ON THE ATTRACTIVE AND REPULSIVE FORCES OF DILUTED MAGNETIC SUSPENSIONS: APPLICATIONS TO NUMERICAL SIMULATIONS

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Abstract. *In this work we use computational tools to model a monodisperse diluted colloidal suspension of permanently magnetized nanoparticles in carrier liquids that do not present magnetic properties. Three models are used to simulate repulsive forces acting on the particles, namely, the Screened-Coulomb potential based repulsive force, the classic Lennard-Jones potential based repulsive force and a electrostatic repulsion force that is meant to emulate the behavior of surfactants adsorbed onto the particle's surface. The approaching of the particles submitted to these repulsive force models is examined. The suitability of each repulsive force model is determined based on its computational cost, the time necessary for particle approach and, finally, the way the particles do approach when submitted to it. We conclude that the Lennard-Jones repulsive force model is the most suitable for most computational applications that require the particles not to form dimers, and the Screened-Coulomb potential based repulsive force is the most suitable for the situations where dimer/chain formation is desirable. The surfactant repulsive force model, although more expensive, allows one to examine the effects of parameters such as temperature and surfactant concentration on the particle's approach and so might be most suitable for simulations that aim to optimize experimental procedures.*

Keywords: *Ferrofluids, Computational Simulation, Lennard-Jones, Screened-Coulomb, Surfactant*

1 INTRODUCTION

Some natural phenomena are too complex to emulate on a laboratory. It can also happen that its performing would be excessively expensive or take too much time to be completed. For this kind of situation there is computational modelling, that consists basically in using computational tools to simulate processes that occur in the physical world, contributing to its understanding and consequence prediction without the need of performing a physical experiment on the laboratory.

Computational modelling can drastically reduce the residue production from scientific experiments that often use dangerous and/or environmentally unfriendly reagents. It can also reduce the costs of production and speed the development of virtually every product and technique that requires previous setting of parameters, since the simulation of properties, behaviors and efficiencies would eliminate the need for countless expensive prototypes that generally precede the solution itself.

According to Rozensweig (1985), the interdisciplinary study between fluid mechanics and electromagnetic fields can be divided into three main areas:

1. Electrohydrodynamics (EHD), which deals with the motion of electrically charged particles or molecules in a liquid medium;

2. Magnetohydrodynamics (MHD), which investigates the magnetic properties of electricity conducing fluids, and

3. Ferrohydrodynamics (FHD), which deals with the mechanics of fluid motion influenced by strong forces of magnetic polarization, on the magnetic fluids.

Whereas the two former fields have already had its characteristics and potential uses well established, investigation of the properties, the flow and the application possibilities of magnetic fluids is a very active research field (Odenbach,2004).

The most important magnetic fluids that arise with FHD are the colloidal suspensions of magnetic nanoparticles (diameters from 5 to 15 nm and volume fraction up to about 10%) that exhibit normal liquid behavior in the absence of magnetic fields but respond to imposed moderate magnetic fields by changing their viscosity without loss of fluidity. These are also called ferrofluids. The influence of external applied magnetic fields in the magnetorheological behavior of the ferrofluid enables it to be used in such diverse areas as medicine, electronics, acoustics, tribology, nanomotors, particle separation and thermal sciences. The magnetic susceptibility, or how much it tends to modify its structure when under a magnetic field gradient, depends not only on the ferrofluid composition and mass fraction but also on the size and shape of the particles, their crystalline structure, their orientation relative to the field and the intensity of the applied field (Usachev,1981).

Because the magnetic particles in such suspensions are so small, they do not form sediment under regular gravitational field or under moderate magnetic field gradients nor do they agglomerate due to magnetic dipole interaction. However, in experimental set ups and in commercial ferrofluids a surfactant is added to the system in order to prevent the nanoparticles from agglomeration due to the Van der Waals attraction forces. If the particles are not coated with a surface layer of surfactant of adequate thickness, they might form chains and clusters when put under magnetic gradients or discontinuities. If this phenomena, which is called correlation

phenomena, is not to be stopped, the nanoparticles may go under sedimentation and therefore lose its usefulness as sealant, printer ink and coolant, only to cite a few.

