Simulation of DLVO theory

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1 Abstract

In this project the focus is on developing code that will simulate the behaviour or the DLVO theory, in order to observe the behaviour of agglomeration of suspended nano particles. This would be done by taking the values for the different constants of the equations of free surface energy of Van der Waals forces and dual layer forces, using the constant values of gold nano particles.

2 Introduction

The objective of this project is to simulate the behaviour of suspended particles acting under the DLVO theory. This theory consist on the effect that the double layer forces (DLF) and the Van der Waals forces have on the behaviour of the particles, where the DLF represents the repulsion forces, and the Van der Waals forces represent the attraction between the particles. Under the effects of these two forces, the nano particles collapse together to a minimum level of energy, where they become clumped with one another, causing for the particle size to increase, and nano particles to loose their properties on the quantum level.

There are different methods to prevent the agglomeration of nano particles. One of them is known as electromagnetic stabilization, and it consists of charging the nano particles with an electromagnetic charge, this in order to cause repulsion between them. The other popular method is known as steric stabilization, and it consists on creating an outer layer of polymer molecules around the nano particle, which have an electromagnetic interaction at a further distance than the energy minimum, where the particle would otherwise become stuck with another, preventing such scenario.

3 Background

3.1 DLVO theory

The DLVO theory is an explanation given to the behaviour of colloidal stability, developed during the 1940's by scientists Boris Derjaguin, Lev Landau, Everet Vervey, and Jan Overbeek, hence the innitials DLVO from their respective last

names. This theory explains the behaviour of aggregation between particles, whether the systems are of homogeneous particles of the same kind interacting together, or heterogeneous systems of different kinds of particles. [2]

The DLVO theory describes the free energy in the surface of the particles can be described by two contributions of the Van der Waals forces and the dual layer forces thus:

$$W(h) = W_{vdw}(h) + W_{dl}(h)$$

The Van der Waals forces are given by the effect of the poles of the molecule in question, and the force of this interaction is given by the value H, the Hamaker constant, which is usually positive, meaning that the Wan der Waals forces are usually that of atraction.

$$W_{vdw}(h) = -\frac{H}{12\pi h}$$

The double layer force depends on the charge of the surface of the particles interacting with one another, given by σ_+ and σ_- to each respective particle. ϵ_0 is the permittivity of vaccum and the ϵ is dielectric constant of water.

$$W_{dl}(h) = \frac{2\sigma_+\sigma_-}{\epsilon_0\epsilon k}$$

Both the attraction from the Van der Waals forces and the repulsion from the double layer work together to form the behaviour we can see in the figure 1.

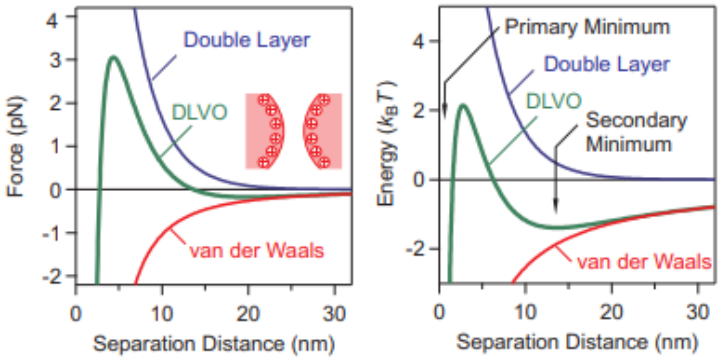

Figure 1: Visualisation of the change of energy and force to the distance

In the case of this simulation the particles will be homogeneous, thus, the particular phenomenon described by the DLVO theory will be that of homoaggregation.

3.2 Steric stabilization

Steric stabilization as a method of preventing aggregation is very common in the world of applied nanoscience. It consists on surrounding a nano particle with macromolecules (polymers) that prevent the interaction with the minimum aglomeration distance with the DLVO energy minimum. By having this additional interface between the nano particles the agglomeration is prevented and allows the colloidal solution to be stabilized and used in different applications with the full extent of the benefits on the nano scale of the particles. [3]

4 Related works

A similar worked was developed by our teacher E. Schaeffer [5] on the 9th assignment of the simulation course with the goal of studying the behaviour of charge and mass in the agglomeration of nano particles. This phenomenon was straight forward, making particles with opposite charges repulse each other, while particles with similar charges would attract each other, and particles with mass would tend towards attracting each other based on the Newtonian formula for gravity.

5 Proposed model

For this simulation, the model that will be used will be based on the repulsion and attraction of the DLVO theory, where the more complex formulas used earlier will be applied once more, by using approximated values, as well as values found in papers studying the colloidal behaviour of gold nano particles [4] visualized in figure 2.

6 Implementation of simulation

The full code used in this project can be found on the repository of the student E. Edgardjfc [1].

The code starts by defining the different functions that will be used to describe the behaviour of the DLVO effect. Using the formulas for the force affecting the particles.

7 Experiments

The experiment will consist on producing a simulation that will behave under the effects of repulsion and atraction of the DLVO theory. Over the duration of a 100 steps and producing 10 different particles within the system.

