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Numerical study of the effect of particle size dispersion on order within colloidal assemblies

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Abstract

The formation of colloidal crystals is of interest in many fields, especially because of their optical properties. These properties are dictated by the colloidal arrangement. It is known that introducing particles with different size can change the structure of crystals and thus their resultant optical properties. To better understand how specific arrangements of particles can be obtained, a detailed understanding of the formation mechanisms is needed.

The influence of particle size distribution on the formation of colloidal crystals is studied by means of Brownian dynamics simulations performed with different types of interaction potentials. Crystal formation is first analyzed in systems containing homogeneous particles, then in systems with a size distribution.

It is shown that the interaction potential has a strong influence on the colloidal arrangement. For homogeneous particles, the width of the potential well affects the aggregate shape: a larger width leads to more elongated structures. When a size distribution is introduced, aggregation becomes more difficult, since the number of isolated colloids increases, and aggregates become disordered regardless the interaction potentials. Depending on the interaction potential, differences in the aggregates are observed. These differences are rationalized in terms of the specific features of the different potentials.

Keywords: Brownian dynamics simulation; colloidal crystal; size distribution; disordering

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1. Introduction

The understanding of the colloid behavior is important in many fields ranging from food industry to pharmacology and ceramics. To better understand this behavior, mesoscopic simulations using colloids as elemental entities can be performed. Numerous simulations have already been done for example in Brownian dynamics simulations [1, 2, 3, 4]. Generally, in such simulations, a homogeneous size is chosen for each kind of particles. However, experimentally, there is always a size distribution for the particles. To better understand how a size distribution can affect the results of simulations, it is proposed here to perform simulations for which ordering of colloids can be obtained.

Ordered aggregates or colloidal crystals have already been intensively studied because of their use in various fields ranging from optics to ceramics [5, 6, 7, 8, 9]. Numerous studies both experimental and numerical have shown that hard-sphere or repulsive colloids are able to form ordered structures when concentrated [5, 10, 11]. Experimentally, ordered structures can be obtained for example by sedimentation or by evaporative self assembly [12, 8]. More recently, it has also been shown that weakly attractive particles are also able to form ordered structures. For example, binary systems where particles interact via a weakly attractive potential can form colloidal crystals [13]. Another example is the possibility to order colloids modified by DNA via low energy attractive interactions [14]. From the point of view of numerical simulations, Boichichio *et al.* have already shown that ordered aggregates can be observed with a weakly attractive potential based on the DLVO theory by choosing a well depth of around 3-4 $k_B T$ [15].

For colloidal crystals, structural defects have consequences for the desired properties. For example, defects can lead to a change in the reflective color of the crystals [16]. A key factor in minimizing the formation of defects is the use of homogeneous particle sizes. Nakawaga *et al.* have shown, that the crystallinity of the colloidal crystals they synthesize is strongly linked to the size uniformity of the nanoparticles used [17]. Disparity in size leads to a reduction in crystallinity. Liu *et al.* have studied in details the effect of particle size distribution on the formation of colloidal crystals based on polystyrene particles [18]. By adding irregularly sized particles to their system, they showed that crystallinity depends on both the concentration and size of the added particles. Modifying the size distribution of the particles enables them to control defects, which could be a way of controlling the optical properties of the resulting

32 crystals.

33 In this paper, we propose to study the effect of particle size inhomogeneity in Brownian
34 dynamics simulations. To this end, we focus on a system similar to that studied by Bochi-
35 chio *et al.*, which features particles interacting with weakly attractive interaction potentials
36 and capable of forming ordered aggregates [15]. First, we will analyze how aggregates are
37 ordered when all particles have the same size, as a function of different interaction potentials.
38 Then we will analyze how particle size distribution modifies the simulation results focusing
39 in particular on the organization of aggregates.

40 2. Simulation methods

41 In this paper, the aggregation and organization of colloids subjected to low-intensity at-
42 tractive interactions is studied. The effect of two kinds of interaction potentials is analyzed:
43 the DLVO potential [19] and the generalized Lennard Jones potential [20].
44 The system used in this paper is similar to the one presented in reference [15]. Alumina par-
45 ticles with a mean radius of $a = 250$ nm suspended in water are considered. The interaction
46 between particles will first be modeled using a DLVO potential. This potential is composed
47 of an attractive part due to van der Waals forces and a repulsive part due to electrostatic
48 repulsion. The van der Waals component can be expressed as [19]:

$$U_{ij}^{\text{vdW}}(r_{ij}) = -\frac{A}{6} \left[\frac{2a_i a_j}{r_{ij}^2 - (a_i + a_j)^2} + \frac{2a_i a_j}{r_{ij}^2 - (a_i - a_j)^2} + \ln \left(\frac{r_{ij}^2 - (a_i + a_j)^2}{r_{ij}^2 - (a_i - a_j)^2} \right) \right], \quad (1)$$

