

# SRD-MD modelling of hydrodynamic interactions in colloidal systems: playing between computational cost and resolution

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## ABSTRACT

A ubiquitous problem that has always been a subject of intensive research is the role played by hydrodynamic interactions (HIs) in several fundamental problems in colloid rheology and aggregation kinetics. However, the high computational demand that is often associated with HIs modelling presents a huge challenge. Even with the computer power that is available today, a full molecular dynamics simulation is still unsustainable. Meanwhile, there is a diverse number of technological applications that call for a means to address this limitation. To that end, we use a hybrid Stochastic Rotation Dynamics - Molecular Dynamics (SRD-MD) method, which can provide a compromise between computational efficiency and molecular dynamics resolution.

We present our SRD-MD simulation results in two parts. The first one is modelling of the rheological behaviour of colloidal suspensions. We successfully reproduce, both qualitatively and quantitatively, the divergence of the suspension viscosity from linear behaviour when HIs are properly included. The second part deals with the aggregation kinetics of colloidal suspensions. We show that HIs speed up the aggregation process of colloids and slow down the reorganization of the clusters formed. Consequently, we demonstrate that the probability of percolation is higher for systems with HIs in comparison with systems without.

**Keywords:** simulations, rheology, shear viscosity, percolation, colloidal suspension

## 1 INTRODUCTION

The significant progress in numerical methods over the recent years has provided a better understanding of the various applications of colloids in natural and industrial settings [1]. Nevertheless, due to the increasing complexity of materials that are being discovered everyday, there is a considerable effort devoted to the development of advanced numerical methods that can keep up with technology's rising demands.

A straightforward technique that can be used to obtain the dynamic properties of many-particle system is Molecular Dynamics (MD). However, there is an extensive class of complex fluids where the timescale separa-

tion, between the motion of the embedded solid and the underlying solvent, presents a challenging task. Since this can be a serious problem with MD, several coarse-grained models have been proposed to resolve this issue. Examples are Brownian Dynamics (BD), BD with Yamakawa-Rotne-Prager tensors (BD-YRP), Dissipative Particle Dynamics (DPD) and Lattice Boltzmann (LB) technique. Among them, the most popular method is BD, mostly because of its simplicity. This is achieved by representing the effects of the solvent particles on the solute by a combination of random forces and frictional terms [2]. In reality however, hydrodynamic forces are omnipresent in complex fluids and while the extension to BD-YRP incorporates hydrodynamic interactions (HIs), its validity is constrained to relatively dilute suspensions. This is because the computational cost of BD-YRP increases drastically with the number of colloid particles  $N$  i.e. it requires a tensor evaluation that scales as  $\mathcal{O}(N^2)$  and diagonalization that scales as  $\mathcal{O}(N^3)$  [3, 4]. Alternatively, HIs can be solved using particle-based or lattice-based methods. Among the widely-celebrated models are DPD and LB. In DPD, the system is completely defined by specifying all the positions and momenta of the solvent particles making it almost similar to MD. The difference is that instead of using an explicit force term, it uses a weight function to define the collision rule [5]. In LB, a linearized and preaveraged Boltzmann equation is discretized and solved on a lattice. Here, the position and velocity probability density functions of each of the nodes are calculated every time step [6, 7].

A versatile model should include all the relevant aspects of the dynamics of the system, i.e. thermal fluctuations and HIs, and still be computationally reasonable to be of value in predicting transport properties, testing physical theories and offering insights to experiments. To this end, we use a hybrid Stochastic Rotation Dynamics - Molecular Dynamics (SRD-MD) method that is first introduced by Malevanets and Kapral over a decade ago [8]. While it can be argued that the cost of computation still depends on the system being modeled, the main advantage of SRD-MD over the previously mentioned methods is that it is generally simpler and faster. Ref. [9] referred to it as the "Ising model" of hydrodynamics. Moreover, its simplified dynamics has allowed

the analytic calculation of several transport coefficients [10, 11]. In comparison to the other methods mentioned above, SRD-MD is a relatively new technique so that most of the work are still in the development stage. But due to its promising potential as a simulation model for complex fluids, it has been gaining a lot of attention and is continuously being developed. In this study, we show that despite the simplicity of SRD-MD, the fundamental rheological and structural behaviors of colloidal systems are still reproduced.

