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## Aggregate formation on polydisperse ferrofluids: A Monte Carlo analysis

L.L. Castro<sup>a</sup>, M.F. da Silva<sup>a</sup>, A.F. Bakuzis<sup>b</sup>, R. Miotto<sup>a,\*</sup>

<sup>a</sup>*Instituto de Física, Universidade de Brasília, Caixa Postal 04455, CEP 70919-970, Brasília, DF, Brazil*

<sup>b</sup>*Instituto de Física, Universidade Federal de Goiás, Caixa Postal 131, CEP 74001-970, Goiânia, GO, Brazil*

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### Abstract

In this work, we report three-dimensional Monte Carlo simulations of a polydisperse magnetic fluid sample based on magnetite nanoparticles surface coated with dodecanoic acid dispersed in hydrocarbon. Monodisperse simulations are also performed and indicate that polydispersity is a key issue. Our simulations are consistent with both static magnetic birefringence and magnetic resonance measurements for a particle volume fraction smaller than 4%.

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A stable colloidal dispersion of (roughly) spherical, magnetic particles in a nonmagnetic solvent is usually called a ferrofluid. The interaction between these particles is mainly governed by attractive dipole–dipole and van der Waals forces, which might lead to the formation of agglomerates [1]. Stability as a colloid is an important property that ensures the formation of a well-defined material suitable for fluid application. As the presence of various types of aggregates influences the macroscopic properties of magnetic fluids, these nanosized particles are strongly stabilized in

order to avoid permanent aggregation (and in some cases flocculation). They either suffer a steric hindrance provided by a surfactant coating (surfacted ferrofluids), or they are charged in order to provide electrostatic repulsion (ionic ferrofluids). Biocompatible magnetic fluids are believed to be stabilized through both mechanisms, i.e. it is an ionic-surfacted ferrofluid. However, even after these treatments aggregates had been experimentally observed by Butter et al. [2] using cryogenic electron microscopy. In addition, the dimension of the particles plays a crucial role in the behaviour of different magnetic fluids under different magnetic fields. In this sense, a systematic study of aggregate formation is essential in order to help the understanding and prediction of magnetic fluid

\*Corresponding author. Tel.: +55 61 3072900;  
fax: +55 61 3072363.

E-mail address: [romiotto@fis.unb.br](mailto:romiotto@fis.unb.br) (R. Miotto).

properties. In this work, we report preliminary results of three-dimensional Monte Carlo simulations of polydisperse  $\text{Fe}_3\text{O}_4$ -based nanoparticles for different concentrations and under zero field conditions. In addition, we have also considered a monodisperse system in order to evaluate the importance of polydispersity.

Monte Carlo simulation is a label used to designate a stochastic technique for solving mathematical problems and constitutes an important simulation technique in many areas of physics and chemistry [3]. In this type of simulation, values for uncertain variables are randomly generated over and over to simulate a model. Multiple scenarios of this model are generated by repeatedly sampling values from the probability distributions for the uncertain variables and using those values for the cell, in order to obtain the thermodynamic properties, the minimum-energy structures and/or rate coefficients. In Monte Carlo simulation, the random selection process is repeated many times to create multiple scenarios. Each time a value is randomly selected, it forms one possible scenario and solution to the problem. Together, these scenarios give a range of possible solutions, some of which are more probable and some less probable. When repeated for many scenarios, the average solution will give an approximate answer to the problem. Accuracy of this answer can be improved by simulating more scenarios. If one is interested in minimum energy configurations, as is the case in the present work, a Monte Carlo simulation will allow us to evaluate the Boltzmann energy distribution. The use of Monte Carlo algorithms in the study of magnetic fluids is not new (see, for example, a comprehensive discussion of two-dimension simulation in Ref. [1]). However, contradicting results [4–6] and novel algorithms for simulating these systems [7] are still being reported in recent investigations. In the following, we briefly discuss the main characteristics of the studied systems considered in our implementation of an algorithm similar to the Metropolis one [8]. In all simulations, we have considered 5 million Monte Carlo steps and the random seed generator is reinitialized every 5000 steps. This is statistically equivalent to a series of 1000 different ensembles of particles.

