Hydrodynamic effects in self-assembly processes of superparamagnetic particles

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Abstract: In this paper we are going to discuss the self-assembly process of superparamagnetic micro-metric particles in a deterministic kinetic domain, where the magnetic interaction exceeds the thermal effects. First of all we are going to study the self-assembly process and the behavior of the particles and chains without taking into account the hydrodynamic interactions and at the end we will discuss and compare what happens if we consider the hydrodynamic interactions.

I. INTRODUCTION

Magnetophoresis is the motion of the magnetic particles in a viscous medium under the influence of an external magnetic field gradient. This motion is also determinated by self-assembly processes. Our main objective is to study the motion of the superparamagnetic micrometric particles under an intense external field, and the self-assembly process in the deterministic kinetic domain, where the magnetic interaction dominates over the thermal effects, and understand how the hydrodynamic interaction affects the self-assembly process.

A. Interactions

Before talking about the process of self-assembly we have to know what interactions rule the motion of the particles. The main interactions are the magnetic dipolar, thermal and hydrodynamic.

To describe superparamagnetic particles we use the Aligned MacroDipole model (AMD)[1]. First of all this model assumes that the colloid is spherical. The colloid is described like a dipole, so under an external field the colloid has a net magnetization in the direction of the field M(H). Then we can characterize the colloid with the magnetic dipolar moment m(H):

$$m(H) = \frac{\pi}{6} d^3 \chi H \tag{1}$$

where d is the colloid diameter, and χ is the magnetic susceptibility.

Two colloids with magnetic moment m have a magnetic interaction which depends on the angle θ between the direction of the magnetic field and the line that link the two colloids, and the distance of separation. The energy given by this kind of interaction can be repulsive or attractive depending on the angle.

$$U(r,\theta) = \frac{-\mu_0 m^2}{2\pi r^3}(1 - \frac{3}{2} sin^2(\theta)) \tag{2}$$

The formation of the structures depends also on the thermodynamics conditions.The thermal energy only depends on the temperature of the particles,and determine if the dipolar interaction is strong enough to maintain the particles together. In the next section we are going to discuss in detail how to compare these two interactions.

The hydrodynamic description can be complex, so we have introduced some simplification. We are going to work only with Newtonian fluids under incompressibility condition. With this type of system the Navier-Stokes equation become:

$$\rho \frac{\partial}{\partial t}\mathbf{u}(\mathbf{r},t) + \rho \mathbf{u}(\mathbf{r},t)\cdot\nabla\mathbf{u}(\mathbf{r},t) = \eta\nabla^2\mathbf{u}(\mathbf{r},t) - \nabla p(\mathbf{r},t) + \mathbf{f}_{ext} \tag{3}$$

Where ρ is the constant mass density of the fluid, $\mathbf{u}$ its velocity, η the viscosity of the fluid, p the pressure and $\mathbf{f}_{ext}$ the external force.
The Reynolds number is a dimensionless number that compares the viscous forces and the inertial ones, if we calculate it in our case we obtain:

$$Re = \frac{vL\rho}{\eta} \sim 1.6 \cdot 10^{-13} \tag{4}$$

We have obtained a Re$\ll$ 1, which indicates that the viscose forces are dominant, and produce a laminar flow, and this allows us to introduce the low Reynolds number approximation, and obtain the Creeping flow equations(5)[2], which derive from the Navier-Stokes equation. These equation are linear with $\mathbf{u}$, which we will uses later in the treatment.

$$\begin{aligned} \nabla p(\mathbf{r},t) - \eta\nabla^2\mathbf{u}(\mathbf{r},t) &= \mathbf{f}_{ext}(\mathbf{r}) \\ \nabla\mathbf{u}(\mathbf{r},t) &= 0 \end{aligned} \tag{5}$$

These two equations define the hydrodynamic flow generated by the motion of the magnetic particles. We can think that every particle moving in the fluid induces a flow field which propagates through the fluid and affects the particles surrounding the initial particle. The linearity property of the Creeping Equations(5), allows us to obtain new solutions with the superposition of solutions. Approximating our particles to point particles, the fluid flow $\mathbf{u}$(r), generated by a collection of particles solution

of Eq. (5) is given by [2]:

$$\mathbf{u}(\mathbf{r}) = \sum_{i=1}^{N} \mathbf{T}(\mathbf{r}\text{-}\mathbf{r}_i) \cdot \mathbf{F}_i$$

$$\mathbf{T}(\mathbf{r}) = \frac{\mathbf{G}(\mathbf{r})}{8\pi\eta} \quad with \quad \mathbf{G}(\mathbf{r}) = \frac{1}{r}\hat{\mathbf{I}} + \frac{\mathbf{rr}}{r^3} \tag{6}$$