49 where A is the Hamaker constant (here $A = 4.76 \times 10^{-20}$ J)[21], a_i the radius of particle i and
50 r_{ij} the distance between particles i and j . The electrostatic repulsion is described by [22]:

$$U_{ij}^{\text{el}}(r_{ij}) = 2\pi\epsilon \frac{a_i a_j}{a_i + a_j} \psi^2 \left[\ln \left(\frac{1 + e^{-\kappa h_{ij}}}{1 - e^{-\kappa h_{ij}}} \right) + \ln (1 - e^{-2\kappa h_{ij}}) \right], \quad (2)$$

51 where ψ is the surface potentials of the particles, $\epsilon = \epsilon_0 \epsilon_r$ the dielectric constant of the solvent
52 (here $\epsilon_r = 81$), and κ the inverse Debye screening length. In the following, $\psi = 0.1$ V and
53 $\kappa = 2.8 \times 10^8 \text{ m}^{-1}$ are used. The well depth of the interaction potential is then $3.3 k_B T$, with
54 k_B the Boltzmann constant and T the temperature (here $T = 293$ K). This value allows us to
55 observe the organization of aggregates [15]. A plot of this potential is shown in Figure 1(a).

56 The well depth of the DLVO potential is size dependant. If the interacting particles are

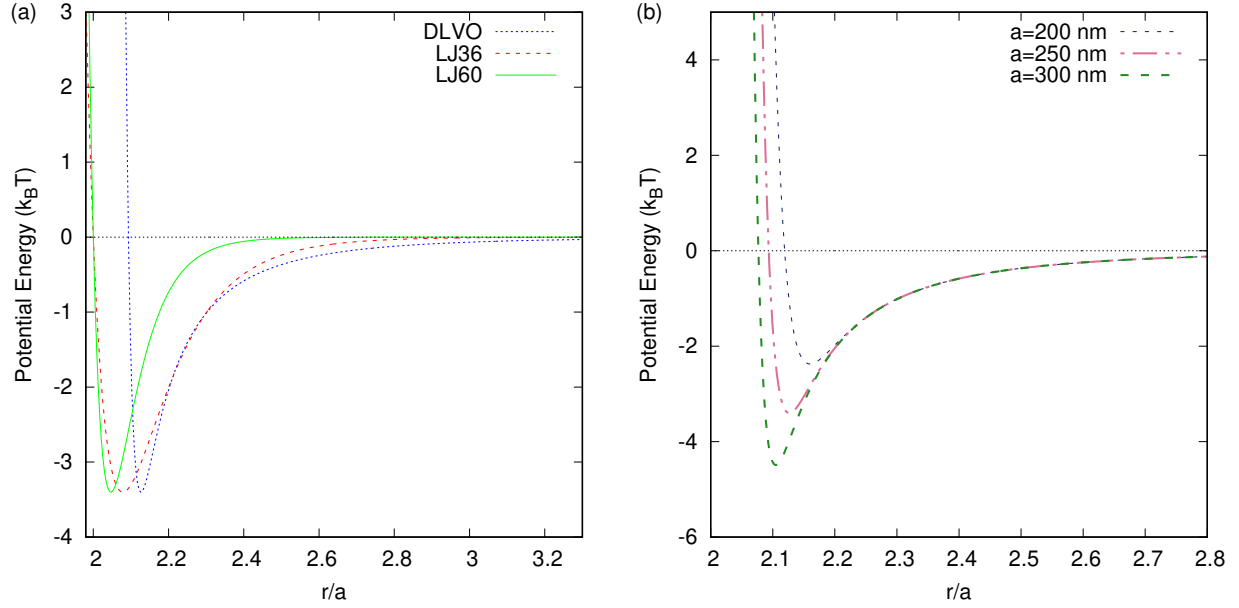


Figure 1: a) Interaction potentials in units of $k_B T$ as a function of distance between particles. (b) DLVO potential in units of $k_B T$ as a function of distance between particles for particles of size 200, 250 and 300 nm.

larger, the potential well becomes deeper. Conversely, for interactions between smaller particles, the well is shallower (see plots of DLVO potential with $a = 200$ nm and $a = 300$ nm in Figure 1(b)).

The aggregation obtained using the DLVO potential will be compared to those obtained using a generalized Lennard Jones potential defined as follows:

$$U_{ij}^{\text{LJ}}(r_{ij}) = 4\epsilon \left[\left(\frac{a_i + a_j}{r_{ij}} \right)^n - \left(\frac{a_i + a_j}{r_{ij}} \right)^{n/2} \right] \quad (3)$$

with ϵ the well depth. The value of n influences the shape and the range of the interaction potential. Initially $n=36$ will be used, as it has already been done in a previous work [20]. This value allows us to obtain the same range of interaction as for the DLVO potential, that means that particles will interact over similar approach distances. However, the width of the potential well depth is larger than that of the DLVO potential. As a comparison, $n=60$ will also be used, which gives a width of well depth similar to that of DLVO potential. In this case, the range of interaction will be shorter. In order to compare only the impact of the shape of the potential, all the simulations are carried out with $\epsilon = 3.3 k_B T$ which is the value of the DLVO potential well depth for particles with $a = 250$ nm. Thereafter, LJ36 and

LJ60 refer to simulations carried out with $n=36$ and $n=60$ respectively. In contrast to the DLVO potential, the potential well depth of LJ36 or LJ60 do not vary with particle size. The different potentials used in this study are shown in the Figure 1(a). All the potentials will be cut at $r_{ij} = r_c = 1.15(a_i + a_j)$.