## 2 SRD-MD

Simply put, the fluid dynamics is treated using SRD and the colloid dynamics is treated using MD. SRD consists of a two-step process that involves the streaming and collision of fluid particles. In the streaming step, the positions of the particles evolve according to [8]:

$$\mathbf{r}_i(t + \Delta t_{\text{SRD}}) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\Delta t_{\text{SRD}}, \quad (1)$$

where  $\mathbf{r}_i$  is the particle position,  $\mathbf{v}_i$  is the particle velocity and  $\Delta t_{\text{SRD}}$  is the SRD time step. In the collision step, the coarse graining is done by dividing the simulation box of side length  $L$  into manageable collision cells, where all the particles in the same cell undergoes the same rotation:

$$\mathbf{v}_i(t + \Delta t_{\text{SRD}}) = \mathbf{v}_{\text{cm}} + \mathbf{R}(\alpha) [\mathbf{v}_i(t) - \mathbf{v}_{\text{cm}}], \quad (2)$$

where  $\mathbf{v}_{\text{cm}}$  is the average velocity of the cell and  $\mathbf{R}(\alpha)$  is a rotation matrix. The SRD parameters that define the dynamics of the fluid are the cell size  $a_0$ , which we choose to be half the radius  $a = 300$  nm of the colloid that is embedded in the fluid, the rotation angle  $\alpha = 90^\circ$ , the dimensionless mean-free path  $\lambda = 0.1$ , the time step  $\Delta t_{\text{SRD}} = 7.37 \times 10^{-4}$  s and the mass of the individual fluid particles  $m_f = 6.75 \times 10^{-19}$  kg. The SRD parameters used in this study are the same as in Refs. [12, 13], where a more detailed discussion can be found.

The coupling of embedded colloids in the fluid can be done in two ways. The first is to couple by SRD, where the colloids are treated as point particles and are rotated along with the fluids in the SRD collision steps [14]. The second one is to couple by MD, where the colloids have a defined interaction radius  $\sigma$  and are evolved along with the colloids during MD steps [15]. In the MD procedure, the colloid-fluid and colloid-colloid interactions obey Newton's equations of motion. The potentials used are of the form:

$$V_{cf} = \begin{cases} \varepsilon \left(\frac{\sigma}{r}\right)^{12} & (r < r_c) \\ 0 & (r > r_c), \end{cases} \quad (3)$$

for the colloid-fluid interaction; and

$$V_{cc} = \begin{cases} \varepsilon \left(\frac{\sigma'}{r}\right)^{12} & (r < r'_c) \\ 0 & (r > r'_c), \end{cases} \quad (4)$$

for the colloid-colloid interaction. In Eqs. 3 and 4,  $\sigma = 0.8a$ ,  $\sigma' = 2a$ ,  $\varepsilon = 2.5k_B T$ ,  $r_c = 2.5\sigma$  and  $r'_c = 2.5\sigma'$ .

## 3 SHEAR VISCOSITY

When a system is undergoing a linear perturbation, the viscosity can be obtained by using  $\eta = \sigma_{yx}/\dot{\gamma}$ . To introduce shear, we use Lees-Edwards boundary conditions (LEBC) so that the particles in the simulation box follow a planar Couette flow [1]. Here, we demonstrate the method at a shear rate of  $\dot{\gamma} = 50$  s $^{-1}$  ( $\text{Pe} \approx 6$ ), where a linear velocity gradient is produced after 3 s of waiting time. For the calculation of  $\sigma_{yx}$ , we adapt the stress tensor provided in Ref. [16] for our system:

$$\sigma_{\text{kin},yx}^{\text{fluid}} = -\frac{m_f}{V_f} \sum_{i=1}^{N_f} \hat{v}'_{iy} \hat{v}_{ix} - \frac{m_f \dot{\gamma} \Delta t_{\text{SRD}}}{2V_f} \sum_{i=1}^{N_f} v_{ix}^2, \quad (5)$$

$$\sigma_{\text{col},yx}^{\text{fluid}} = -\frac{1}{V_f \Delta t_{\text{SRD}}} \sum_{i=1}^{N_f} \Delta p_{iy} r'_{ix}, \quad (6)$$