To simulate the effects of the surfactant layer on the surface of the nanoparticles the numerical models of repulsive forces can be used. In this work we utilize three models for repulsive force: a) a repulsive force based on a variation of the Screened Coulomb potential that has an exponential decay term; b) a repulsive force based on the classical Lennard-Jones potential and c) a repulsive force based on electrostatic repulsion that intents to simulate the behavior of the surfactant molecules.

Screened-Coulomb potential based repulsive force: The potential from which this force is derived is known as Debye-Huckel potenfial in plasma physics (Cao *et al*,2014). It has been widely used to simulate the interactions between charged particles, molecules or colloidal agglomerates, as well as in liquid metals (Zhang *et al*,2014). The reasons for its widely spread use in computational simulation of interactions between charged elements are mainly: a) its reasonably accurate results for interactions between charged particles, for it is basically a deformation of the classic Coulomb potential, b) the effective screening effect due to an exponential decay term that allows this potential to describe dilution effects on these charges and, finally, c) the low computational cost that comes from its implementation. Although free charge is often absent in ferrofluids, electric charge can be applied to the surface of the nanoparticles in order to reach stability against van der Waals short-range destabilizing attraction forces, thus this repulsive force may be useful in real synthesis.

Classic Lennard-Jones potential based repulsive force: The Lennard-Jones potential has the advantage of being very simple, having only two parameters and a relatively low computational cost. This potential describes correctly the behavior of two neutral atoms approaching each other. Due to its simplicity, it is often used as initial step to fitting experimental data, even when the approaching objects are not atoms nor neutral (Blaney & Ewing,1976).

Surfactant-like electrostatic repulsive force: Van der Waals attraction forces are very short-ranged, however, they can cause the destabilizing of a ferrofluid by promoting the agglomeration of the nanoparticles. In order not to let the particles touch each other, hence causing the van der Waals attraction force to prevail and cause agglomeration, long chain molecules are absorbed onto the surface of the nanoparticles. They exert short range steric hindrance and electrostatic repulsion, thus impeding the nanoparticles to attach to each other, which could led to clustering and sedimentation (Rinaldi *et al*,2005).

Fatty acids such as oleic acid can be used as surfactants. These kind of molecules have a polar head that is adsorbed onto the surface of the nanoparticle, physically or chemically, and a non-polar tail that interacts with the medium, and change the nature ot time changing in magnetic susceptibility. When choosing a molecule to act as surfactant two things must be taken in account: the nature of the surfactant molecule and the nature of the medium. It is appropriate that the non-polar tail of the surfactant be similar to the medium, hence hiding the the nanoparticle from the influence of the medium, acting like elastic bumpers.

2 METHODS AND GOVERNING EQUATIONS

This work presents a comparison between the computational models for three repulsive forces used in ferrofluid behavior simulating. A diluted colloidal monodisperse suspension of

permanently magnetized nanoparticles carried on a viscous, non-conducting liquid approach each other, impelled by magnetic attraction and are repelled due to simple hysterical hindrance and possibly by action of eletrostatic and surfactant effects. These three repulsive forces, namely the Screened-Coulomb potential-based repulsive force, the Lennard-Jones potential-based repulsive force and the repulsive force due to the action of surfactants are implemented and evaluated for their efficiency (their ability to prevent overlap), computational cost (the processing power required to perform the calculations, which can be estimated by the time required to complete them), numerical stability and suitability for several sets of non-dimensional parameters.

The ferrofluid is modelled by two spheres with equal radius with permanent magnetic momentum dipoles that have fixed spacial orientations. This model was used because the colloidal solution is monodisperse and very diluted (ϕ 5%, where ϕ represents the particle's volumetric fraction), thus the probability that three or more particles interact at the same time is very small. Moreover, it is considered that the particles cannot rotate around themselves, so their magnetic momentum dipole's orientation in space would not change. This is a wild simplification that can only be made because the main point of this work is comparing several repulsive force models instead of investigate in details the exact behavior of the particles in the ferrofluid. The non-dimensional approach was chosen for sake of generality, so this solution would be suitable for several sets of dimensional parameters. The time step used on this work is equal to 10^{-3}.