Brownian dynamics simulations are performed with 10,000 particles in a cubic box with periodic conditions. Initially, particles are randomly distributed in the simulation box. The size of the box is defined so that the volume fraction of particles is equal to 6%. To understand the influence of particle size dispersion on aggregation, a particle size distribution is introduced by randomly choosing the particle size in a normal distribution with mean $a = 250$ nm and standard deviations ranging from $0.01a$ to $0.1a$. More specifically, the distribution effect with a standard deviation of $0.01a$, $0.025a$, $0.05a$ and $0.1a$ will be studied. One condition to use the Brownian dynamics simulations is to choose a time step being higher than the velocity relaxation time of each particle, while being also sufficiently small to ensure that the interaction forces do not change significantly during one integration step [2]. To satisfy these conditions, it was chosen to restrict the particle size between $0.8a$ and $1.2a$. Examples of the size distributions used in simulations for the different standard deviations mentioned before are shown in Figure 2. In the following, simulations carried out with a standard deviation of $0.01a$, $0.025a$, $0.05a$ and $0.1a$ will be denoted by $\sigma = 0.01$, 0.025 , 0.05 and 0.1 , respectively. The time step of the simulations has been fixed at 1.5×10^{-7} s. Simulations have been performed with different home-made simulations codes running on CPU or on GPU based on OPENCL [23] or on CUDA. Results are averaged over three independant simulations.

3. Results and discussion

3.1. Aggregation without size dispersion

First, the aggregation without size dispersion is analyzed. Snapshots of Brownian dynamics simulations obtained at $t = 300$ s are shown in Figure 3.

Whatever the interaction potential used, the aggregates are organized and isolated particles remain. To quantify the organization, order parameters P12 indicating the percentage of particles with 12 first neighbors and P6 indicating the percentage of particles with 6 second

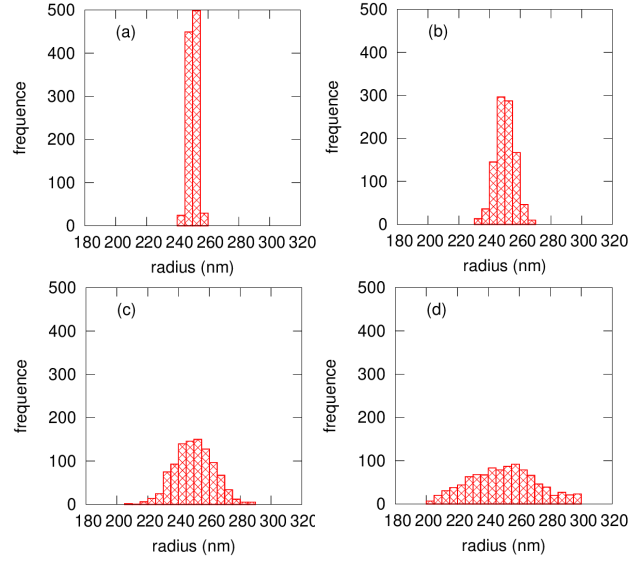


Figure 2: Examples of the size distributions used in simulations for the different standard deviations: (a) $\sigma = 0.01$, (b) $\sigma = 0.025$, (c) $\sigma = 0.05$ and (d) $\sigma = 0.1$.

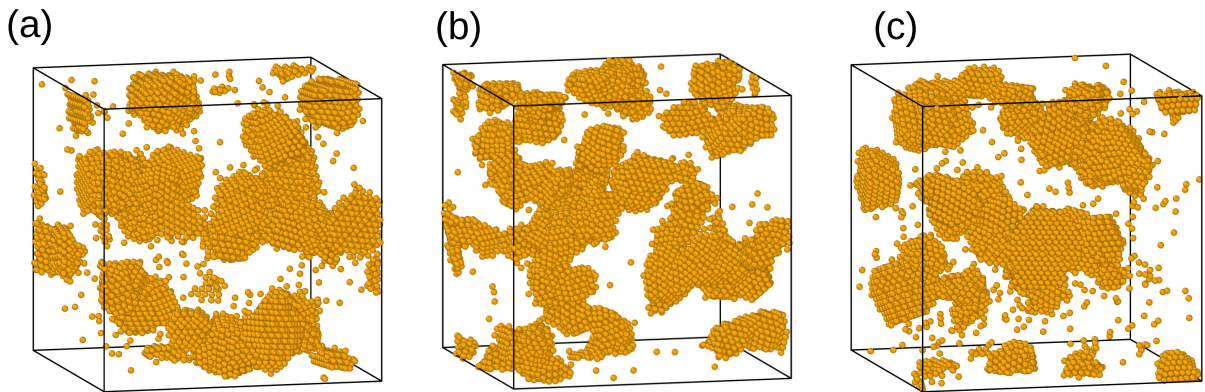


Figure 3: Snapshots of Brownian dynamics simulations at 300 s: (a) DLVO, (b) LJ36 and (c) LJ60.

