Dynamics of Magnetic Colloid Aggregation Under Magnetic Fields

Author: Albert Ortega Bartolomé.
*Facultat de Física, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain.**

Advisor: Carlos Calero Borrallo

Abstract: Colloid self-assembly processes are quite difficult to predict; in spite of that, because of its relevance in material science such as building complex materials, it is an important subject of study. In this work the superparamagnetic colloid (SPC) self-assembly process in 2D under magnetic fields was studied using brownian dynamics simulations. The dynamics and the equilibrium states properties were studied for different concentrations and magnetic field conditions. Chains where formed for low magnetic field values (for every density studied) and bundles of chains appeared when magnetic field increased for higher densities. In both cases equilibrium was reached.

I. INTRODUCTION

Colloidal self-assembly is a relevant alternative to chemical synthesis route and an important factor in fabrication techniques for building increasingly complex structures and materials [1]. Studying the behaviour of these particles may help to clarify crystallisation and phase transition mechanisms because, thanks to their mesoscopic size, their dynamics are slowed down sharply in comparison with atomic systems, making its study much more accessible and efficient.

Among the variety of strategies for guided assembly of colloidal matter, magnetic-field induced assembly represents a unique route due to the instantaneous and anisotropic nature of magnetic interactions [1]. This assembly process occurs mostly due to dipole-dipole interactions (which can be either attractive or repulsive). In addition, the strong response to an external magnetic field makes aggregation a fast process. Furthermore, their interaction is at a distance, implying independence of changes in experimental conditions. Finally, magnetic fields can be easily created and manipulated. Moreover, being easily torqued by an external field and the corresponding orientation being visualized by simple optical techniques is one of the main reasons that encourage the study of colloid assembly. These properties can be employed in several applications [4–6, 10], where anisotropic magnetic particles are used as force sensors, microstirrers, active components in constrained geometries, micro-rheological probes or externally actuated micropropellers. Moreover there is a special interest in the medical field where different techniques use magnetic colloids in diagnosis and medical imaging. In addition, assembling colloids into 1D chains, 2D arrays and 3D superlattices continues to be one of the grand goals in colloid and nanomaterial science owing to the inspiring properties found in their microscale and macroscale assemblies [10].

Specifically, colloids treated in this study are superparamagnets. The main attribute of superparamagnetic materials is having an exceptionally strong response to applied magnetic fields. Moreover, superparamagnets do not present magnetic hysteresis and, in the absence of external field, their magnetization is zero (they do not have remnant magnetization) [2]. Such colloids are particles of typical size in the range $50\,nm$ to $2\,\mu m$.

The aim of this work is to study with numerical simulations the aggregation and the equilibrium state of a set of N SPCs randomly distributed on a plane with certain density under static magnetic fields applied in the plane. Since the field is only applied on the plane, we expect SPCs to form chain or bundle structures along the field direction. The objective is to observe in what conditions the equilibrium is reached, what properties do the formed structures have and under what conditions chains or bundles appear. The study was done with Brownian dynamics simulations, which could be used since SPC have micrometric size and therefore their dynamics is overdamped ($Re \ll 1$) and thermal agitation is important.

II. METHODS

A. Model

The superparamagnetic colloids are described as spherical particles which interact through finite volume (aka steric) interactions and magnetic interactions. To evaluate colloidal magnetic interactions it is mandatory to know the value of the magnetic moment $\vec{m}$ of each colloid. We can consider that $\vec{m}$ can be obtained from:

$$\vec{m}_i = \chi V(H_{ext} + H_{dip}) = \chi V\left(H_{ext} + \sum_{j\neq i} H_{dip}^{(j)}(r_i)\right) \tag{1}$$

Here χ is the volume magnetic susceptibility of the paramagnetic particle, $V = \pi\sigma^3/6$ its volume where σ represents the diameter of the SPC, and H_{ext} and H_{dip} the external field and the dipolar field caused by the other

*Electronic address: aortegba9@alumnes.ub.edu

magnetic particles. Note that Eq. 1 is an implicit equation, since H_{dip} depends on the value of the magnetic moments $\{m_i\}$. In order to solve it, it will be necessary to use an iterative procedure. Then, starting from a magnetic moment of a SPC under an external field $H_{ext} = H_0$ that can be expressed as $m_0 = \chi V H_0$ we can obtain a first approximation by inserting m_0 into Eq. 1 which also depends on m. Once this new m is obtained we could simply replace it in Eq. 1 to have a better approximation an so on. In this work, the iteration stops at the first approximation. Notice that near neighbours effect is considered in the dipole-dipole interaction. In this approximation, the magnetic moment is then given by:

$$\vec{m_i} \approx \vec{m_i}^{(0)} + \vec{m_i}^{(1)} = \chi \frac{\pi\sigma^3}{6} H_0 \times \\ \times \left[\left(1 - \frac{\sigma^3 \chi \mu_0}{24} \sum_{j \neq i} \frac{1}{r_{ij}^3} \right) \hat{h} + \frac{\sigma^3 \chi \mu_0}{8} \left(\sum_{j \neq i} \frac{\hat{h} \cdot \hat{r}}{r_{ij}^3} \hat{r} \right) \right] \tag{2}$$