We describe our ferrofluid by considering an ensemble of 200 polydisperse nanoparticles surface-coated with dodecanoic acid and stably dispersed in hydrocarbon in a cubic box with periodic boundary conditions. The grafting ( $\chi$  = number of molecules adsorbed on the nanoparticle surface) was considered to be  $1 \times 10^{18}$  molecules/m<sup>2</sup> [1], and for the Hamaker constant ( $A$ ) the value of  $4 \times 10^{-20}$  J was used [9]. Different concentrations were obtained by varying the box size. The hard spheres are considered to be homogeneously magnetized and translational and rotational degrees of freedom are assumed for these particles. The interparticle interaction potential is expressed [9] in terms of a steric repulsion  $U_s$ , a van der Waals attraction  $U_w$ , and a dipole–dipole interaction of the magnetic moments of ferroparticles  $U_d$ . We have also considered the possibility of the external potentials  $U_m$  and  $U_g$ , due to the presence of external magnetic (Zeeman term) and gravitational fields, respectively. Thus, our total energy potential can be written as

$$U = U_s + U_w + U_d + U_m + U_g,$$

where [1,9]

$$U_s = \frac{\pi d_{ij}^2 \chi k_B T}{2} \left[ 2 - \frac{1+2}{t} \ln \left( \frac{1+t}{1+1/2} \right) - \frac{1}{t} \right],$$

with  $d_{ij}^2$  defined as the mean particle diameter ( $(d_i + d_j)/2$ ),  $k_B$  is the Boltzmann constant,  $T$  is the temperature,  $l = (2s)/d_{ij}$  ( $s$  = surface–surface particle distance) and  $t = (2\delta)/d_{ij}$  ( $\delta$  = the coating layer thickness),

$$U_w = -\frac{A}{12} \left[ \frac{d_{ij}^2}{r^2} + \frac{d_{ij}^2}{r^2 - d_{ij}^2} + 2 \ln \left( \frac{r^2 - d_{ij}^2}{r^2} \right) \right]$$

and

$$U_d = \frac{\mu_0}{4\pi} \left[ \frac{\vec{m}_j \cdot \vec{m}_i}{r^3} - 3 \frac{(\vec{m}_j \cdot \vec{r})(\vec{m}_i \cdot \vec{r})}{r^5} \right],$$

where  $r$  is the particle–particle distance (centre to centre),  $\mu_0$  is the magnetic permeability of free space, and  $m_i$  is the magnetic moment of particle  $i$ .

In order to reflect as close as possible the real ferrofluids samples that had been experimentally investigated by our group [10–13] via static magnetic birefringence and magnetic resonance,

we have carefully chosen the relevant physical parameters with reference to them, e.g. a log-normal particle distribution  $f_{\log n}$  with a modal diameter  $\bar{D} = 8.9$  nm and a diameter dispersity  $\sigma = 0.34$ . To ensure that our equilibrium configurations are comparable to the experimental data the thickness of the surfactant layer was also chosen as to reflect the samples investigated by our group (1.2 nm). It is worth emphasizing that in contrast to previous calculations (including very recent ones [7]), where polydisperse samples were simulated considering a bidisperse system (i.e., the polydisperse sample is simulated as a mixture of particles with only two different sizes, so-called small and large particles [7]), our Monte Carlo simulations consider a real polydisperse system with the particle diameter distribution following a log-normal function:

$$f_{\log n}(D) = \frac{e^{-2\sigma}}{\bar{D}\sigma\sqrt{2\pi}} \left[ e^{-\ln(D/\bar{D})/2\sigma^2} \right],$$

where  $\bar{D}$  and  $\sigma$  define the size distribution. An example of such distribution is shown in Fig. 1. The polydispersity of the particles is obtained as follows: (a) for a given modal diameter and dispersity we estimate the maximum frequency of the log-normal function ( $f_{\log n}(\bar{D})$ ); (b) a random diameter between 0 and 25 nm is generated ( $d_{\text{rand}}$ ) and we calculate the log-normal function value at this point ( $f_{\log n}(d_{\text{rand}})$ ); (c) a random number between 0 and 1 is generated and compared with

the ratio ( $f_{\log n}(d_{\text{rand}})/f_{\log n}(\bar{D})$ ). If this ratio is greater than or equal to the random number, this diameter is accepted; otherwise the process is repeated until a diameter is attributed to all particles from our ensemble. It is important to note that step (c) is crucial in order to guarantee that the random generated sequence corresponds to a log-normal distribution function. Indeed, with this scheme it is possible to generate any given distribution function.