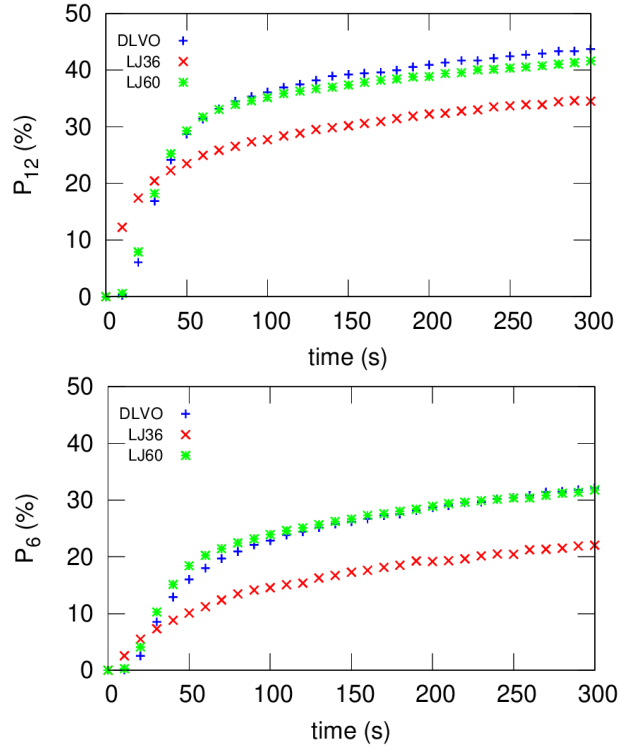


Figure 4: Evolution in time for the two order parameters P_{12} and P_6 obtained for the different potentials DLVO, LJ36 and LJ60.

neighbors are analyzed (see Figure 4). The distance used to identify the first and second neighbors are based on an analysis of the radial distribution functions.

In all cases, P_{12} and P_6 increase during the simulations confirming an ordering in the simulation. The values seem to indicate that order is more important in the aggregates obtained with the DLVO and LJ60 potentials than with the LJ36 potential. On the other hand, the shape of the aggregates obtained is different for LJ36 compared to DLVO and LJ60 (see Figure 5). The aggregates obtained with LJ36 are more elongated.

The aggregates obtained with LJ36 are the result of the coalescence of smaller aggregates that seem to rearrange little into a compact shape. Various tests are carried out to understand this difference in organization. Previous studies have shown that the ability of an aggregate to reorganize may be linked to the ability of the particles to detach [15]. To examine this property with different potentials, simulations are carried out to quantify the average dissociation time of a dimer. To do this, Brownian dynamics simulations are carried out by considering only two particles initially placed so that their separation distance is that of the minimum of the interaction potential. The dissociation time corresponds to the time

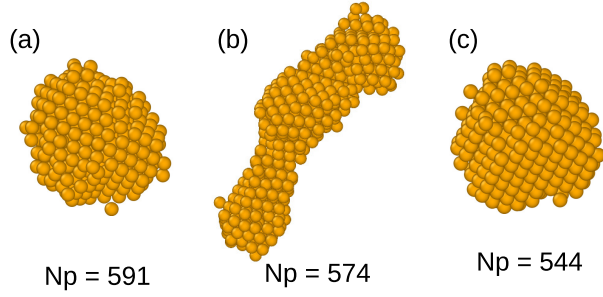


Figure 5: Snapshots of representative isolated aggregates obtained at 300 s in Brownian dynamics simulations: (a) DLVO, (b) LJ36 and (c) LJ60. N_p is the number of particles in the aggregates.

taken for the particles to stop interacting, i.e. the time required for them to be at a separation distance greater than $3.3a$. The average dissociation time obtained over 200 simulations was measured at $t = 6.42 \times 10^{-2} \text{ s}$, $t = 8.93 \times 10^{-2} \text{ s}$ and $t = 3.02 \times 10^{-2} \text{ s}$ respectively for DLVO, LJ36 and LJ60. The dissociation times are lower for the latter potential, indicating a greater ability of the particles to dissociate in these systems, allowing the aggregates to locally reorganize better. However, the dissociation times obtained with LJ36 and DLVO are not so different and do not fully explain the difference in aggregate shape. The main difference between these two potentials is the width of the well depth, which is larger for LJ36. Because of the potential width, not only neighbor particles but also second neighbors may play a role in the ordering. The second-neighbor interactions on nucleus has thus been investigating by analyzing the energy of a compact aggregate made up of 13 particles (icosaedre) during a Brownian dynamics simulations. This structure has been chosen because it is compact and can be considered as a first nucleus. Results show that the energy of the system is lower when using LJ36 than when using DLVO or LJ60. The lowest energy obtained in DLVO is $-199.6 k_B T$, in LJ60 $-203.2 k_B T$ and in LJ36 $-227.0 k_B T$. As already discussed, this difference can be attributed to the interaction width of the LJ36 potential well depth. Since this width is larger than that of the two other potentials, with LJ36 the second neighbors will also interact and organize themselves locally to minimize the total energy of the aggregate. As a consequence with this potential, nuclei may form more easily and have a sufficiently low energy to allow rapid crystal growth. Once the crystal nuclei are formed, aggregates continue to grow by coalescence, resulting in the formation of elongated aggregates. The narrower well depth of the LJ60 and DLVO potential wells, on the other hand, makes the reorganization of