In Eq. 2 $\hat{h}$ is the direction of the applied field, $r_{ij} = |\vec{r_i} - \vec{r_j}|$, $\hat{r} = (\vec{r_i} - \vec{r_j})/r_{ij}$ and μ_0 is the permeability of vacuum. As previously stated, the magnetic moment in Eq. 2 gives the necessary information to determine the dipolar magnetic force on each particle due to the other colloids, $\vec{F}_i^{(m)}$. On the other hand, we use the WCA potential ($\mathcal{U}_0(r)$) [11] to generate the steric force ($\vec{F}_i^{(r)}$). $\mathcal{U}_0(r)$ is similar to the Lennard-Jones potential, being $\mathcal{U}_0(r) = 0$ for $r > 2^{1/6}\sigma$ and:

$$\mathcal{U}_0 = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] + \epsilon, \qquad \text{for} \quad r < 2^{1/6}\sigma \tag{3}$$

Here ϵ is a characteristic energy and its order is of $K_B T$ (specifically $\epsilon = 10 k_B T$ was used). This potential grants that no overlapping occurs. The dynamics of the problem is that of a forced Brownian motion in a 2D plane with a diffusion constant D_t. The equation that needs to be solved is:

$$\frac{d\vec{r}_i(t)}{dt} = \beta D_t (\vec{F}_i^{(r)} + \vec{F}_i^{(m)}) + \sqrt{2D_t}\vec{\xi}_i(t) \tag{4}$$

Here, $\beta = 1/K_B T$ and the last term is a random force which takes into account thermal noise, computed with $\vec{\xi}_i(t)$ which takes the form of a Gaussian random noise. To solve the dynamics it is convenient to write Eq. 4 in a dimensionless form. Then we define $T = \sigma^2/D_t$ as a temporal unit and $L = \sigma$ as a length unit. Defining $\vec{x} = \vec{r}/L$ i $\tau = t/T$ we can rewrite (4) as:

$$\frac{d\vec{x}(\tau)}{d\tau} = \beta\epsilon \vec{f}_i^{(r)} + \beta\sigma f_m \vec{f}_i^{(m)} + \sqrt{2}\vec{\xi}_i(\tau) \tag{5}$$

Where the relations $\vec{F}_i^{(r)} = \frac{\epsilon}{\sigma}\vec{f}_i^{(r)}$ and $\vec{F}_i^{(m)} = f_m \vec{f}_i^{(m)}$ have been used. Now (5) is written as a function of the following dimensionless parameters:

$$\varepsilon = \beta\epsilon, \qquad \Gamma = \beta\sigma f_m = \frac{4\pi\chi^2\mu_r}{3}\mu_0 H_0^2 \sigma^3 \beta \tag{6}$$

These parameters are defined as the energy and magnetic parameters, respectively and govern the dynamics of the problem.

B. Analysis

The dynamics of the system are integrated numerically using an in house *Fortran* program which numerically solves Eq. 5 with a discrete time of $dt = 10^{-4}\tau$. At each time step all stated interactions are being evaluated plus the random noise is generated using the Marsaglia polar method [12]. Then Euler's algorithm is used to advance to the next time step. This process is iteratively repeated until the final time of integration t_{fin} is reached.

The particle system is initialized in a random configuration in the XY plane in accordance with the desired number of particles (N) and the desired density and magnetic parameter in Eq. 6 while the energy parameter is maintained fixed at a value of 10. Moreover, the program used Periodic Boundary Conditions (PBC) so if a particle was to exit the "box" from one side, it would appear in the opposite end of the simulation box.