Where $\mathbf{F}_i$ is the force acting on particle i and $\mathbf{G}(\mathbf{r})$ is the so-called Oseen tensor, which connects the point force at **r'** to a resulting fluid flow at **r**.
Once the fluid flow is known we can calculate the drag force made by the fluid on a particle i, $\mathbf{F}_{iH}$, which is given by:

$$\mathbf{F}_{iH} = -\gamma(\mathbf{v}_i - \mathbf{u}(\mathbf{r}_i)) \tag{7}$$

Where $\gamma = 3\pi\eta d$ is the drag on a particle of diameter d. There is also a third interaction that is the repulsive steric interaction, which prevents particles from overlapping.

B. Parameters

Now that we know the interactions which determine the motion of the particles we need to define the domain we are going to work on.
The formation of structures, as said before, does not only depend on the magnetic interaction, but also on the temperature of the system. To compare the thermal and magnetic energy, we use the parameter called: magnetic coupling parameter(τ). As we work at constant temperature, we also have to consider the entropy. In this conditions the self-assembly process not only depends on the magnetic coupling parameter, but also depends on the fraction of occupied volume(ϕ_0) [1].

$$\phi_0 = \frac{\pi}{6} d^3 n \tag{8}$$

$$\tau = \frac{\mu m^2}{2\phi d^3 k_B T} \tag{9}$$

To characterize the aggregation we can use the dimensionless aggregation parameter N* [1], which depends directly on τ, ϕ_0.

$$N^* = \sqrt{\phi_0 e^{\tau - 1}} \tag{10}$$

The parameter N* also allows us to determine when self-assembly is going to happen and which type of structures are going to appear. If the magnetic interaction is weaker than the thermal agitation, N*<1 (τ <1), the entropy wins and the self-assembly will not occur. Then we will have structures if N*>1. At values around N*>10, the magnetic interaction will be strong enough to unite chains of particles and create bundles. And at values N*$\gg$10 there will only be bundles[1].
As we have seen the kinetics of the particles is going to be described by the relation between the thermal agitation and the magnetic interaction. This allows to distinguish two domains, deterministic kinetic, in which the magnetic interaction dominate, and diffusive kinetic dominated by diffusion. In our case we will only work in the deterministic kinetics domain. In diffusive kinetics self-assembly processes due to the weak magnetic interaction, the destruction of structures may be possible, but in deterministic kinetics the interaction between the particles is strong enough to maintain the particles together.

C. Simulation

Using the simulation program which is written in C, and the Visual Molecular Dynamics(VMD) program allows us to visualize the motion of a system of particles under the conditions discussed in the previous sections.
The main program starts reading the initial position of each particle and the problem parameters. This is made by two python scripts: The initial condition script generate a random distribution of a determinate number of particles separated at least a distance d, inside the volume of an L side cube centered at the origin of coordinates. The main parameters to create the initial conditions are the system length(L), and the density (ρ). The second script is the one which gave the parameters to the main program, this parameters include the particles parameters, the fluid parameters and the field parameters. We have used typical parameters for the study of superparamegnetic micro-metric particles(viscosity of water, susceptibility, densities typical of this kind of particles, and a magnetic field of 0.1T).
Once it has the initial conditions and the parameters, it calculates the forces between particles(magnetic, and steric), and using the Eq.(6) of the fluid flow it calculates the hydrodynamic flow generated by all the particles. Knowing the interaction that affects the particles we solve the Newton equation using the Verlet algorithm(11)[3], which uses the position, velocity, and forces of each particle to solve the Newton equations:

$$\begin{aligned} \mathbf{r}_i(t+dt) &= \mathbf{r}_i(t) + dt\mathbf{v}_i(t) + \frac{dt^2}{2m}\mathbf{F}_i(t) \\ \mathbf{v}_i(t+dt) &= \frac{2m-\gamma_0 dt}{2m+\gamma_0 dt}\mathbf{v}_i(t) + \frac{dt}{2m+\gamma_0 dt}[\overline{\mathbf{F}}_i(t)\overline{\mathbf{F}}_i(t+dt)] \end{aligned} \tag{11}$$