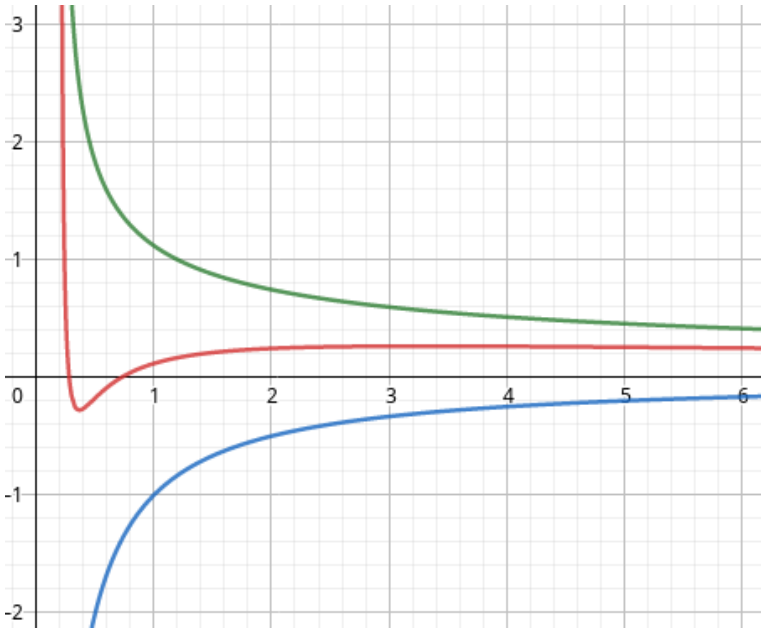

Figure 2: Aproximation of the DLVO theory

7.1 Design

By applying the following functions designed after the formulas for the force between particles.

```
def freeEnergyDL(h):
    return (2*sigma*sigma)/(consts.epsilon_0*dielectric*debyeLength)*exp(-debyeLength*h)

def freeEnergyVDW(h):
    return -(hamaker)/(12*pi*h*h)

def freeEnergy(h):
    return freeEnergyDL(h) + freeEnergyVDW(h)

def force(h):
    return pi*radius*freeEnergy(h)
```

The following function is in charge of calculating the force for each of the step in order to make a movement that is consistent with that of the formulas previously established

```
def forceStep(space):
    timeInterval = 3e-11 # time step; the force is assumed to be linear at steps of this le
    nextSpace = []
```

```
    for p1 in space:
        forceSumX, forceSumY = 0, 0
        for p2 in space:
            if p1 == p2:
                continue
            dist = p1.distance(p2)
            (dirx,diry) = ((p1.x-p2.x)/dist,(p1.y-p2.y)/dist)
            f = force(dist)
            forceSumX += f * (p1.x-p2.x) / dist
            forceSumY += f * (p1.y-p2.y) / dist
        #print("Force on {:s} is ({:e},{:e})".format(str(p1),forceSumX,forceSumY))
        dx = forceSumX * timeInterval*timeInterval / (2*mass)
        dy = forceSumY * timeInterval*timeInterval / (2*mass)
        ddist = sqrt(dx*dx+dy*dy)
        print("Particle {:s} moved by ({:e},{:e})".format(str(p1), dx, dy))
        nextSpace.append(Particle(p1.x-dx, p1.y-dy))
    return nextSpace
```

These last two functions are set in place to form the initial conditions of the simulation and to simulate the different steps within it.

```
def initial():
    return [Particle() for i in range(10)]

def simulate(steps):
    space = initial()
    for i in range(steps+1):
        print(i)
        if i % 10 == 0:
            plt.scatter([p.x for p in space], [p.y for p in space])
            plt.title("Step {:d}".format(i))
            plt.xlim(-0.1e-6,1.1e-6)
            plt.ylim(-0.1e-6,1.1e-6)
            plt.savefig("step{:d}.png".format(i))
            plt.close()
        space = forceStep(space)
```

7.2 Results

The results produced were the following figures 3-6. Where we can observe the development of the experiment over the 100 set steps.

7.3 Discussion

We could observe in the result section how there was a period of stability between steps 10 and 70, where the particles maintained their distance from one another, until finally collapsing and agglomerating with one another.

