

Ground state geometries and hysteresis loops of small granular ferrofluids as function of coating

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Abstract

A simple numerical algorithm to identify lowest energy configurations of a ferrofluid is presented. We consider the ferrofluid as a cluster formed by magnetic particles with constant magnetic moments and interacting through van der Waals and dipolar interactions. The minimal structure search is based on two strategies: to identify local minimum by simulated annealing methods and to search the energy potential surface by means of genetic algorithms. The mixing of these two methods improves the survey over the potential energy surface. In the non-magnetic limit, our algorithm recovers all known results for mono atomic clusters interacting through van der Waals forces, whereas in the presence of the magnetic interaction new structural geometries are found.

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1. Introduction

A ferrofluid is a composite of single magnetic nanoparticles immersed in a carrier fluid [1–3]. These nanometric particles are coated by a thin layer of a polymer and suspended in a non-magnetic fluid solvent. Due to the particle size, the resulting mixture is quite uniform and behaves as a two-phase liquid. The surfactant used to cover the magnetic particles is very important to avoid agglomeration mainly due to a decreasing of the magnetic dipole interaction. The nanometric size of the nanoparticles competes with the exchange magnetic size, giving them a monodomain character; even though, the magnetic properties strongly depend on the particle volume (diameter and shape). When these magnets are thermally activated, they show a paramagnetic behavior (following the Langevin law) with a very large susceptibility (much larger than other paramagnetic fluids), i.e., a larger magnetic response to small changes in the applied magnetic field.

There have been a large number of applications based on ferrofluids. Among them, the cooling of loudspeakers [2,4,5], in sealing technology by bringing a drop of ferrofluid into the gap between a magnet and a high permeable rotating shaft. In the cancer treatment, as magnetic targeting (drugs and radiopharmaceuticals), MRI imaging, diagnostics, immunoassays, molecular biology, RNA and DNA purification, cell separation and purification, cell adhesion research, and hyperthermia, etc. [1–3,6].

These unique magnetic properties have attracted a lot of interest, opening a diverse number of possibilities to enable magnetic control of their flow and other transport properties. The perspectives on different technological applications by applying external fields is large. In order to pursue this type of research, underlying microscopic mechanisms, the dependence on applied fields and flow-induced structure have to be understood. The interplay between theoretical and experimental approaches will provide a lot of information between structure and rheology [7–9].

The choice of a ferrofluid with appropriate properties is one of the most important questions in the preparation of experiments with magnetic fluids for novel applications [5,10,11]. In addition, the control and determination of the

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fluid magnetization and viscosity is a necessary basis for any work on these type of magnetic systems. In this article, we investigate by means of a classical model, the minimal energy configurations that can be obtained by changing the properties of the polymer used to coat the magnetic particles. The presence of a different type of polymer changes the intensity of the van der Waals attraction term, which changes the structure due to the competition between the dipolar interaction and the long range van der Waals interaction.

In Section 2 we discuss the physical model we have used to simulate the magnetic particles. Section 3 presents in detail the computational algorithm we have implemented to search the different structural minimum as a function of the model introduced previously. Section 4 is a summary of our findings in the case of small clusters, where the competition between the long range forces, considered here, can influence the final structural geometry. We end up in Section 5 by concluding and discussing future work.

2. Theoretical model

We model the ferrofluid as a system consisting of spherical particles of radius R , which have a permanent magnetic dipole moment μ . By assuming that each ferrofluid magnetic particle has a single magnetic domain, the particle magnetic moment μ is given by its volume times the saturation magnetization per unit volume M_S (1.7×10^6 and $0.48 \times 10^6 \text{ Am}^{-1}$ for bulk iron and magnetite, respectively [1]) as

$$\mu = \frac{4}{3}\pi R^3 M_S. \quad (1)$$

On the other hand, the short range repulsive interaction between two magnetic nanoparticles i and j is modeled by a Lennard-Jones pair potential:

$$E_{\text{LJ}} = \frac{1}{2} \sum_{i \neq j}^N 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (2)$$

where ϵ is the energy parameter, σ is the equilibrium distance parameter, and r_{ij} is the interparticle distance between particle i and j . Since the equilibrium distance between two particles in a Lennard-Jones potential is $2^{1/6}\sigma$, we can model the coating of the magnetic particle by setting $R = \sigma/2$, such that the difference between the equilibrium distance and $2R$ (distance in which the two particles are in physical contact) mimic the size of the surfactant layer. Summarizing, we define $R = \sigma/2a_s$, where a_s is now a parameter that controls the surfactant layer thickness.

The dipole–dipole interaction between magnetic moments $\boldsymbol{\mu}_i$ is given by

$$E_D = \frac{1}{2} \sum_{i \neq j}^N \frac{\mu_0}{4\pi} \left[\frac{\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j}{r_{ij}^3} - 3 \frac{(\boldsymbol{\mu}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\mu}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} \right], \quad (3)$$

where μ_0 is the vacuum permeability.