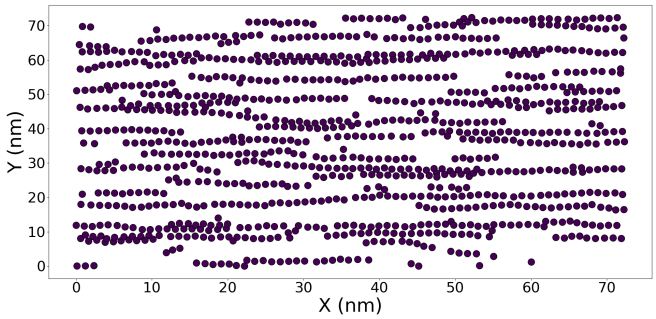

FIG. 1: Snapshot of a simulation of a system with $\Phi = 0.22$ and $\Gamma = 18.5$. Chains and bundles can be spotted.

The output returned by the simulation code consists of a trajectory file which contained the positions of every colloid whenever a time step iteration (snapshot) finished and could be visualized graphically. In Fig. 1 we can observe a snapshot of the simulation where colloids form aggregates in the shape of chains.

To analyze the trajectory a *Python* program was used. This program should be able to identify all the aggregates that appear for every snapshot using a certain criteria of distance between particles that was set after manually analysing some snapshots where chains were formed. In this process it is mandatory to have extreme care with

PBC since they can widely modify the results obtained. We can see different aggregates in Fig. 2.

The output returned by the program is a distribution of the different sizes of the aggregates and the average aggregate size $\langle n \rangle$ for every snapshot. This information allows us to follow the dynamics of the system on the basis of the initial random configuration and to identify when the equilibrium state is reached.

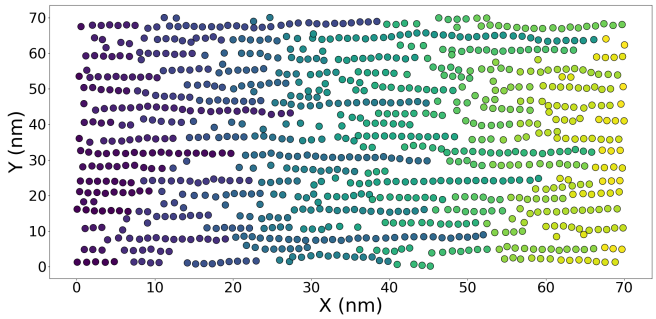

FIG. 2: In this frame of a system with $\Phi = 0.16$ and $\Gamma = 18.5$ we can see that the analysis program has identified 224 different bundles (represented in different colors).

III. DISCUSSION

To identify the different structures reached in equilibrium we represent in Fig. 3 a phase diagram where the average number of colloids per aggregate $\langle n \rangle$ is plotted as a function of the density (Φ) and magnetic (Γ) parameters. The phase diagram is divided in two zones by a red line. This line was plotted using from each density the $\langle n \rangle$ where bundle structures started forming.

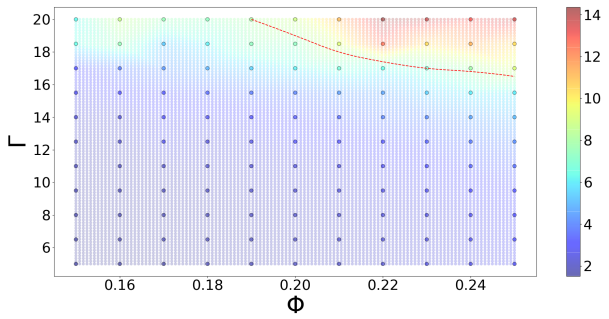

FIG. 3: Phase diagram obtained as a function of magnetic parameter Γ and density Φ for systems of N=100 particles. Interpolation points have been shaded. The color-bar shows the average particles per chain ($\langle n \rangle$) for every system. A red-dashed line marks the systems from which bundle formation appears.

Observing the phase diagram we notice that, at low values of Γ, we obtain low values for the average of particles per bundle. However, maintaining a fixed value of Γ, $\langle n \rangle$ increases with the density. Moreover, as Γ grows higher, density becomes more relevant and the difference with $\langle n \rangle$ becomes significant. In addition, we can observe that at low Γ values thermal agitation is dominant against dipolar magnetic interaction and not even chains get formed.

On the one hand, observing the different simulations of magnetic colloids departing from random initial configurations, we notice that a stationary state is reached. In this state chains are being formed and destroyed dynamically and the $\langle n \rangle$ oscillates about a fixed value, which might indicate an equilibrium state. On the other hand at high values of Γ and Φ, we can distinguish some chains that stick together in what seems a different dynamical structure (bundles). Therefore, there are two kind of self-assembled structures that may be studied: chains and bundles.

A. Chains

First of all systems with chain formation were studied. The aim of this section is to find if there is any stability at all (if the system reaches equilibrium) and to see how it evolves with time.