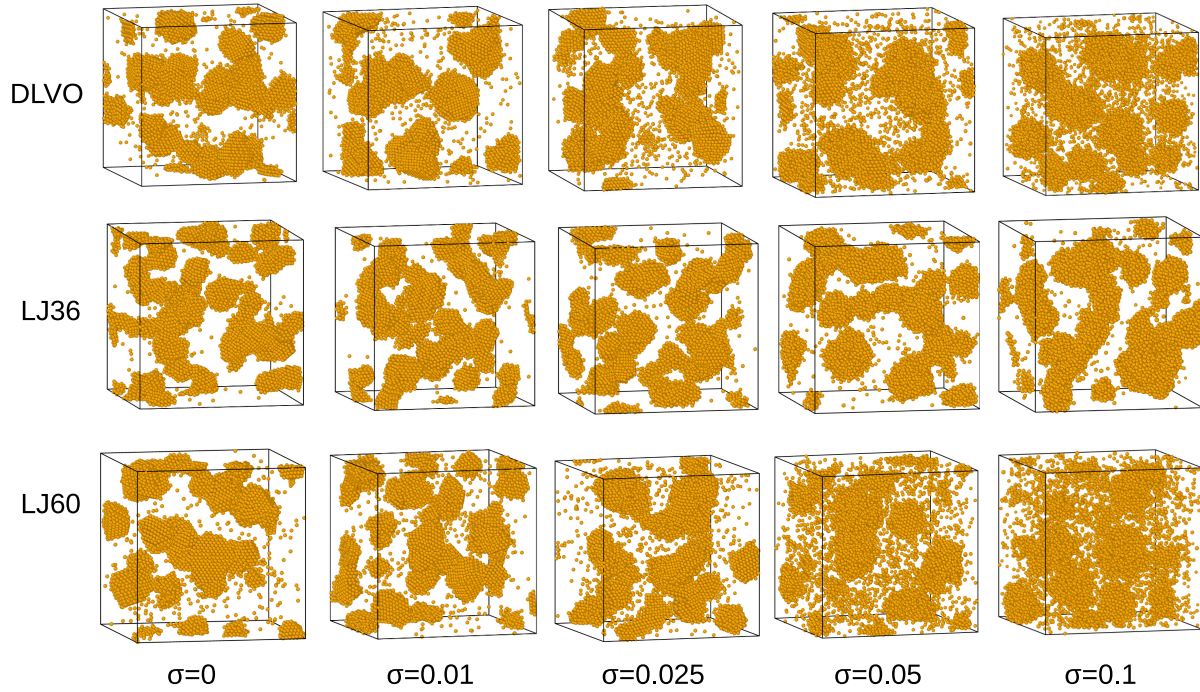


Figure 6: Snapshots of simulations at $t = 300\text{s}$ as a function of the radius dispersion: first row: DLVO potential, second row: LJ36 potential and third row: LJ60 potential.

aggregates more difficult, and the nuclei should be less energetically stable. Nuclei should be more difficult to stabilize, leading to later crystallization (see Figure 4). At the initial stage of aggregation, the P6 and P12 parameters increase indeed faster for LJ36 than for LJ60 and DLVO. In summary, the LJ60 and DLVO potentials, which have similar well potentials in terms of well value and width, give similar simulation results. On the other hand, the LJ36 potential results in a different aggregation which can be explained by a larger potential well width.

3.2. Aggregation with size dispersion

Experimentally, particles are always dispersed in size. Studies have already shown that differences in particle size lead to changes in crystallization. To understand the impact of particle size dispersion in the previous simulations, the simulations were repeated with particle sizes varying according to a Gaussian distribution. The results obtained are shown in Figures 6 and 7.

For the dispersion $\sigma = 0.01$, there is no significant effect on the aggregates' organization.