At this point, it is useful to write the total energy as function of the following adimensional quantities: energy $\xi = 2E/\epsilon$, spatial coordinates $\mathbf{r}^* = \mathbf{r}a_s/\sigma$, and the dipolar parameter $\lambda_D = \pi\mu_0 M_S^2 R^3/18\epsilon$. By introducing $R = \sigma/2a_s$ and Eq. (1) into the total energy of the system, this can be written as

$$\xi = \sum_{i \neq j}^N \left[\left(\frac{a_s}{r_{ij}^*} \right)^{12} - \left(\frac{a_s}{r_{ij}^*} \right)^6 \right] + \lambda_D \left[\frac{\mathbf{u}_i \cdot \mathbf{u}_j}{r_{ij}^{*3}} - 3 \frac{(\mathbf{u}_i \cdot \mathbf{r}_{ij}^*)(\mathbf{u}_j \cdot \mathbf{r}_{ij}^*)}{r_{ij}^{*5}} \right], \quad (4)$$

where \mathbf{u}_i is the unit vector along the magnetic moment in particle i . Now, the energy becomes a unique function of the adimensional parameter λ_D , which measures the intensity of the dipolar–dipolar interaction with respect to the Lennard-Jones energy.

In this work, we are interested in characterizing the zero temperature physical state of a ferrofluid (particle positions and magnetic moment directions of each particle) by minimizing the total energy in Eq. (4). It is important to emphasize that λ_D is proportional to the coating thickness and therefore it is a function of the polymer type used to coat the ferrofluid. All the structures here reported are characterized as function of it.

3. Computational method

Conventional minimization techniques are very useful in searching minimal energy configurations when the energy surface changes very smoothly and there is a state with much lower energy than any other [12]. However, they are very limited due to a large probability of getting trapped in metastable states. Recently, new methods have been explored, but one that has called a lot of attention is the denominated genetic algorithm (GA). This method is aimed to locate the global minimum instead of obtaining a local minimum. As suggested by its name, this method is based on a natural selection among the different possible structures, as it happens in biology. A set of possible structures are called the population and every element (an individual) in the population is constructed from the real atomic position of the ferrofluid particles (normalized to a cubic box system size L , much larger than the cluster size) and the orientation of the magnetic moments. A given element in the population is encoded in a vector of real numbers $X_i = (x_1, y_1, z_1, \theta_1, \phi_1, \dots, x_N, y_N, z_N, \theta_N, \phi_N)$, where x_i, y_i, z_i are the normalized atomic positions of the i ferrofluid particle and (θ_i, ϕ_i) are the angular spherical coordinates of the magnetic moment with respect to a Cartesian axis and normalized to π and 2π , respectively. With the imposed normalization, all vector components are treated on the same footing.

In order to obtain the lowest energy configuration, we proceed along the following lines. A fixed initial population N_{pop} is generated (usually 20). The population members are chosen according to the following criteria: (a) published optimized Lennard-Jones cluster [13], (b) a linear chain,

(c) a packed FCC cluster, (d) randomly positioned and oriented particles on a cubic box of size L , and (e) a previous run (if it applies). After the members have been selected, local minimizations by using simulated annealing are performed to every member. In the early stages of the numerical procedure, the number of local minimizations is low (between 1000 and 5000) and in the later stages the precision is increased by applying more than 15 000 steps to every member.

After the local minimum are determined for all individuals in the population, a GA step is performed as follows:

- The energy of every individual, ξ_i , is evaluated by using Eq. (4). A predefined percentage of the lowest energy configurations are passed through the new population. This is called the elitism rule (20% was the value used).
- A fitness function, f_i , is assigned to every member as

$$f_i = \frac{\sum_{j=1}^i (\xi_{\max} - \xi_j)}{\sum_{j=1}^{N_{\text{pop}}} (\xi_{\max} - \xi_j)}, \quad (5)$$

where ξ_{\max} is the maximum value of the set $\{\xi_i\}$ and N_{pop} is the population size. This functionality gives rise to a discrete probability distribution, used to select members from the population.

- The new population is completed by randomly selecting members of the previous population according to the probability distribution and applying some genetic operators (also randomly selected) until the size N_{pop} is repopulated. The operators we have considered are modifications from Ref. [14] and can be summarized as follows:
 - *Inversion.* A single member is selected (the father) and two locations in the vector are randomly chosen. A new individual (the child) is created by copying the previous member and between the two selected locations, a mirror image of the previous is copied.
 - *Arithmetic mean.* A pair is selected from the population and a single one is produced as the average of every vector position.
 - *Geometric mean.* A pair is selected from the population and a single individual is produced as the geometrical average of every vector position.
 - *Two-point crossover.* A pair is selected and a pair of new individuals is produced. A random integer is chosen between one and the vector size. The new two members are produced by crossing over one part of a first parent and the second part of the second parent.
 - *N-point crossover.* A pair is selected and a pair is constructed. The new individuals are built such that every vector site is selected randomly from the two parents.