First we studied the $\langle n \rangle$ stability for different systems that evolve into an equilibrium state with chain formation. In order to do so, multiple simulations with a thousand particles were performed. A representative example starting from a random distribution (therefore with $\langle n \rangle = 1$) is shown in Fig. 4. It is noticeable that $\langle n \rangle$ grows higher monotonously until it reaches a plateau where it oscillates around a stable value.

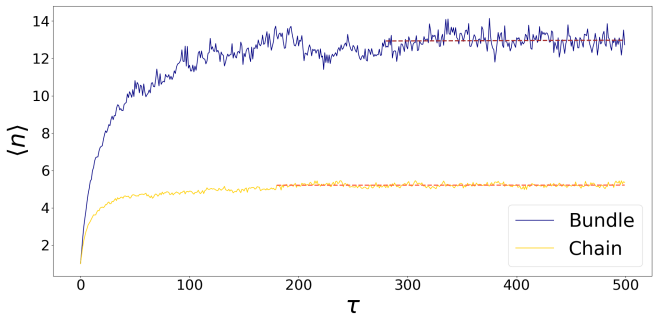

FIG. 4: Mean plot of the average number of particles per aggregate versus time for a system with $\Phi = 0.16$ i $\Gamma = 18.5$ (Chain, in yellow) and a system of with $\Phi = 0.23$ i $\Gamma = 18.0$ (Bundle, in blue) obtained from 10 simulations each. Regression lines are represented which interception values indicates the stability values of the systems and have slopes compatible with 0 within the statistical error.

In Fig. 4 we can distinguish a regime where equilibrium has been reached. Furthermore, we can see that equilibrium has been reached in a time around $\tau_{eq} = 180$ which means that it is $t_{eq} = 180 \cdot \sigma^2 / D_t \; s$. Here we can do a estimation for a colloid of typical size $\sigma = 1 \mu m$ using the Stokes-Einstein formula for the diffusion coef-

ficient for an spherical particle $D_t = k_B T/(3\pi\eta\sigma)$, where $\eta \approx 0.001 Pa \cdot s$ is the viscosity of water and we assume a temperature $T = 300K$. Then, we obtain $t_{eq} \approx 40.91\ s$.

It is also of interest the equilibrium distribution of probability for a chain to be formed of n particles using the snapshots where the $\langle n \rangle$ fluctuates around a fixed value, see Fig. 4).

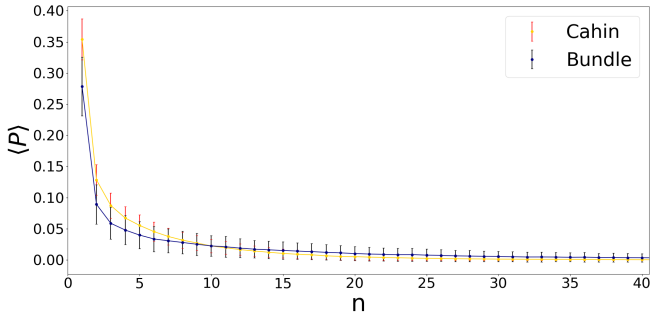

FIG. 5: Average probability $\langle P \rangle$ of finding a chain of a certain length (n) in equilibrium for a system with $\Phi = 0.16$ i $\Gamma = 18.5$ (Chain, in yellow) and a system of with $\Phi = 0.23$ i $\Gamma = 18.0$ (Bundle, in blue) obtained from 10 simulations each.

In *Fig. 5* the probability of finding a chain of length n in equilibrium is plotted against n for a representative case where chains are formed. The average value of particles per chain in equilibrium is marked in yellow. The average probability of finding a chain of length n in equilibrium is marked with a larger point and its standard error is plotted. We can see that P decreases as n increases monotonically. The probability of finding a non aggregated particle in equilibrium is pretty high.

B. Bundle

Now we will consider those cases where two or more chains stick together an become a single aggregate this happens only when we have high values of Γ and Φ (as marked in Fig. 3). As we can see in Fig. 10 in [2], when chains have a certain number of colloids, it is energetically favorable to form bundle structures instead of longer chains. For these cases, we see that chains prefer to aggregate in zip formation instead of in parallel.