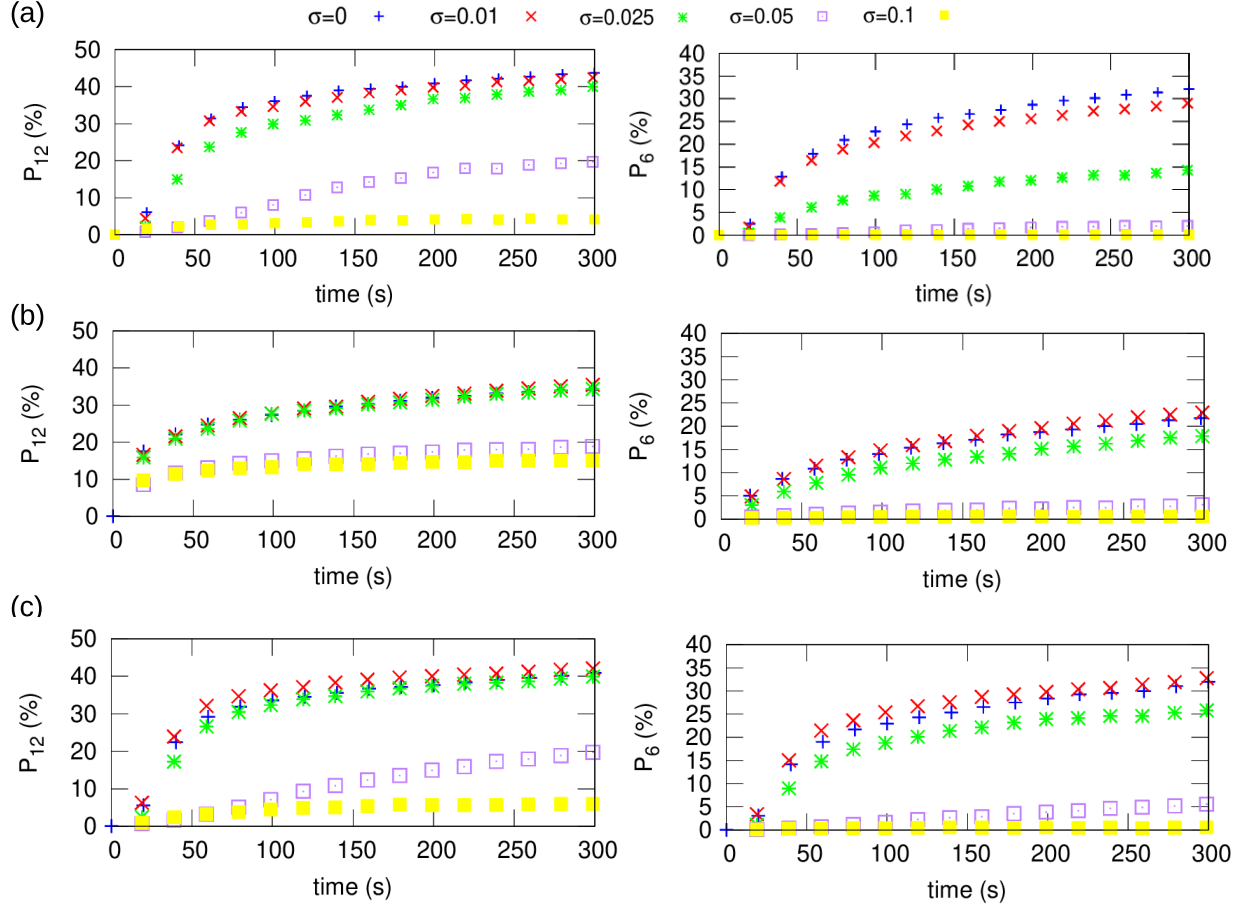


Figure 7: Evolution in time for the two order parameters P_{12} and P_6 obtained with different radius distribution for : (a) DLVO potential, (b) LJ36 potential and (c) LJ60 potential.

Aggregates can accommodate the small size variations. However, whatever the interaction potentials used, results show that the aggregates become disordered with a dispersion greater than or equal to $\sigma = 0.05$. This observation is in agreement with experiments, which demonstrate that size dispersion leads to disorganized aggregates [17]. As for $\sigma = 0.025$, there is a difference between the potentials. According to the analyses of P6 parameters, with this dispersion, aggregates obtained with DLVO seem more disordered than the ones obtained with the two kinds of generalized Lennard Jones potentials. Given that the size distributions are the same in the different simulations, this observation is due to the interaction potential. When the size dispersion increases, an increase in the number of isolated particles is also observed, whatever the potential (see Table 1). An analysis of the average size of the isolated particles shows that their average radius is smaller than that of the distribution ($a = 250$ nm).

Table 1: Averaged number of isolated particles $n_{isolated}$ and averaged radius of isolated particles $a_{isolated}$ observed in Brownian dynamics simulation at $t = 300$ s for the different interaction potentials. Results are averaged over three independant simulations

	DLVO		LJ36		LJ60	
distribution	$n_{isolated}$	$a_{isolated}$ (nm)	$n_{isolated}$	$a_{isolated}$ (nm)	$n_{isolated}$	$a_{isolated}$ (nm)
$\sigma = 0$	321.7	250.0	61.3	250.0	346.3	250.0
$\sigma = 0.01$	310.0	249.8	72.3	249.5	384.0	249.9
$\sigma = 0.025$	534.7	248.5	118.3	249.4	630.3	249.7
$\sigma = 0.05$	1039.7	246.5	210.0	247.8	1426.3	247.5
$\sigma = 0.1$	1416.0	232.5	210.0	249.5	1624.3	246.6