$$\sigma_{yx}^{\text{colloid}} = -\frac{M_c}{V} \sum_{i=1}^{N_c} \hat{v}'_{iy} \hat{v}_{ix} - \frac{M_c \dot{\gamma} \Delta t_{\text{SRD}}}{2V} \sum_{i=1}^{N_c} v_{ix}^2 - \frac{1}{V} \sum_{i=1}^{N_c} F_{iy} r'_{ix}, \quad (7)$$

where  $V = L^3$ ,  $N_f = 163840$  is the number of fluid particles,  $M_c = 2.49 \times 10^{-16}$  kg is the mass of the colloid and the shorthand notations  $\hat{v} = v(t - \Delta t)$  and  $\Delta p_{iy} = m_f(v_{iy} - \hat{v}_{iy})$  are used [12].  $F_{iy}$  is obtained from  $\partial(V_{cc,i} + V_{cf,i})/\partial r_y$ . The apostrophe symbol (') is for quantities measured after LEBC are imposed.

Because of the coupling used, the free volume accessible to the fluid is now defined as  $V_f = L^3 - N_c \frac{4}{3} \pi \sigma^3$ , where  $L = 32a_0$  and  $N_c$  is the number of embedded colloids. Consequently, we define the volume fraction occupied by the colloids as  $\phi = (N_c/L)4\pi\sigma^3/3$ . Note that because of our definition of  $\phi$ , we use  $\sigma$  as our best approximation of the hydrodynamic radius of the colloids.

The continuous pumping of energy from shearing increases the kinetic energy of the system. To ensure that the kinetic energy is conserved, a Monte-Carlo thermostat [17] is also implemented.

Finally, the total stress tensor of the suspension is calculated from the sum of the contributions from the embedded colloids and the suspending fluid:

$$\sigma_{yx} = \sigma_{\text{kin},yx}^{\text{fluid}} + \sigma_{\text{col},yx}^{\text{fluid}} + \sigma_{yx}^{\text{colloid}}. \quad (8)$$

The results are shown in Fig. 3 and are superimposed with the results of Refs. [18, 19]. We are able to reproduce the divergence from Einstein's linear equation  $\eta_R = 1 + 2.5\phi$ , which is only valid for dilute suspensions.

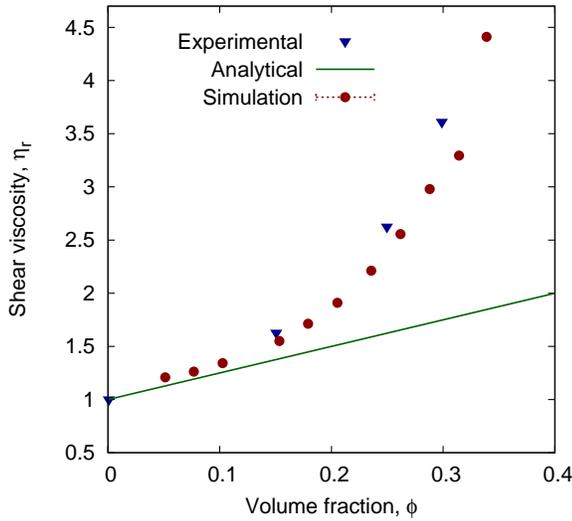


Figure 1: Shear viscosity as a function of volume fraction for  $\dot{\gamma} = 50 \text{ s}^{-1}$  superimposed with the experimental results of Ref. [19] and Einstein's equation  $\eta_R = 1 + 2.5\phi$  [18].

Moreover, we are able to demonstrate the SRD-MD calculation of shear viscosities even for the concentrated cases.

## 4 AGGREGATION KINETICS

To compare the differences in the aggregation kinetics of colloidal systems, we performed two sets of simulations: BD for systems without HIs and SRD-MD for systems with HIs. For the colloids to be attractive, we substitute the  $V_{cc}$  in Eq. 4 by a generalized Lennard Jones potential of the form:

$$V_{cc} = \begin{cases} 4\varepsilon_{LJ} \left[ \left(\frac{\sigma'}{r}\right)^{36} - \left(\frac{\sigma'}{r}\right)^{18} \right] & (r < r'_{LJ}) \\ 0 & (r > r'_{LJ}), \end{cases} \quad (9)$$

where  $\varepsilon_{LJ} = 14k_B T$  and  $r'_{LJ} = 1.6\sigma'$ .