The behavior of the ferrofluid will be investigated using the fourth order Runge-Kutta method to solve the following governing equation:

$$
\begin{aligned}
m\frac{d\boldsymbol{v}}{dt} \;=\; & -6\pi\mu a\boldsymbol{v} \;+\; \sum \frac{3\mu_0 \mathrm{M}_i \mathrm{M}_j}{4\pi r_{ij}^4}[(\boldsymbol{d}_i \cdot \boldsymbol{d}_j)\boldsymbol{r}_{ij} \;+\; (\boldsymbol{d}_i \cdot \boldsymbol{r}_{ij})\boldsymbol{d}_j \;+ \\
& +\; (\boldsymbol{d}_j \cdot \boldsymbol{r}_{ij})\boldsymbol{d}_i \;-\; 5(\boldsymbol{d}_i \cdot \boldsymbol{r}_{ij})(\boldsymbol{d}_j \cdot \boldsymbol{r}_{ij})\boldsymbol{r}_{ij}]
\end{aligned}
\tag{1}
$$

This equation describes the movement of each particle in a diluted magnetic suspension, modeled by two particles approaching each other. It takes in account the magnetic force due to the magnetic interactions between the magnetic dipole moments of two particles. The following parameters are utilized: $\boldsymbol{v}^* = \frac{\boldsymbol{v}}{U_s}$, $t^* = \frac{tU_s}{a}$, $r_{ij}^* = \frac{r_{ij}}{a}$.

U_s represents here the Stokes velocity or the terminal velocity of the particle, $\frac{U_s}{a}$ represents the time the particle takes to undergo a distance that is equal to its radius at terminal velocity and r_{ij} is the distance between the centers of two particles. Thus, the following equivalence is observed:

$$
\frac{d\boldsymbol{v}}{dt} = \frac{U_s^2}{a}\frac{d\boldsymbol{v}^*}{dt^*}
$$

From this point on the asterisk mark will be removed for the sake of clarity. One can rewrite the Eq (1) as:

$$
\begin{aligned}
St\frac{d\boldsymbol{v}}{dt} \;=\; & -\boldsymbol{v} \;+\; \sum \psi_m \frac{1}{r_{ij}^4}[(\boldsymbol{d}_i \cdot \boldsymbol{d}_j)\boldsymbol{r}_{ij} \;+\; (\boldsymbol{d}_i \cdot \boldsymbol{r}_{ij})\boldsymbol{d}_j \;+ \\
& +\; (\boldsymbol{d}_j \cdot \boldsymbol{r}_{ij})\boldsymbol{d}_i \;-\; 5(\boldsymbol{d}_i \cdot \boldsymbol{r}_{ij})(\boldsymbol{d}_j \cdot \boldsymbol{r}_{ij})\boldsymbol{r}_{ij}]
\end{aligned}
\tag{2}
$$

One can also define a non-dimensional magnetic parameter, ψ_0, as:

$$\psi_m = \frac{\mathrm{M}_i \mathrm{M}_j \mu_0}{8\pi^2 a^5 U_s \mu} \tag{3}$$

And also the Stokes number:

$$St = \frac{mU_s}{6\pi\mu a^2} \tag{4}$$

The repulsive force can be modeled in the following ways:

Screened-Coulomb potential based repulsive force: $f_r = C_1 u_j e^{\frac{(\zeta - 2*a)}{C_2}}$, where u_j is the adimensional velocity of the particle *j*, defined as $u_j = \frac{v_j}{U_s}$ and ζ is the distance between the particle's centers at a given moment, C_1 is 1 and C_2 is 0.22. This model was used in the work of Gontijo and Cunha, (2015), and adaptations were made for the present work.