In Fig. 2, we present Monte Carlo simulation snapshots for a polydisperse surfactated magnetic fluid considering a modal diameter  $\bar{D} = 8.9$  nm and a diameter dispersity  $\sigma = 0.34$  at zero magnetic field for two different concentrations, namely (a)  $\Phi = 0.04\%$  and (b)  $\Phi = 6.40\%$ . Different colours indicate different nanoparticle diameters. The difference in the size of the nanoparticles for different concentrations reflects the fact that in our simulations the concentration is defined by the box size. The formation of aggregates is not clear from these snapshots. In order to make a careful analysis of the three-dimensional figures, we have defined an agglomerate as an aggregate with a surface particle–particle distance smaller than 2.6 nm. When two particles fulfil these criteria, we have a dimer, for three particles a trimer, and so on. From this approach, it was possible to infer that cluster formation increases with increasing concentration. Our quantitative analysis is summarized in Fig. 3, where the fraction of monomers, dimers and agglomerates (i.e. dimers, trimers and other possible aggregates) are presented as a function of the particle volume fraction.

We understand that the choice of the aggregate criteria is an important issue in the study of the clusterization process. We believe that the definition of agglomerate should not be simply related to close proximity between particles, at least when considering magnetic nanoparticles, mainly due to the magnetic nature of the material. A magnetic system often reacts to the presence of an external magnetic field. The mechanism of rotation of the magnetic moment of the nanoparticle, for example, is an important issue to be considered. As an emblematic example, consider the case where two particles are close together and the magnetisation reversal mechanism is the coherent rotation, as

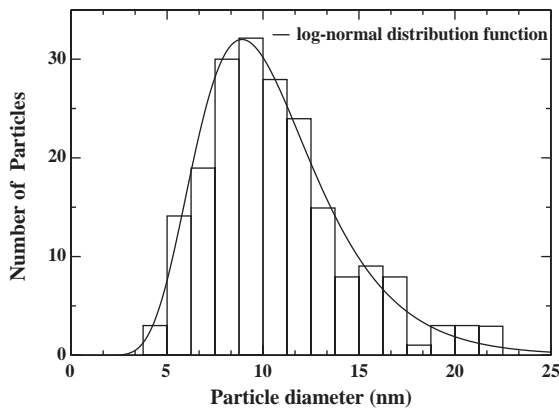


Fig. 1. Particle diameter histogram considering size distribution parameters  $\bar{D} = 8.9$  nm and  $\sigma = 0.34$ .