At every GA step, all new members of the population are locally minimized. In the process, the number of step used in the local minimization is increased to improve the

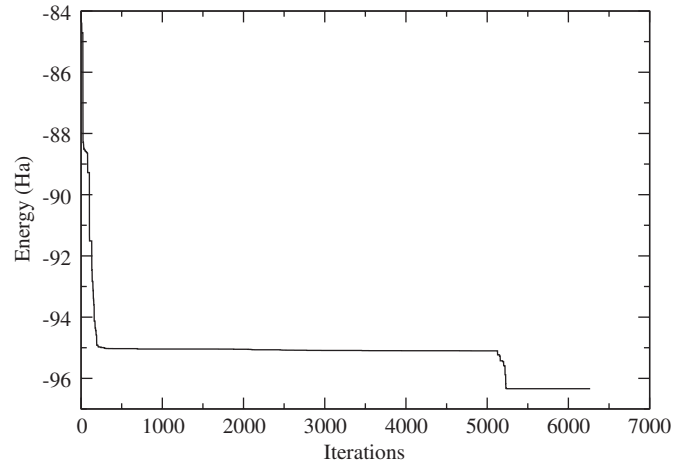


Fig. 1. Convergence rate as function of number of genetic algorithm steps.

convergence to the local minimum. The GA search is finished when the energy remains constant for more than 500 GA steps. Population number is kept constant during all steps. Due to the random nature of this algorithm, we have repeated the process several times and the best configuration found in a previous run was entered to the next one. The number of GA steps and local minimizations are also increased. This process is stopped until the energy difference between one run and the next one was less than 0.01 per particle.

An example of the energy convergence is shown in Fig. 1. At first, the energy changes very rapidly between GA steps. This shows that our search is efficient. After some steps, the energy remains constant for a large number of iterations, which means that the instantaneous configuration has a good potential of being the lowest energy configuration. The importance of using GA is demonstrated around step 5000, where there is a large jump in energy, which means that after the GA mixing, a new lowest energy structure is found.

4. Results

By using the previously described algorithm we have obtained the lowest energy configurations of a ferrofluid of 10 particles. As discussed previously, the important parameter is λ_D . This parameter summarizes the strong competition between wire type of structures when the dipole–dipole interaction is dominant and compact structures when Lennard-Jones interaction prevails. Large system sizes will be discussed elsewhere. Fig. 2 shows the minimal energy configurations we have obtained and Table 1 shows the cluster symmetry and their total magnetic moment. It is clear the effect of λ_D on the topological structure of the ferrofluid. As λ_D increases, the cluster becomes less compact up to a point where a wire of particles is obtained (see Fig. 2). In the particular case of 10 particles, it becomes a circle wire with spins forming a vortex around the center of mass. In intermediate values of