Figure 8 shows the percentage of isolated particles as a function of their size in the case $\sigma = 0.1$. For the two generalized Lennard Jones potentials, the percentage of isolated particles decreases slightly with the size of particles. However, for the simulation with the DLVO potential, it is clearly observed that the smallest particles are more isolated than the largest ones. These evolutions are in agreement with the observation of the average radius of isolated particles. The decrease in the percentage of isolated particles with their size suggests that regardless of the potential used, the smallest particles have more difficulty to aggregate and remain more isolated. This can explain the increase of the number of isolated particles with

the increase in size dispersion. Indeed, whatever the interaction potential used, an increase in size dispersion leads to an increase in the number of smaller-than-average particles, which will have more difficulty in aggregating and thus will tend to remain isolated. Different reasons could explain this phenomenon. First, smallest particles, because of their smaller mass, could have a higher vibration frequency in the well and escape more easily from the potential well depth and therefore not be bound. Moreover, because of their size, small particles are more difficult to bind to several other particles. Insertion of small particles into an aggregate could also create geometric constraints, which results in larger network distortions often less stable. It has already been shown experimentally that the insertion of small particles of irregular size leads to more disordered structures than larger particles [18]. This should lead to a preferential localization of small particles on the surface of aggregates, or even to their isolation, to minimize distortion and therefore the system energy. However, it can be noted that the smallest particles are more isolated when using the DLVO potential. This can be explained because the DLVO interaction is size dependant and when the particle become smaller, they interact by a shallower potential well (see Figure 1(b)). The decrease of the well depth makes the bonding of small particles less stable compared to the other potentials, resulting in more small particles remaining isolated with the DLVO potential.

Let's now look at how size distribution affects the distribution of particles in aggregates. This analysis is carried out more specifically on systems with $\sigma = 0.1$. In the Figure 9a, isolated aggregates are represented with particles colored according to their radius. The images in the top row show the aggregate from the front, allowing us to analyze the aggregate surface. To better understand the distribution of particles within the aggregates, cross-sections are also shown below. In the case of the DLVO potential, there are fewer large particles on the surface than with the generalized Lennard Jones potentials (see red or orange particles in Figure 9a). On the other hand, particles with the largest radii are clearly present at the cross-sectional level. To better quantify this, the number of coordination of the aggregated particles as a function of their radius is reported in Figure 9b. The general trend is an increase of the coordination number with the radius of particles. Geometrically, larger particles are likely to have more neighbors than smaller ones. However, it can be noticed that the curves for LJ potentials do not show a monotonic increase, while the trend observed for

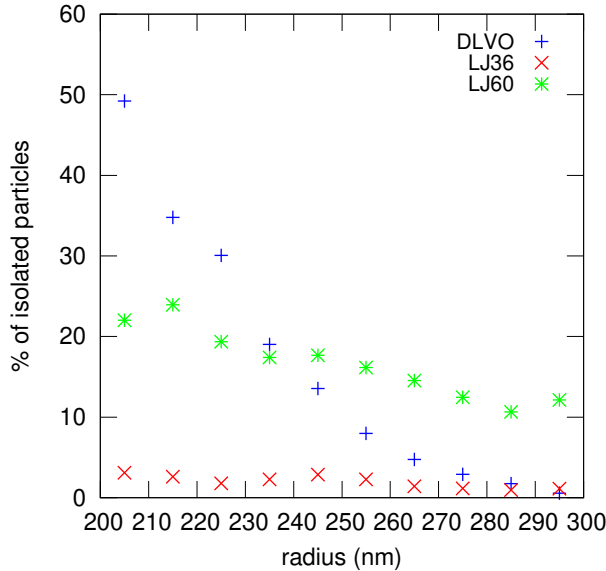


Figure 8: Percentage of isolated particles as a function of size at $t = 300$ s for $\sigma = 0.1$. Results are obtained on one simulation. The percentage is expressed as the ratio of the number of isolated particles with a size within the interval under consideration to the total number of particles with a size within this interval.

DLVO is continuous and monotonic. For DLVO potential, the larger the particle radius is, the greater is the coordination number. This is consistent with the fact that large particles are located preferably inside the aggregates. The curves of the coordination numbers show also that the trend is less pronounced for the generalized Lennard Jones potentials and particles of different sizes are better distributed in the aggregates.

According to these results, including a size distribution has not exactly the same effect when using the DLVO or the generalized Lennard Jones potentials. The difference can be explained by the dependency of the well depth with the size of particles. As already mentioned, for the Lennard Jones potentials, changing the sizes of particles has indeed no effect on the interaction potential. The effect of size dispersion can be explained only by geometrical constraints and by the higher mobility of small particles. However, as already mentioned the DLVO potential is size dependant and when particles size increases, the well becomes deeper (see Figure 1(b)). To reduce the energy of the system, with the DLVO potential, it is then better to have aggregation between the largest particles. Thus, the biggest particles will tend to aggregate together with the maximum compacity and the smallest ones will essentially be expelled from the aggregate center and even detached. This will result