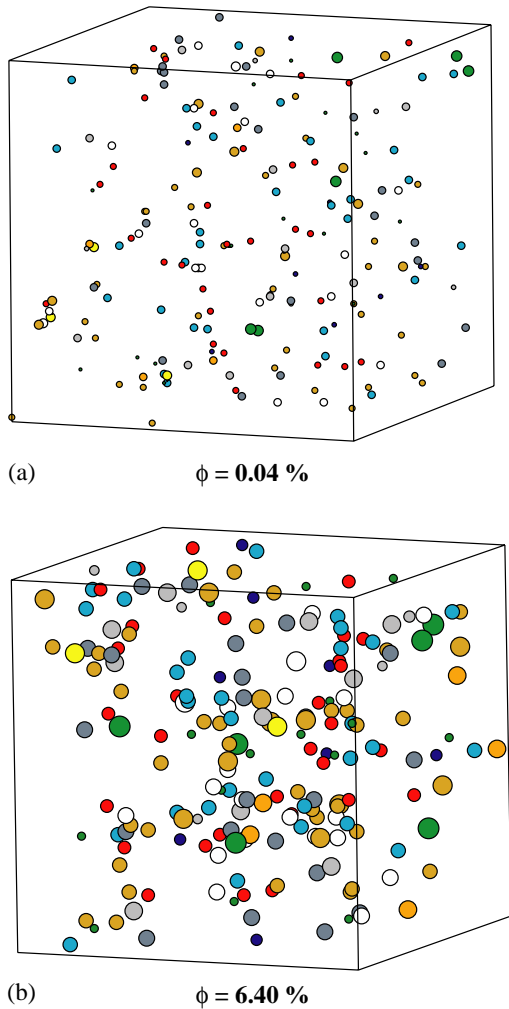


Fig. 2. Visualization of two simulated equilibrium configurations for a polydisperse ferrofluid, at zero magnetic field condition, considering different particle volume fractions: (a)  $\Phi = 0.04\%$  and (b)  $\Phi = 6.40\%$ .

observed for isolated nanoparticles. In this case, even when the particles are close together they should not be treated as agglomerates. However, if the particles rotate through an inhomogeneous mechanism, as for instance through the fanning mechanism, then the dipole–dipole interaction has to be taken into consideration and the particles should be treated as an agglomerate [14]. Experimental data from static magnetic birefringence confirm the presence of dimers in ferrofluids [10–12,15]. In addition, recent analysis from

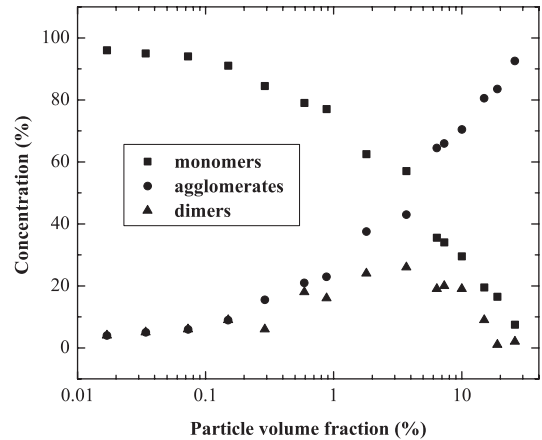


Fig. 3. Concentration of monomers, dimers and agglomerates (i.e. dimers, trimers and other aggregates) as a function of particle volume fraction (%).

magnetic resonance experiments shows dimers with a surface–surface particle distance larger than the coating layer thickness [13,16]. However, the same experiments also indicate dimers where this distance is smaller than the coating layer thickness, suggesting an interpenetration of the coating layers. This interpenetration was also clearly observed from cryogenic transmission electron microscopy (CTM) [2]. Having all those points in mind, it is important to consider a dimer with a surface–surface particle distance slightly larger than the coating layer thickness and also the possibility of interpenetration of the coating layers, i.e. a dimer formation criterion with surface–surface particle distance slightly larger than 2.4 nm (in the present case) but also smaller than this value. In our study of the influence of the dimer formation criteria, our Monte Carlo data suggest that when considering a 2.4 nm surface–surface particle distance, the results do not change significantly. For a particle volume fraction of 3.7%, for example, the results agree within 2%.

It is clear from Fig. 3 that for a particle volume fraction smaller than 1%, all the agglomerates are dimers. This is consistent with static magnetic birefringence measurements of magnetic fluids at this concentration range [11,12] where only dimers are observed. For higher particle volume fraction, our results indicate that the number of monomers decreases (as an example, for  $\Phi = 0.017\%$  the

number of monomers decreases from 96% to 7.5% at  $\Phi = 26\%$ ). The decrease of the number of monomers as a function of the increasing particle concentration is also consistent with static magnetic birefringence data [10–12]. It is interesting to note that the decrease in the number of monomers is also associated with the formation of other aggregates (dimers, trimers, tetramers, etc.). Our data also indicate the formation of larger agglomerates for higher particle concentrations (as an example, for a  $\Phi = 6.4\%$  we found a fraction of dimers close to 19%, trimers  $\sim 13\%$ , tetramers  $\sim 4\%$ , and smaller fractions of other agglomerates). As expected, in all the ensembles simulated in our studies we have found no evidence of magnetic order under zero field condition, i.e. for all final configurations in the concentration considered in this work, the magnetisation of the system is zero.