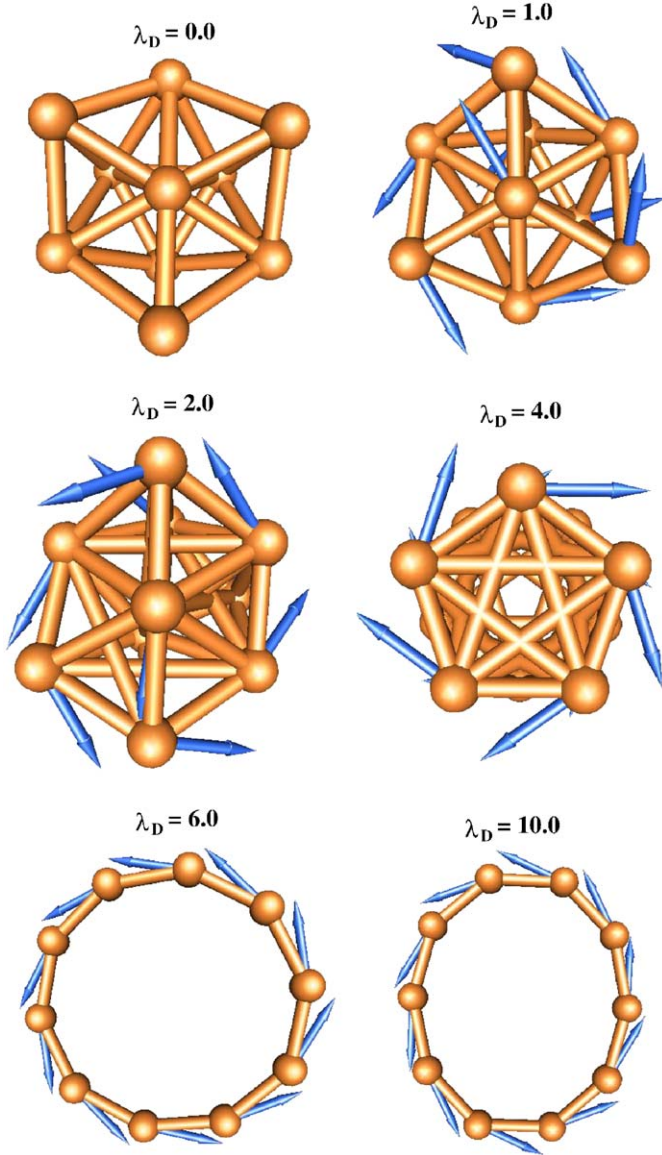


Fig. 2. Minimal optimal structures obtained by the genetic algorithm (see text) for a ferrofluid of 10 particles. Different values of the parameter λ_D are considered.

Table 1
Energies in units of ϵ , total magnetic moments and symmetry of the lowest energy configurations

λ_D	Symmetry	Energy	Total magnetic moment
0.0	C3v	-28.422531	0.000
1.0	C3v	-43.015445	0.496
2.0	C2	-59.487148	0.347
4.0	D5d	-96.339002	0.000
6.0	D10	-137.276952	0.001
8.0	C2h	-182.060477	0.002
10.0	D2h	-227.347544	0.001

λ_D , there is a strong competition between dipole energy and Lennard-Jones energy, and important changes on the cluster symmetry, with a total magnetic moment of zero. The plane, where the vortex state is developed, it is

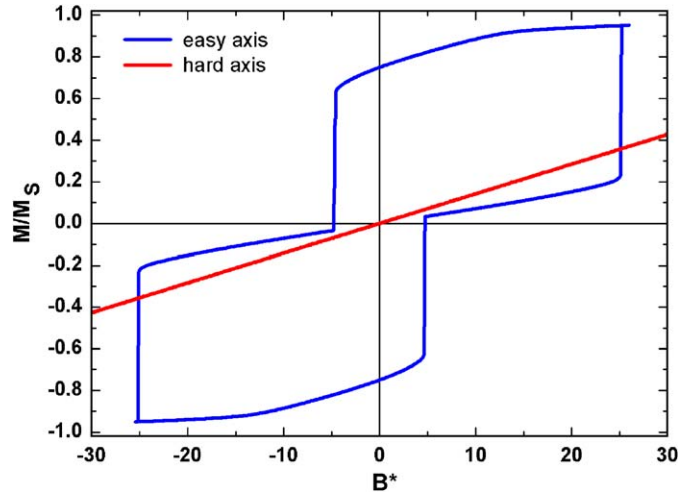


Fig. 3. Hysteresis loop of ten particle ferrofluid with $\lambda_D = 10.0$ along the easy axis and the hard axis.

denominated as the *easy plane*, whereas the perpendicular axis is called the *hard axis*. In general, the effect of changing the coating of a ferrofluid particle should produce a similar effect by modifying the compactness of the structure. Long particle wires and aggregated clusters have been reported in the literature (see for example Refs. [10,15,16]).

In Fig. 3, we demonstrate the effect of the coating on the magnetic properties, where we have calculated the magnetic hysteresis loops for the minimal structures. The hysteresis loop has been obtained by using Monte Carlo methods as described in Ref. [17]. In the case of more compact structures, we observe no coercivity and large jumps on the hysteresis curve. This last observation comes from changes of individual magnetic moments, as the applied field decreases. Similar jumps have been reported in molecular magnets. As λ_D increases, the dipolar interaction becomes dominant and now the magnetic moments can change direction with respect to the applied field by forming domains. This makes more difficult to observe jumps in the hysteresis curve and a large coercivity value is obtained.

5. Outcome and future work

In summary, we have introduced a methodology to study minimal ground geometries in a simple model of ferrofluids. This model includes the dipole–dipole interaction and a Lennard-Jones potential as the more important contributions to the ferrofluid. We scale the total energy as function of adimensional variables and express the ratio between the two competing energies (dipolar and Lennard-Jones) through a single parameter λ_D . In the case of a small ferrofluid cluster, when λ_D is small, the Lennard-Jones interaction dominates and the resulting geometrical structure is compact. Whereas, when λ_D increases, the dipole–dipole becomes much larger than the Lennard-Jones energy and the cluster tends to form wires. This

suggests that if new coatings are produced which reduce the dipole–dipole interaction, different and compact structures can be obtained with novel magnetic properties [18–20]. We also demonstrate that, depending on the structure, the hysteresis loops reveal different behavior. For example, in susceptibility measurements, the magnetic response would depend on the structure, which also could modify the fluid transport properties under the influence of external fields.

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