Lennard-Jones potential based repulsive force: $f_r = 4\Delta \left[\left(\frac{\sigma_{LJ}}{\zeta}\right)^{13} + \left(\frac{\sigma_{LJ}}{\zeta}\right)^7 \right]$ where σ_{LJ} and ϵ mean, respectively, the finite distance at which the interparticle's potential is zero and the depth of the Lennard-Jones potential well. σ_{LJ} is set as 1.76681995 and ϵ is 100. The Δ parameter can be defined as $\Delta = \frac{\sigma_{LJ}}{\pi m u a U_s \epsilon}$.

Surfactant-like electrostatic repulsive force model: $f_r = \varphi log \left(\frac{2a + 2\delta}{\zeta} \right)$, where φ can be defined as $\varphi = \frac{4k_b T \sigma_S a}{12\mu U_s \delta}$, k_b is the Boltzmann constant, T is the absolute temperature of the system, set as 298K, σ_S is the surface concentration of absorbed molecules of the surfactant and has the value of $\approx 10^{18}$, and δ is the thickness of the absorbed molecule, set as 5×10^{-10}. This model was used in the work of Liu *et al* (2010), and adaptations were made in this work.

3   RESULTS AND DISCUSSION

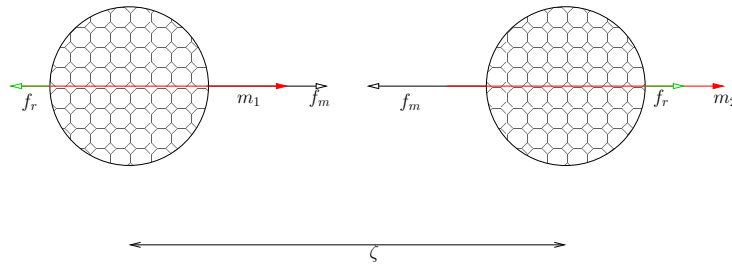The physical situation that is being modeled can be represented in the following way:

Figure 1: Schematic representation of the problem.

Where f_m is the magnetic force responsible for attracting the particles towards each other, f_r is the repulsive force that prevents the overlapping, m_j is the dipolar magnetic momentum of the particle *j* and ζ is the distance between the particles's centers.

The graphic below shows the behavior of the ferrofluid's particles when submitted to three different repulsive force models. As a particle with unitary radius was used in this simulation, it is possible to see that all the three models succesfully avoided particle overlapping. Henceforth, η represents the particle's position in a bidimensional plane.
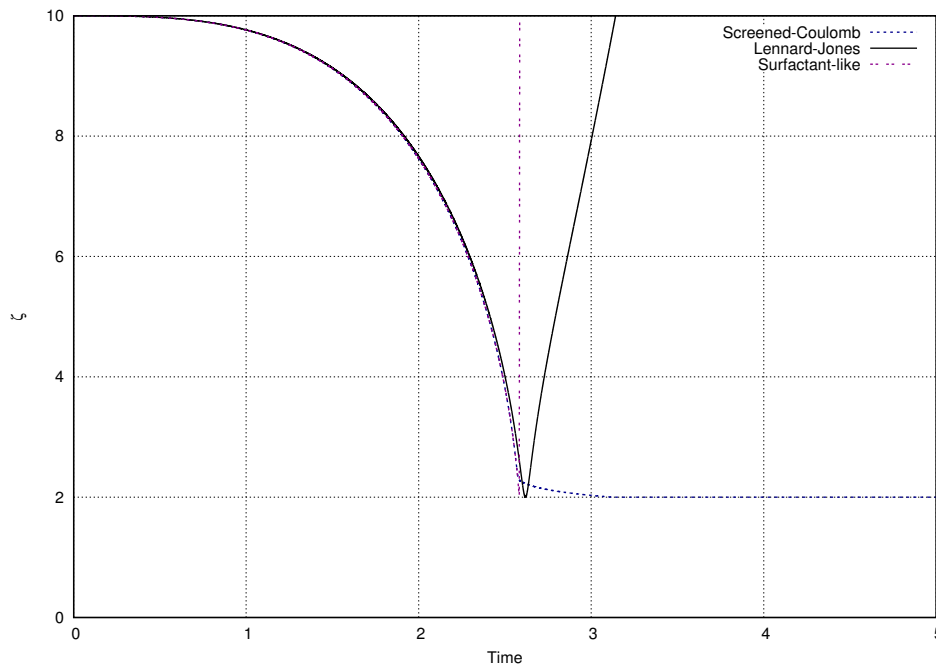