Where t is the time, dt the time step, m the mass, γ_0 is the friction factor of the particle, and $\overline{\mathbf{F}}_i$ is the force component which does not depend on the velocity
The process of solving the Newton equation through the Verlet algorithm is repeated every time step dt, which gives us the position of each particle in that instant of time. Finally we convert the data obtained with the main program with a python scrip turning it to an "xyz trajectory", which the VMD can read easily .
We have modified the initial program including periodic boundary conditions[4] to simulate a real system. Our volume with N particles represents the main cell of the

system formed by an infinite lattice of identical cells. So with this conditions we limit our particles movement in the 3D cube with a determinate length, but we can obtain the motion given by an infinite system of identical cells. As our system is dominated by short-ranged interactions we ignore the interactions with the particles at large distance using a cutoff r_c, which with periodic boundary conditions has to be less than L/2, where L is the system length scale. With this we also reduce the execution time.
To analyze the results we have developed a python script capable of characterizing the chain distribution. This means that we can know the quantity of chains and their length at any time in the simulation allowing us to obtain a more exhaustive analysis.

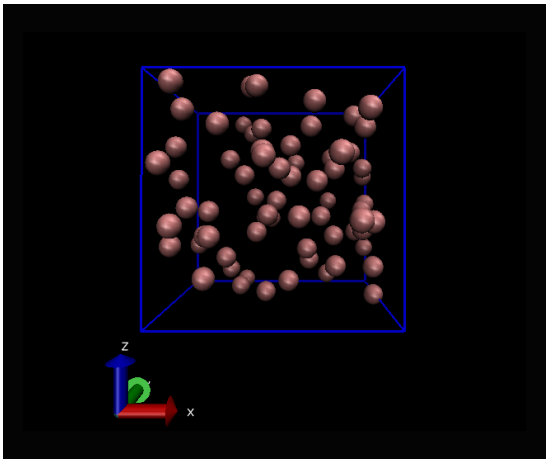

FIG. 1: Snapshot of the initial state of a simulation of a $7{\cdot}10^{-2}$ part/μm^3 system.

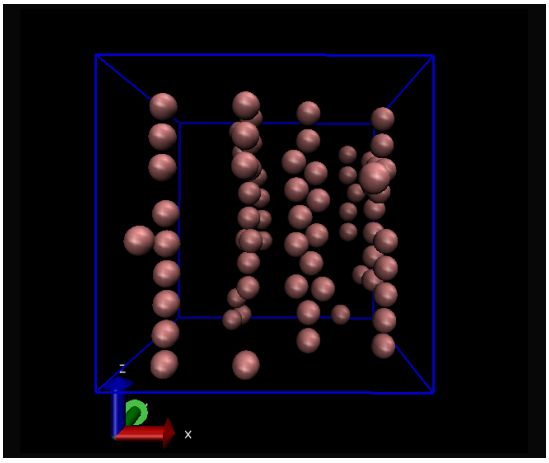

FIG. 2: Snapshot of the $7{\cdot}10^{-2}$ part/μm^3 system after a 10^7 step simulation.

II. COMPUTER SIMULATIONS

A. Aggregation without hydrodynamic interactions

To study and understand the behavior of the particles and the self-assembly process under the deterministic kinetic domain, first of all we are going to analyze different systems without taking into account the hydrodynamic interactions. And after knowing the behavior and how the self-assembly processes occurs we are going to compare the first results with the results applying the hydrodynamic interactions.

Before talking about the simulation we have to talk about the initial conditions and the parameters of the problem. We have used densities between 10^{-2} and 10^{-1} part/μm^3, and a constant system length of L=20μm, which produce systems with a range of particles between 10 to 100. The initial velocity of the particles is fixed at 0.

The number of steps is a crucial parameter to consider. A 10^{-2}part/μm^3 system with a 10^7 simulation steps is going to run an order of ten minutes, but the simulation time has a quadratic dependence on the number of particles, so increasing the number of the particles is going to increase the time simulation an order of n^2.

First we study the aggregation of paramagnetic particles in absence of hydrodynamic interactions. In this case, we do not consider the effect of the motion of the particles on fluid flow given by Eq. (6). The results obtained show us the behavior that we expected. The velocity of the dynamics of the self-assembly process decrease with the formation of larger chains, because of the increase in the distance between them. As we do not consider the thermal effects, the system can not reach the equilibrium, what implies that in a very long time limit we should expect to get an unique chain with all the particles in it.

Figures 1 and 2 represent the initial conditions and the 20% state of a simulation with a density $7{\cdot}10^{-2}$ part/μm^3, a system length of 20μm, and $5{\cdot}10^7$ simulation steps without hydrodynamic interactions. In the first figure the particles have a random distribution over all the space, and in the second figure most of the particles are joined together in larger chains. Due to the magnetic field direction the self-assembly process only occurs in the z-direction. In figure 2 there are a few chains being formed by two or more particles, and in the center a bundle is starting to form. The interaction of the other particles is not strong enough to gather it together and create more larger chains in the simulation time.