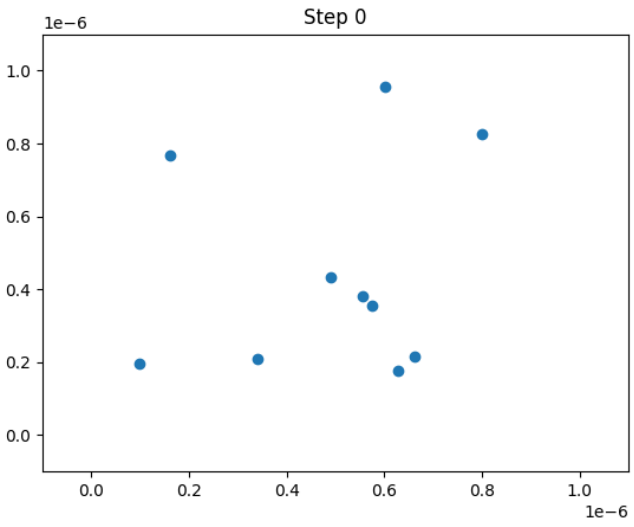

Figure 3: Initial condition of the simulation

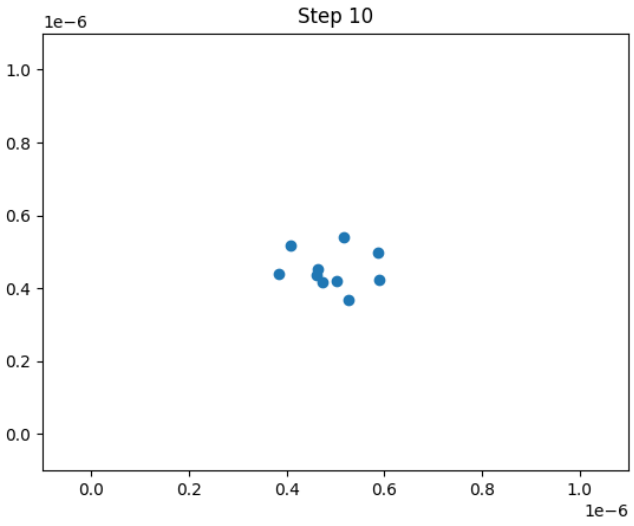

Figure 4: Initial condition trends towards agglomeration

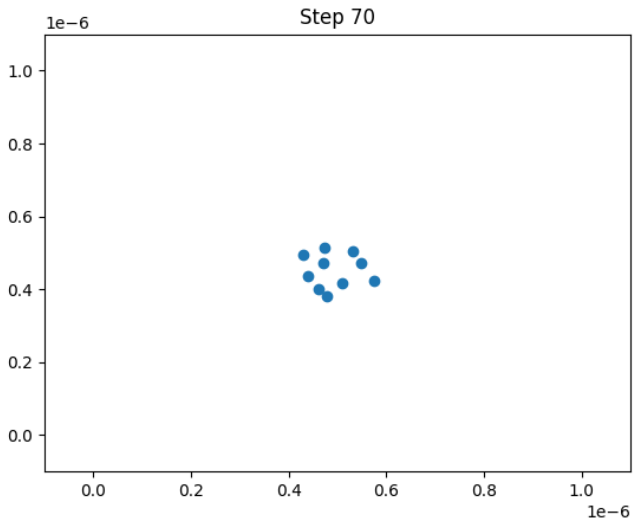

Figure 5: Repulsion force prevents them from fully agglomerating

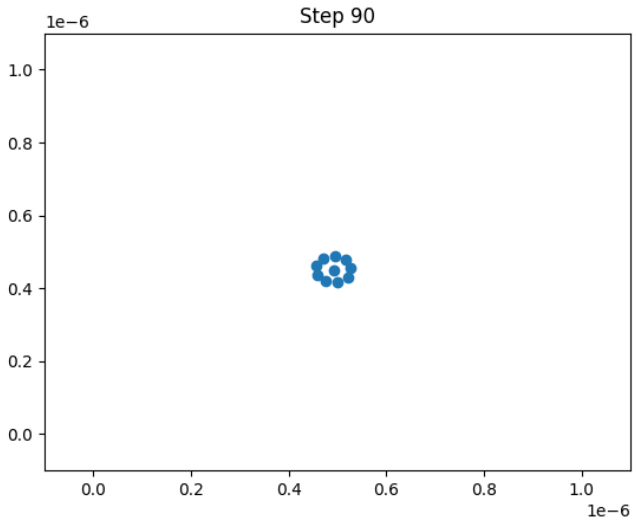

Figure 6: Particles reach the energy minimum

8 Conclusions

We proved the behaviour of the DLVO theory by applying the formulas of the theory into the simulation, and observed the expected behaviour within the experiment.

9 Future work

From this code we can further develop different possible methods for preventing the agglomeration, such as electromagnetic stabilization and steric stabilization. By developing a way to simulate the change of behavior on either scenario. For instance, an example for the steric stabilization being simulated could be by adding additional particles around the main particle, where these prevent the agglomeration.

References

[1] E. Edgardjfc. *GitHub,P11*. URL: https://github.com/edgardjfc/Simulacion-Nano-2022/tree/main/P12.

[2] M. Borkovec G. Trefalt. "Overview of DLVO Theory". In: (2014). DOI: https://archive-ouverte.unige.ch/unige:148595.

[3] D.H Napper. "Steric stabilization". In: *Journal of Colloid and Interface Science* 58.2 (1977), pp. 390–407. DOI: doi:10.1016/0021-9797(77)90150-3.

[4] Louis H. Haber Raju R. Kumal Tony E. Karam. "Determination of the Surface Charge Density of Colloidal Gold Nanoparticles Using Second Harmonic Generation". In: *The Journal of Physical Chemistry C* 119.28 (2015), pp. 16200–16207. DOI: https://doi.org/10.1021/acs.jpcc.5b00568.

[5] E. Schaeffer. *GitHub,Particles*. URL: https://github.com/satuelisa/Simulation/tree/master/Particles.