Figure 2: Distance between the particles' centers when submitted to three different repulsive force models.

As the processing time is an important variable in the simulation processes, it was also measured for the three models. This data is on Table 1 below, together with ζ_m, that is the minimal distance reached between the particle's centers, it is, the distance between them at the closest point of their trajectories. The CPU time considered here is the time necessary to process all iteractions of the simulation, in a Intel ® Core™ i7-2600 CPU @ 3.40GHz × 8, with memory of 3,8 GiB.

Table 1: Processing time and minimal distance reached between particle's centers for the three repulsive force models.

	CPU time (s)	ζ_m **(radius)**	**Time step**
Screened-Coulomb	$2.79999990.10^{-2}$	1.99999428	0.0001
Lennard-Jones	$2.79999990.10^{-2}$	1.99998188	0.0001
Surfactant-like	0.175999999	2.00253701	0.0001

The *Screened-Coulomb potential based repulsive force model* could be used when dimer or chain formation is desirable. This model offers a very smooth approaching and stabilizes the particles at a distance (Figure 3) that is determined by the C_1 and C_2 parameters.
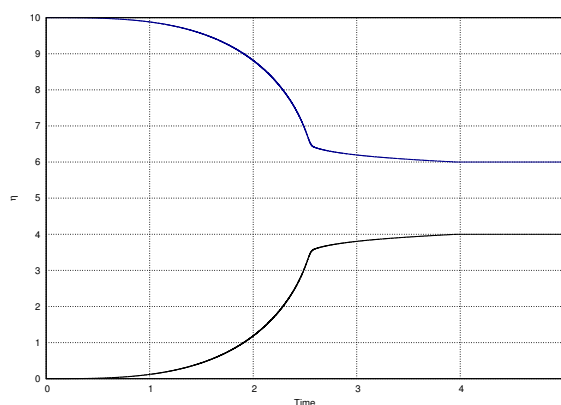
Figure 3: Particle approaching when submitted to Screened-Coulomb potential based repulsive force model.

The parameters might be adjusted appropriately (Fig. 4). When not considering the small flutuations at particle's positions around their equilibrium position, it could be said that the particles undergo an inelastic collision.
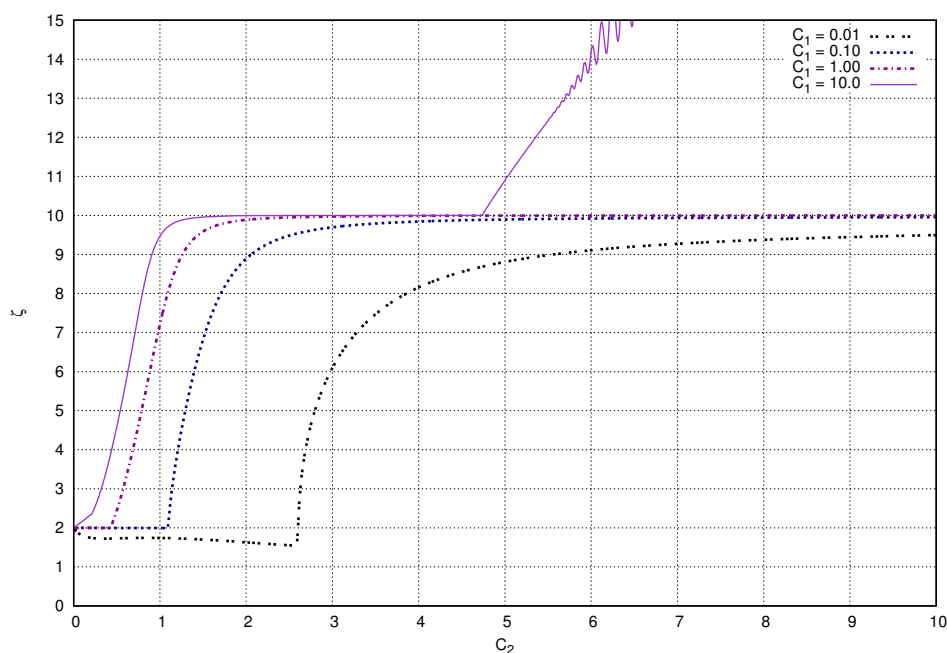