Fig. 4 shows the aggregation kinetics of a 500-particle colloidal system in a simulation box of side length  $L = 55a_0$  with a volume fraction of 10%. By considering an aggregate as an assembly of at least two colloids, we can quantify the aggregation kinetics by observing the temporal evolution of the number of aggregates ( $N_A$ ) in the system. We divide the aggregation process in two stages. Stage I is determined by the increase in  $N_A$  due to the formation of small clusters from individual colloids. From Fig. 4, we can observe that the increase in  $N_A$  is faster for the system without HIs. This is attributed to the slow dimer formation observed in the SRD-MD simulation [20]. A maximum number of clusters is then achieved which marks the beginning of Stage II.  $N_A$  starts to decrease because the clusters coalesce

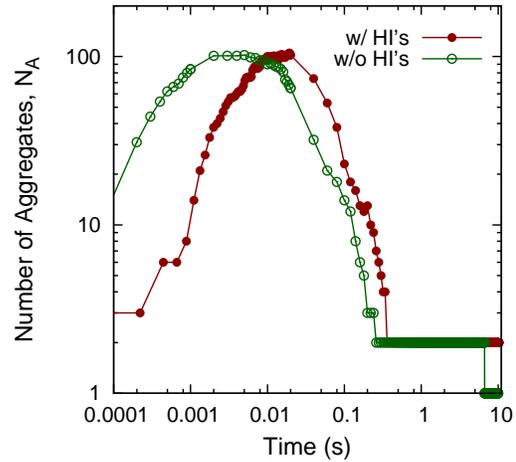


Figure 2: Comparison of the aggregation kinetics between the system with HIs simulated using SRD-MD and the system without HIs simulated using BD. The volume fraction used is 10%.

to form bigger aggregates. In Ref. [20], it was found that the diffusivity increases when HIs are taken into account. This therefore explains the faster coalescence of aggregates in Stage II for the case with HIs.

The two stages of aggregation kinetics both contribute to the final structure of the colloids. Hence from our knowledge of the aggregation process, we turn our attention to percolating networks. Several studies [21, 22] have suggested that the probability of percolation may increase due to the mere presence of hydrodynamic forces. Our results are shown in Fig. 3. This is a snapshot of the colloids at  $\approx 0.5 \text{ s}$ , where the biggest aggregate is shown in red. For the case with HIs, the red aggregate is connected in all 3 directions; while for the case without HIs, the red aggregate is connected in only 2 directions. The difference observed may be due to the rapid formation of big aggregates in Stage II, which does not provide enough time for the colloids to reorganize. Therefore, the reorganization process is another stage in the aggregation kinetics of colloids that needs to be considered. Because of this, we also note that the structures presented here can be considered as transient structures and may change given a longer time scale.

## 5 CONCLUSIONS

We have demonstrated that SRD-MD is an effective simulation technique for the study of the rheology and structure of colloidal suspensions. The calculation of shear viscosity as a function of volume fraction is one of the benchmarks for the effectiveness of the method in modelling hydrodynamics.

In our simulations, BD remains to be the fastest method for the study of aggregation kinetics. However