In table 1 we have represented the results of six simulations with different particle densities after 10^7 simulation steps with a system without considering hydrodynamic interactions.

The number of chains with more than two particles and the length of these chains increase with the density. At low densities the number of chains larger than two particles increase a lot between the different densities, but in larger densities the this number doesn't change a lot or does not even change. This is because in the larger systems first of all chains with few particles are created, and with the time these chains join, and create

TABLE I: Number of chains with more than one particle and distribution of chain length for systems of different particle densities after $1{\cdot}10^7$.

Density(10^{-2}part/μm^3)	**Chains(n>1)**	**Chains Length**						
		2	**3**	**4**	**5**	**6**	**7**	**8**	**9**
1.0	1	1	0	0	0	0	0	0	0
2.0	2	1	1	0	0	0	0	0	0
3.0	5	4	1	0	0	0	0	0	0
4.0	11	6	3	1	1	0	0	0	0
5.0	13	8	3	1	0	0	1	0	0
6.0	13	6	3	2	1	1	0	0	0

larger chains. We are going to study the evolution of the systems more in detail later, and this will be clear.

We have to keep in mind that the results of this simulations depend on the initial conditions of the system, the initial distribution of the particles affect the results, so table 1 reflects only and example of how the self-assembly process work, to obtain better results we have to do statistics using several realizations of the same simulation.

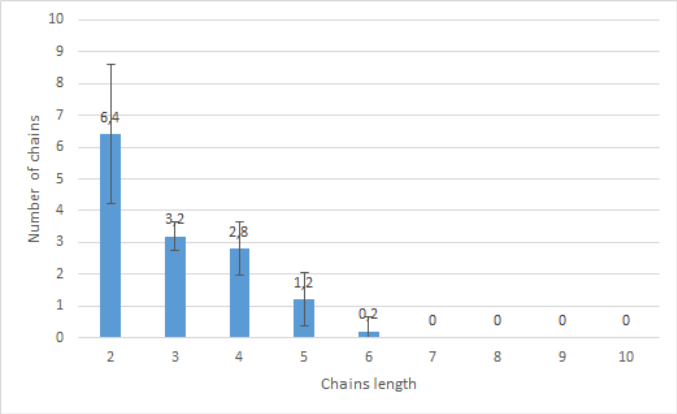

FIG. 3: Histogram representing the average number of chains of each length $1.25{\cdot}10^7$ steps, of a $7{\cdot}10^{-2}$ part/μm^3 system.

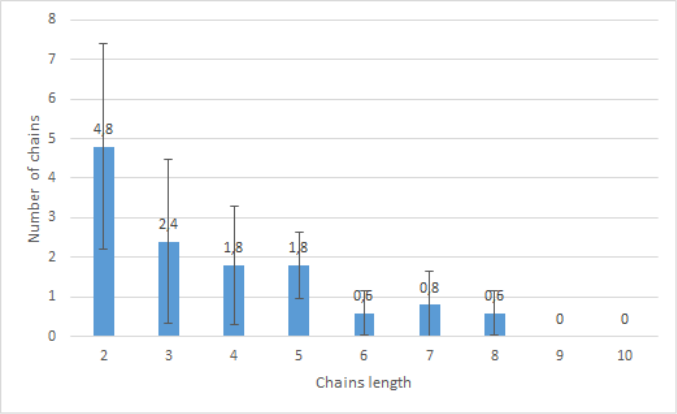

FIG. 4: Histogram representing the average number of chains of each length $5{\cdot}10^7$ steps of a $7{\cdot}10^{-2}$ part/μm^3 system.

In figures 3 and 4, we have represented the number of chains with two or more particles, with a particular length in the same system, in a different state of the simulation. The first one is a representation of the chains with two or more particles created in the system on the 25% state of the total steps in the simulation, and the second one is the final state. The simulation corresponds to an average of five systems with $2.5{\cdot}10^{-2}$ part/μm^3, after $5{\cdot}10^7$ simulation steps.