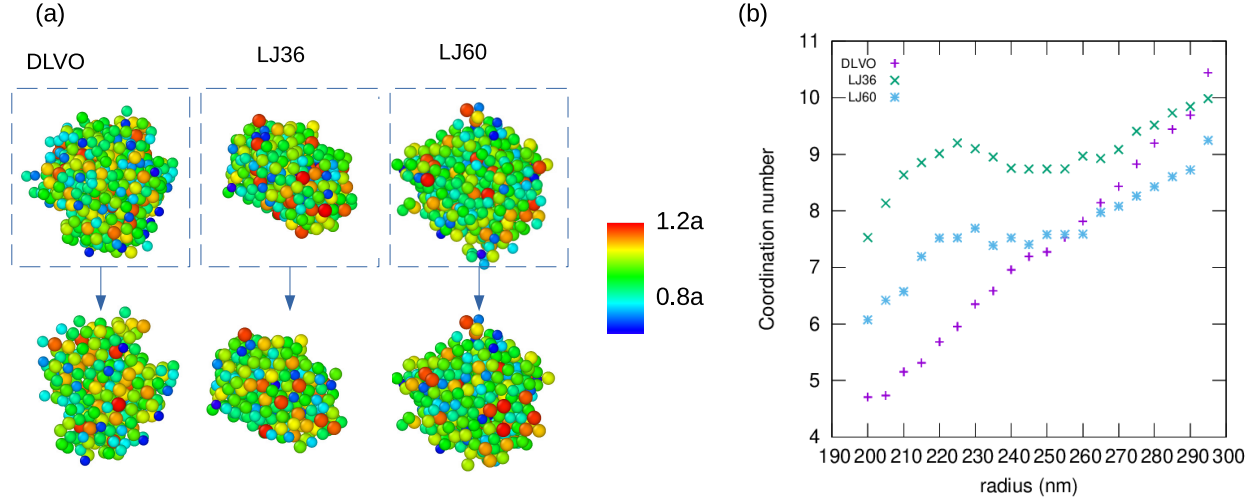


Figure 9: (a) Snapshots of an isolated aggregate obtained in simulations at $t = 300$ s for $\sigma = 0.1$: on the top aggregate seen from front and below, cross-section of the aggregate. Particles are colored according to their radius. (b) Coordination number of particles in aggregates as a function of their radius at $t = 300$ s for $\sigma = 0.1$. Results are averaged over 3 simulations.

in a different distribution of particles in the system to that observed with the generalized Lennard Jones potentials. As already mentioned, Figure 7 shows that aggregates obtained for $\sigma = 0.025$ are more disordered with the DLVO potential than with the generalized Lennard Jones potentials. This can also be explained by the interactions between particles. According to Figure 1(b), the separation distance where is found the minimum of well depth of DLVO potential, decreases with the size of particles. In that case, even if the size of particles is not so different ($\sigma < 0.05$), when aggregating, larger particles will tend to approach more each other. This will cause some distortions in the particle network and render more difficult the ordering and the values of the order parameters will decrease. On the contrary, particles interacting with the generalized Lennard Jones potentials will be able to maintain an ordered network until the size dispersion implies geometrical constraints because they will stay at the same distance.

These results show that to understand the effect of size distribution in real systems, it is important to describe the interactions between particles accurately, as they can be size-dependent and consequently induce different behaviors.

4. Conclusion

In this paper, crystallization using attractive potentials is analyzed. First, aggregation between homogeneous particles interacting via different potentials having the same well depth values are studied. It has been shown that the width of the interaction potential well depth has consequences for the shape and degree of organization of the aggregates. A narrow well depth results in more spherical and organized aggregates. A larger width, on the other hand, produces more elongated aggregates. A larger well depth seems to facilitate the formation of nuclei, resulting in numerous small organized aggregates forming and then coalescing to form larger elongated aggregates.

Next, the effect of introducing size dispersion was analyzed. In all cases, size dispersion led to the disorganization of the aggregates and an increase in the number of isolated particles. Aggregates obtained with $\sigma \geq 0.05$ are all disordered regardless the potential used. This result is in agreement with the results found in literature showing that particles of irregular size affect the microstructure of colloidal crystals [16, 18, 17]. However, the study also shows that the interaction potentials between the colloids can affect differently the distribution of particles both in aggregates and in isolated particles. There is a non trivial effect of the interaction potentials. Interaction potentials that give similar results with particles of identical size may give indeed different results when a particle size distribution is introduced. The difference is explained by a change of the potential well depth as a function of particle size.

To conclude, this study opens new perspective to control defects in the crystal and therefore their properties by modifying the interactions between particles. From a more general point of view, it also shows that results of simulations can be impacted by a size distribution. Depending of the properties studied numerically, it can thus be necessary to consider a size dispersion, which is always present in experiments.

CRediT author statement

Manuella Cerbelaud: Conceptualization, Software, Investigation and Formal analysis;
Fabien Mortier: Investigation and Formal analysis; **Hanady Semaan**: Investigation;
Julien Gerhards: Software; **Benoit Crespín**: Software; **Riccardo Ferrando**: Formal analysis and **Arnaud Videcoq**: Conceptualization and Formal analysis.

All authors contributed to writing the paper.

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Figures 3, 5, 6, and 9 have been obtained by OVITO [24].

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