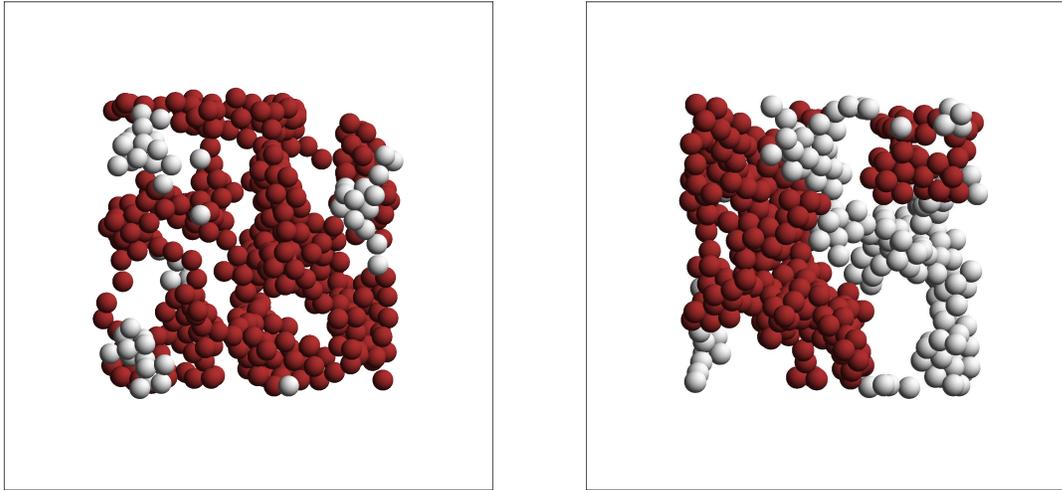


Figure 3: Snapshots at 0.5 s of colloids simulated using SRD-MD (left) and BD (right). The colored spheres corresponds to the biggest cluster present in the system.

in the system described here, HIs also affect the different stages of aggregation of colloids. Thus when HIs cannot be neglected, SRD-MD is an effective approach and can be potentially useful in the study of percolation.

While there is not a single simulation model that can encompass all kinds of systems, we were able to demonstrate that the relevant aspects of the dynamics of colloidal suspensions, especially HIs, are reproduced using SRD-MD despite the approximated fluid and colloid dynamics employed in the model.

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### REFERENCES

- [1] Allen and Tildesley, “Computer Simulation of Liquids,” Oxford University Press, 1987.
- [2] D. L. Ermak and A. J. McCammon, *J. Chem. Phys.* 69, 1352, 1978.
- [3] J. Rotne and S. Prager, *J. Chem. Phys.* 50, 1969.
- [4] H. Yamakawa, *J. Chem. Phys.* 53, 1970.
- [5] P. J. Hoogerbrugge and J. M. V. A. Koelman, *Europhys. Lett.* 19, 1992.
- [6] A. Ladd and R. Verberg, *J. Stat. Phys.* 104, 1191, 2001
- [7] S. T. T. Ollila, C. Denniston, M. Karttunen, and T. Ala-Nissila, *J. Chem. Phys.* 134, 2011.
- [8] A. Malevanets and R. Kapral, *J. Chem. Phys.* 110, 1999; 112 ,2000.
- [9] G. Gompper, T. Ihle, D. M. Kroll, and R. G. Winkler, “Advance computer simulation approaches for soft matter sciences iii,” Springer, pp. 1-88 , 2009.
- [10] J. T. Padding and A. A. Louis, *Phys. Rev. E.* 74, 2006.
- [11] T. Ihle and D. M. Kroll, *Phys. Rev. E.* 67, 2003.
- [12] A. M. K. Laganapan, A. Videcoq, M. Bienia, T. Ala-Nissila, D. Bochicchio and R. Ferrando, *J. Chem. Phys.* 142, 2015.
- [13] A. Tomilov, A. Videcoq, T. Chartier, T. Ala-Nissila, and I. Vattulainen, *J. Chem. Phys.* 137, 2012.
- [14] M. Hecht, J. Harting, M. Bier, J. Reinshagen, and H. Herrmann, *Phys. Rev. E.* 74, 2006.
- [15] G. Batôt, V. Dahirel, G. Méridet, A. Louis, and M. Jardat, *Phys. Rev. E.* 88, 2013.
- [16] R. G. Winkler and C. C. Huang, *J. Chem. Phys.* 130, 2009.
- [17] C. C. Huang, A. Varghese, G. Gompper, and R. G. Winkler, *Phys. Rev. E.* 91, 2015.
- [18] A. Einstein, *Ann. Phys.* 19, 1906; 34, 1911.
- [19] P. N. Segrè, S. P. Meeker, P. N. Pusey, and W. C. K. Poon, *Phys. Rev. Lett.* 75, 1995.
- [20] A. Tomilov, A. Videcoq, M. Cerbelaud, M. A. Piechowiak, T. Chartier, T. Ala-Nissila, D. Bochicchio, and R. Ferrando, *J. Phys. Chem. B* 117, 2013.
- [21] H. Tanaka and T. Araki, *Phys. Rev. Lett.* 85, 2000.
- [22] J. Whitmer and E. Luijten, *J. Phys. Chem. B.* 115, 2011.