In the early state the histogram is concentrated in the left side, chains between 2 and 4 particles predominate, but the largest chain is made of six particles. In the second one there is flatter distribution with larger chains, and the largest is made of eight. So we can observe that through the simulation the number of chains with two or more particles have grown, by the union of two chains,

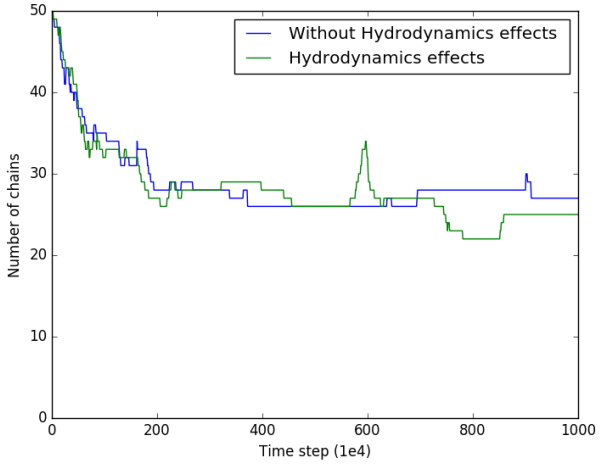

FIG. 5: Dependence of the number of chains on simulated time in a system with $5{\cdot}10^{-2}$ part/μm^3

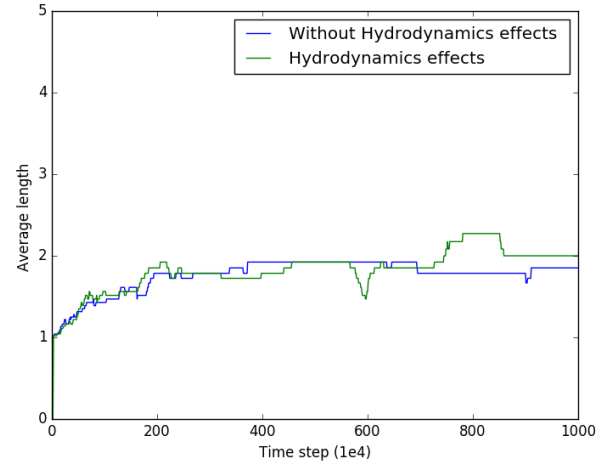

FIG. 6: Dependence of the average length of the chains on simulated time in a system with $5{\cdot}10^{-2}$ part/μm^3

either by the union of a single particle chain with another chain or by the union of two larger chains. The big number of chains with a two particles length indicate that this system could continue to evolve to a system with larger chains.

B. Effect of hydrodynamics in the aggregation process

In order to compare the simulation with and without the hydrodynamic interactions , we are going to use the figures 5 and 6, in which we can see the evolution of two systems with the same initial conditions but the second one takes into account the hydrodynamic effects. This implies solving the equations of motion considering the effect that the motion of the particles have on the fluid flow using Eq.(6).

First of all in a general context, the two behaviors are really similar. In figure 5 the number of chains decrease really fast at the first steps, then the number of chains fluctuates up and down while decrease a little and at the end is apparently stable. In the second figure the behavior is more o less the same. These graphs prove the behavior previously commented, in the first stages of the simulation we have a lot of chains with a fewer particles each one, and through the time the number of chains decrease less or even increase a few, but the chain length increase.

The fluctuations in the two figures can be explained with the union of a single particle chain in a larger chain already formed. When a particle is joining between two particles the interaction between the three of them make the two particles of the chain move in such a way that the third can get between them, this movement breaks momentarily the chain allowing the particle to stand between them and finally be part of the chain. In this process the analysis program does not count the initial chain and the particle as one, it counts as two shorter chains, and this produces a decrease in the average length and an increase of the number of chains.

In the first stages the behavior is really similar between the cases with and without hydrodynamic interactions as we said, but it is not totally the same, this indicates that the self-assembly process is affected by hydrodynamic interactions. In the later stages the hydrodynamic behavior is not stable as the other. But due to the decrease of the speed of the dynamics in the final stages both of them are more stable than in the initial stages.

III. CONCLUSION

To conclude with, we have proven that the self-assembly process of superparamagnetic particles happen under a deterministic kinetic domain, where the magnetic interaction exceeds the thermal effects. And we have been able to analyze and discuss the results.

The self-assembly process depends on the initial conditions of the particles, the density and the system length. As we have seen in the lowest densities systems we obtain a few chains made by two or more particles. As we increase the density, the number of chains decrease and the average length of chains increase, if we continue to increase the density there will be a point where the number of chains will not decrease or even increase but the chains length will increase due to the union of larger chains. We have to keep in mind that these study results have been obtained without taking into account the thermal effects.

Finally we have proven that the hydrodynamic effects weakly affect the behavior of the particles in the self-assembly process, but the self-assembly process will still happen. To understand better the effect of hydrodynamics we would have to do a more exhaustive study, which implies larger simulations, larger systems and larger number of simulations that would allow us to extract better results with good statistics.

Acknowledgments

I would like to thank my advisor Carles Calero for the advice and support through the long work done, that without his guidance would have been not possible. My colleagues for their encouragement, and finally to my family for their support and help over the years.

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