Numerical study of soft colloidal nanoparticles interaction in shear flow – Supporting information

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IMPACT OF SHIFTING OF THE VAN DER WAALS CURVE

As described in the methodology part, the proposed interaction model was built considering an approximation of the van der Waals curve in order to connect the non-contact interactions with the contact interactions in a continuous curve. This approximation consist of shifting the van der Waals curve towards the origin such as the maximum tensile force achieved by the van der Waals curve occurs at the zero inter-particle separation distance, and has a value equal to the maximum adhesive force (pull-off) described by the DMT theory.

Thus the magnitude of the distance, by which the van der Waals curve is shifted, is determined by the value of the pull-off force from DMT model. The pull-off force can be calculated from the Eq. 8 in the main text. As it can be seen, Eq. 8 depends on the effective radius of the particles and the surface energy. Since in our simulations the radius of the particles is constant, the variation of the pull-off force only depends on the surface energy. Hence, the shifting distance of the van der Waals curve depends only on the value of surface energy and is equal to the separation distance, for which the van der Waals force is equal to the pull-off force. The Figure 1 SI shows the value of the shifting distance for different surfaces energies.

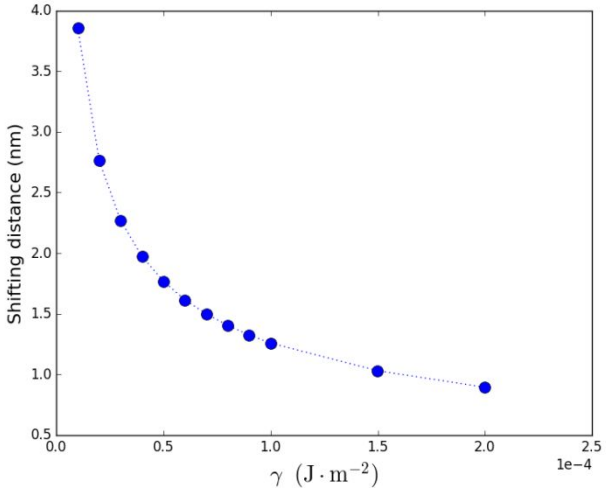

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Figure 1 SI - Magnitude of the shifting distance of the van der Waals curve to meet the DMT curve for different surface energies.

23 In order to understand the impact of the shifting distance on the particles interaction, we evaluated the
24 magnitude of the van der Waals force before and after the shifting, considering different separation
25 distances.

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Table 1 SI – Difference between the original van der Waals force and the used for our model for surface energy $\gamma = 2 \times 10^{-4}$ (mJ/m2)

Separation distance (nm)	Force difference (N)	Difference in % (% of the original vdW force)
1.0	-2.29×10^{-11}	60.94
1.5	-1.11×10^{-11}	52.44
2.0	-6.21×10^{-12}	45.93
2.5	-3.84×10^{-12}	40.83
3.0	-2.54×10^{-12}	36.73
3.5	-1.76×10^{-12}	33.36
4.0	-1.28×10^{-12}	30.56
4.5	-9.53×10^{-13}	28.18

As shown in the Table 1 SI, the relative difference of the used van der Waals force with respect to the original van der Waals force increases when the separation distance decreases. On the other hand, for large values of separation distance, the force difference is smaller, since the van der Waals curve converges asymptotically to zero. It is important to mention that as the simulations presented in this study were performed for fully destabilized primary particles, the values of separation distance shown in the Table 1 SI are larger than the Debye length. When considering typical latex particles prepared by emulsion polymerization, the value of critical coagulation concentration for Magnesium Chloride is around 0.015 mol/L, resulting in a Debye length of about 1.0 nm. For smaller values of separation

distance, the particles would interact due to their surface adhesion. Therefore, in this range, considering van der Waals force is not appropriate.

Furthermore, when considering larger surface energy than that presented in Table 1 SI, the relative difference of the van der Waals force before and after the shift becomes smaller compare to values presented in Table 1 SI.

IMPACT OF SHIFTING OF THE VAN DER WAALS CURVE ON AGGREGATES SIZE

In order to quantify the impact of the van der Waals curve shift in the multi-body simulations, we decided to run a test simulation in which the forces experienced by the particles before contact will be the same as if the van der Waals curve will not be shifted. Then, this test simulation was compared with a base case (Original simulation) using the interaction model as described in this article. In order to isolate the effect of modifying the non-contact forces (vdW), we have to keep in both the Test and Original simulation the same loading conditions in terms of stiffness and pull-off force (interaction after contact).

The strategy used to achieve this scenario, was to increase the initial surface energy in the Test simulation (while using the same interaction model). In this way, the new value of adhesive force will be the same as if the van der Waals curve will not be shifted (see dashed line in Figure 2 SI). The magnitude of this increase was chosen according to the maximum difference reported in Table 1 SI (61%), which is equivalent to a surface energy $\gamma = 3.22 \times 10^{-4}$ mJ/m^2 instead of value $\gamma = 2 \times 10^{-4}$ mJ/m^2 used in Original simulations. Moreover, we choose the conditions in such way, that all the particles in the system undergo plastic deformation. Thus, the pull-off force of the particles in both

cases will be greater than the initial adhesive force set by the given surface energies.