(a) *Zip.* **(b)** *In parallel.*

FIG. 6

This is because zip aggregation is energetically more favorable. If we consider that the dipole field is negligible (since its much weaker than the external field) the main contribution to the total energy is the dipole-dipole pair interaction[9]. Taking into account that colloids have approximately the same magnetic moment, then we can rewrite the dipole-dipole energy between two particles for the whole bundle as a function of the angle θ between the magnetization and the distance between particles $\hat{r}$ as:

$$E_{bundle} = -\frac{\mu_0 |m|^2}{4\pi} \sum_{ij} \frac{3cos^2(\theta_{ij}) - 1}{|r_{ij}|^3}; \qquad (7)$$

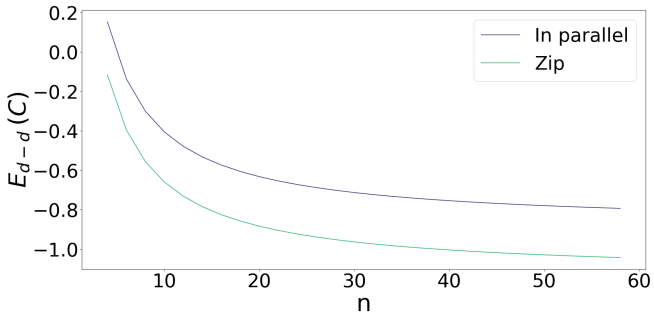

FIG. 7: Energy for a particle in a system where two chains (both of size n) are in parallel E_p or in zip E_z. The result is expressed in function of $C = \frac{\mu_0 |m|^2}{4\pi}$ (in Eq. 7).

To calculate Eq. 7 we have assumed that the distance between particles (in the same chain and with the particles of the other chain) is low enough to consider that they are in contact. In Fig. 7 we represent the energy of a bundle of n particles both in zip and in parallel formation. We can see that $E_z < E_p$ for every n value which confirms what we expected. In Fig. 1 and 2 we can appreciate some zip aggregated structures.

In Fig. 4 we can see the mean value for every frame for systems where zip formation was observed (In blue). We would expect a region with chain formation before they aggregate into bundles but it is not appreciable. However we can see that in equilibrium $\langle n \rangle = 12.88 \pm 0.01\, part/chain$ and that is reached around $t_{eq} = 280 \cdot \sigma^2/D_t\ s$. The fact that equilibrium is reached quite late may be due to the chain equilibrium that should have been reached before the appearance of bundles. In addition we can observe as in the previous case the distribution of the probability when equilibrium is reached (see Fig. 5, in blue).

IV. CONCLUSIONS

In this work superparamagnetic colloids (CPS) self-assembly has been studied under the effect of an external magnetic field on a plane. This external field induces a magnetic dipole on each colloid and can generate self-assembly. Due to the rising interest in colloid self-assembly (CSA) for the wide variety of applications that it has, it is important to predict the collective behavior of colloids under certain circumstances such as temperature or external fields.

The main focus of this work has been the study of CSA by means of simulations of brownian dynamics of a system of CPS in a plane under the effect of a magnetic field in terms of basic particle characterization data (magnetic response) and experimental conditions (concentration and temperature). Then the evolution of this system was studied until a stable state which is identified as equilibrium state was reached. Next, this state was characterized calculating the equilibrium distribution of probability of aggregates in function of its size.

From this analysis it has been observed that depending on the magnetic parameter and the concentration of colloids they stay disaggregated (for low values of both parameters), they form chains along the external field direction (mid values) and bundles of chains (high values). Therefore, an important result is that CSA reaches a stable state when chains are being formed and destroyed systematically around an average chain length that increases with the parameters of the problem Γ, Φ. Equilibrium is reached with a monotonous increase of $\langle n \rangle$ in both studied cases. A relevant remark is that, when bundles were formed, it was impossible to observe a first plateau related to chain formation.

Another important result is that the distribution of probabilities of finding chains of size n in equilibrium decreases with n in the case of chain formation. In the studied case we can clearly see that in spite of forming chains of average size around $\langle n \rangle = 5.14$, the highest probability of finding a chain of size n is for $n = 1$. However, the probability of finding chains of size around $\langle n \rangle$ is pretty high in comparison of the one corresponding to longer chains. When doing the same analysis with bundles we can see that something similar happens since $\langle 1 \rangle$ has the highest probability and that the probability of finding a chain of the equilibrium size is much higher than that of a much longer chain. Finally, we observe that occasionally huge bundles where formed but with a probability of nearly 0. This may indicate an artifact from periodic boundary conditions.

All an all, this study has only delved into one face of many of CSA. For example the magnetic field was maintained static and also in the same direction. Furthermore equilibrium was studied as a dependence of time in one case but it could be extended at different systems and search a relation between the studied parameters and $\langle n \rangle$. Another interesting study that could have been made was to change the intensity of the field with time and study what would happen with equilibrium. In addition, systems with different particles other than colloids (or adding different kinds of colloids or particles to the actual system) may have some interest when trying to achieve the birth of new materials. Anyway, this study is a small step to reach the goal of CSA being fully understood.

Acknowledgments

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