) Temporal evolution of the Sauter diameter computed on the basis of the aggregate outer radii. Each curve was obtained averaging the data relative to three different realizations. The error bars indicate the standard deviation of the data.

Differently, the introduction of a tangential model for the colloidal interaction (model B) had a substantial effect on the growth rate of the Sauter diameter of the population, especially for large times (*Fig. 2b*). Initially the trends of the Sauter diameter relative to the two model aggregates are almost identical: in the first stage of the process the population is, in fact, composed mainly by dimer, trimer and other small aggregates, whose structure is almost independent from the model used for the colloidal interaction. As aggregation proceeds, the curve relative to the population B steeply increases; as it will be discussed soon, this effect has to be related to the peculiar cluster structures which originate as a consequence of the introduction of a model for the tangential interaction.

2.1 Aggregate characterization

Aggregates composed by particles which interact solely by central forces exhibited a closely packed structure; as a measure of the structure compactness, *Fig. 3a* reports the cluster coordination number, defined as the mean number of bonds each primary particle forms inside the aggregate. As apparent, model A aggregates present a substantially larger average coordination number. This effect has to be related to the possibility for primary particles to slide and roll over each other as a response to the shear viscous stresses. On the contrary, primary particles interacting also through a tangential interaction aggregate to form clusters characterized by a more porous and branched

structure, with particles involved in a limited number of bonds. For model B aggregates, as soon as a bond is established, the structure of the generated aggregate is frozen and no rearrangement can occur; occasional restructuring phenomena were detected only for large aggregates. In this case, the coordination number exhibited by most of the smaller aggregates equals 2(*i*-1)/*i* (dotted line in *Fig. 3a*), showing that their structures are isostatic; only the larger ones present a slightly over-constrained structure, with internal loops formed as a consequence of a partial restructuring induced by the shear stresses exerted by the flow field.

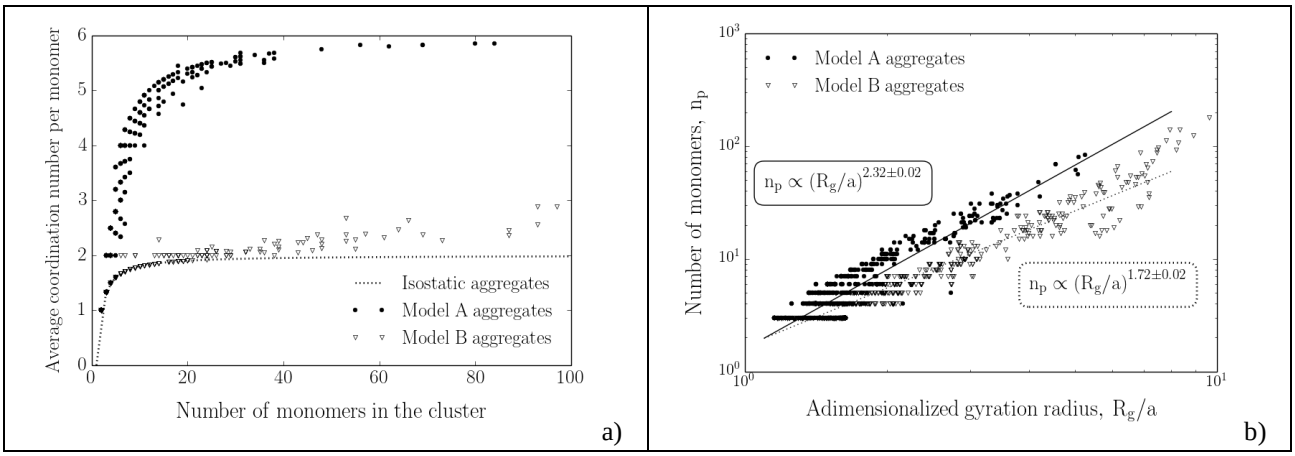

Fig. 3. a) Average coordination number for model A and B aggregates. b) Power-law fits relating the number of monomers composing the aggregates with their gyration radius.

Populations of colloidal aggregates are often described on the basis of their fractal dimension. The fractal dimension is usually considered as an indication of the typical morphologies and of the aggregation mechanism. It is generally recognised that low values (≈1.8) of this parameter are an indication of porous and open structures, whereas larger ones (up to 2.8) are a signal of compact structures. As apparent, *Fig. 3b* confirms what already discussed about the coordination number; the introduction of a model for the tangential interaction is responsible for the generation of porous structures characterised by low values of the fractal dimension (≈1.7). On the contrary, when particles are free to rearrange their position inside the clusters, the fractal dimension increases up to 2.3.

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