Figure 4: ζ **change with the parameters** C_1 **and** C_2**.**

The *surfactant-like electrostatic repulsive force model* causes the particles to approach and then suddenly separate, following different paths with velocities that are different between them and also different from the ones they had before colliding. This behavior is as that of a partially inellastic collision. Besides that, the particles do not touch each other, but remain separate by a small distance even in their trajectories' closest point. This small separation is determined by the lenght of the surfactant molecule's apolar tail, as well as the surface concentration of the surfactant onto the particles' surface. This model offers the possibility to model the effects of several experimental parameters such as temperature of the ferrofluid, surfactant concentration and surfactant molecule's lenght (therefore the surfactant type), so it might be used to optimize

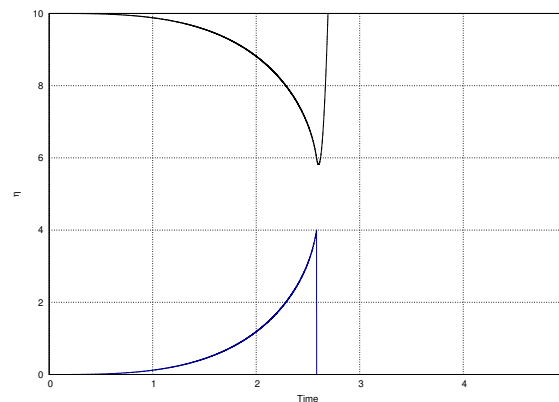experimental procedures, reducing, for example, the time and costs involved in experimental set-ups.

Figure 5: Particle approaching when submitted to surfactant-like repulsive force model

It could be possible to form dimmers and chains using this repulsive model, however, the time steps involved in order to physically capture the smoothness of the motion of two approaching particles would need to be very small time step of order 10^{-9}). Under this time step, the particles approach very slowly and have the time to, at the time of the collision, equilibrate the attractive and repulsive forces and form agglomerates.

The *Lennard-Jones potential based repulsive force model* causes the particles to collide and then separate, therefore it is suitable for modelling the situations when dimer formation is not desirable, as in most applications of ferrofluids. Moreover, the particles only touch each other at the moment of the collision and do not undergo deformation, which accounts for a perfectly ellastic colision.
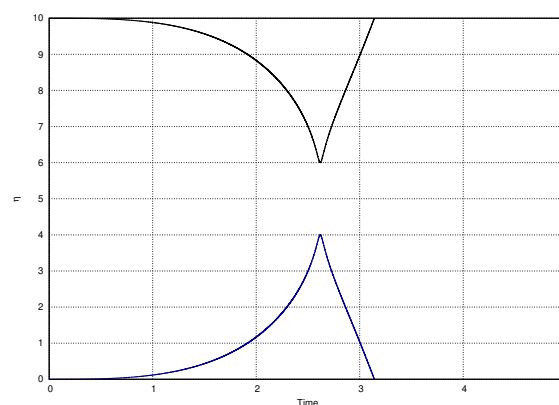

Figure 6: Particle approaching when submitted to Lennard-Jones potential based repulsive force model.