This approach of course has consequences in the contact interaction curve, since the initial value of adhesion determines the starting point of the DMT curve. In order to maintain the same loading conditions during plastic deformation in both cases, we had to modify the onset of plastic deformation in the Test simulation (see dashed and solid line in Figure 2 SI after reaching point of plastic deformation). Additionally, we artificially set a maximum surface energy in the Test simulation in order to keep the same average pull-off force as in the Original simulation. An example of interaction curve of both cases is presented below.

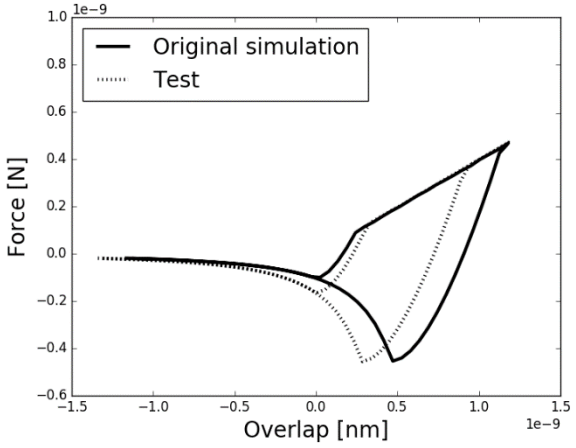
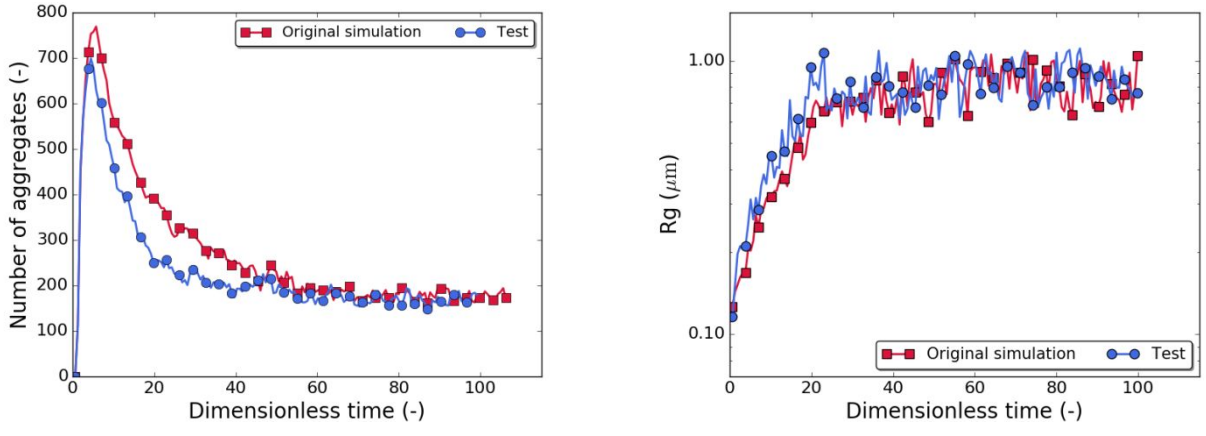


Figure 2 SI – Example of interaction curve used for testing the effect of shifting in the van der Waals curve

As can be observed in the Figure 2 SI, the deformation required to achieve the target pull-off force in both cases is different. On one hand, in the Original simulation, the pull-off force is an outcome from the external forces which lead to a maximum deformation during contact. This deformation depends on the material properties as well as the shear rate. On the other hand, in the Test simulation, we had

to artificially set a threshold to the pull-off force in order to keep it the same as the Original simulation. Even though the pull-off force is set a priory in the Test simulation, the particles can still deform further the point where the unloading starts. One detail to be considered is that any deformation further that point will have a linear unloading along a plastic deformation path until the line meets the unloading curve again.

Thus, we compared two multibody simulations using the same shear rate, material properties but different initial surface energy, as described above. So in both systems the particles experience the same deformation and same pull off-forces, but different attractive forces before contact (vdW). We are especially interested in how this modification affects the macroscopic behavior of the system, particularly in terms of number and size of the aggregates.



(a) (b)

Figure 3 SI – Macroscopic comparison of two systems with different van der Waals forces: (a) Evolution of number of aggregates in time, (b) Evolution of radius of gyration in time. Both simulation were tested considering $K = 0.4$ and $G = 1.60 \times 10^6$ s^{-1}.

As shown in the Figure 3 SI (a) and (b), the difference between both simulations arises in the kinetics of aggregation. In particular, in the case when the van der Waals curve is shifted to higher surface energy (Test simulation), the aggregation occurs faster. In contrast, both simulations reach the same condition at steady state with approximately 200 aggregates in the system with an average size around 0.8 microns. This information is very important, and tells us that the average size of aggregates at steady state in our model depends on the pull-off force at the moment of detachment, which in the case of plastic deformation is always greater than the initial adhesive force set by DMT or van der Waals theory. Thus, we can state that the modification of van der Waals curve does not affect the steady state macroscopic behavior of the system, as long as plastic deformation takes place.