This fact is corroborated by Fig. 7, which shows that the particles have, after the collision, the same speed and opposite movement's directions.
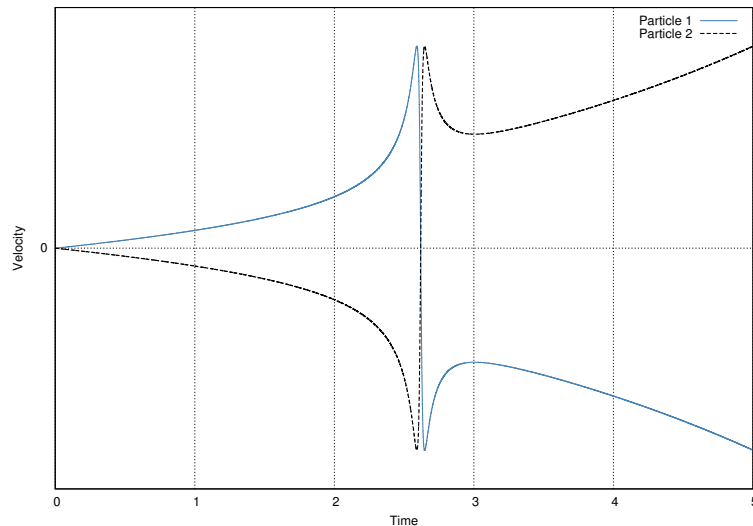
Figure 7: Particle's velocities change with time.

About this repulsive force model it is also interesting to note that there is an easily obtained potential energy associated with it (the Lennard-Jones potential). The Fig. 8 shows the Lennard-Jones potential changing with time. The potential energy decays when the particles aproach, reaching minimal value when they are in ζ_m. If the particles were to undergo a overlap, the potential enery would suddenly rise, showing that a closer approach would require a great amount of energy to take place. As the particles separate after the collision, the potential gradually rises and finally get stabilized at its equilibrium value, that can be interpreted as the potential value when both particles are at an infinite distance.
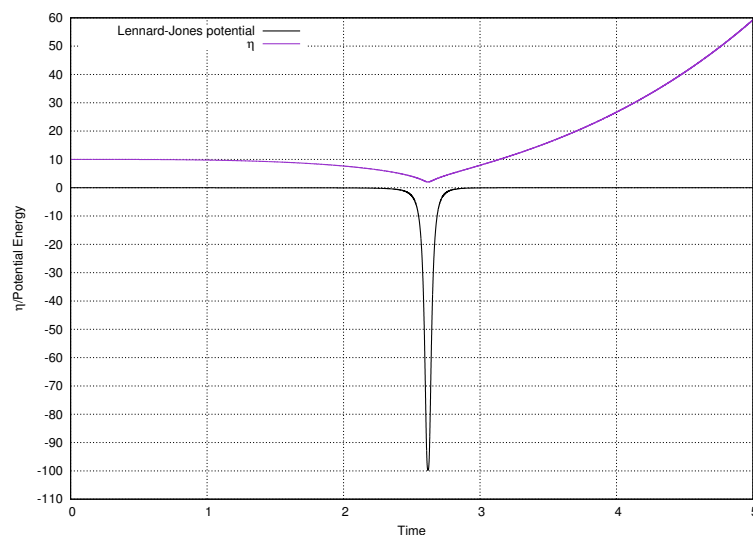

Figure 8: Lennard-Jones potential energy and particle's positions changing with time.

4   CONCLUSIONS

Although all the analyzed repulsive force models avoid significant overlaps, each has specific situations in which their use is more appropriate. The Lennard-Jones potential based repul-

sive force model might be used when dimer formation is not required: its computational cost is low and it causes the particles to have symmetrical velocities. The screened Coulomb potential based repulsive force model, on the other hand, causes the particles to smoothly approach and form a stable dimer with time steps as low as 10^{-3}, and could be used when this property is desired. The eletrostatic repulsive force model that emulates a molecular surfactant might as well form a dimer, but the time step required would make the computational cost too great and its use, therefore, non-viable. At low time steps, this model causes the particles to collide and separate, just as the Lennard-Jones potential based force model.

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