In Table 1, we show a comparison between experimental and theoretical values for the fraction of monomers and surface–surface particle distance, considering both polydisperse and monodisperse systems. The particle size distribution considered in the present simulation was chosen in order to allow a direct comparison with recent magnetic resonance measurements of magnetic fluid sample based on magnetite nanoparticles surface coated with dodecanoic acid and stably dispersed in hydrocarbon [13]. In their paper, the sample was characterized by transmission electron microscopy revealing a particle size distribution equivalent to the one used in our simulation. According to their results the magnetic resonance spectra had contributions from monomers and

dimers. From the analysis of the resonance data, the authors obtained dimers with a surface–surface particle distance between 0.18 and 1.80 nm (0.40–2.94 nm) for a sample with a particle volume fraction of 0.29% (3.70%). This value is consistent with the 1.52 nm (1.45 nm) found in our work, specially considering that our theoretical value corresponds to an average distance for all aggregates. From the area analysis of the magnetic resonance spectra of the same sample  $\Phi = 0.29\%$  (3.70%), Morais and co-workers [16] have found a fraction of monomers of 84% (60.1%) in very good agreement with our Monte Carlo calculated value of 89.5% (57%). However, a similar level of agreement is not found for a higher concentration ( $\Phi = 10\%$ ). Our calculated surface–surface particle distance is 48% higher than the largest experimental value. The fraction of monomers, on the other hand, is found to be much smaller than the experimental value (29.5% in the present simulation against 58.9% for the magnetic resonance data). These differences might be related to the fact that in real magnetic fluids a phase separation phenomenon occurs near this concentration range [9]. Phase separation is a biphasic colloidal system where droplets of highly concentrated particle regions are dispersed in a diluted phase. The homogeneity of the colloid is destroyed by this phase separation. We believe that the present simulation does not correctly describe such a situation, mainly due to the fact that surface interactions (e.g. surface tension) are not explicitly considered.

In order to evaluate the influence of polydispersity, we have compared our results with monodisperse simulations. The percentage of monomers obtained for a monodisperse system is found to be 86.0, 39.0 and 16.5% for a particle volume fraction of 0.29, 3.70 and 10.0%, respectively. When comparing these results with the polydisperse results (Table 1), it is clear that the latter is in agreement with the experimental results than the former for  $\Phi$  smaller than 4%, indicating that polydispersity indeed plays a key role in the properties of these systems. In contrast, we have found a similar level of agreement between the calculated surface–surface particle distance for both the polydisperse and monodisperse systems (see Table 1).

Table 1  
Comparison between experimental and theoretical values for the fraction of monomers and surface–surface particle distance

Concentration $\Phi$ (%)	Monomer %			Distance $d_{\text{surf-surf}}$ (nm)		
	Pol	Mono	Exp [16]	Pol	Mono	Exp [16]
0.29	89.5	86.0	84.0	1.52	0.16	0.18–1.80
3.70	57.0	39.0	60.1	1.45	1.81	0.40–2.94
10.0	29.5	16.5	58.9	3.70	4.25	0.10–2.50

Pol and mono stands for a polydisperse and a monodisperse system, respectively.

Finally, it is important to note that only surfacted magnetic fluids have been simulated. In fact, we plan to develop a systematic experimental–theoretical investigation in collaboration with the authors of Ref. [16], in order to make a full comparison between our Monte Carlo simulations and experimental data. We understand that such analysis will be extremely important in a complete description of the mechanisms involved in such systems. However, this is beyond the scope of the present article and will be published elsewhere. In addition, we are about to simulate ionic magnetic fluids. The results of our simulations will also be compared with experimental data (static magnetic birefringence and magnetic resonance) with a view to allow a better understanding of the influence of the electrostatic repulsion mechanism. After both steps are complete, we will feel confident to perform simulations on biocompatible ferrofluids.

In summary, in this work we report three-dimensional Monte Carlo simulations of both polydisperse and monodisperse magnetic fluid samples based on magnetite nanoparticles surface coated with dodecanoic acid and stably dispersed in hydrocarbon. Our polydisperse simulations are consistent with both static magnetic birefringence and magnetic resonance measurements. Our data indicate that the fraction of monomers decreases with the increase of the particle volume fraction with the formation of various aggregates, i.e. dimers, trimers, etc. It is interesting to note that for  $\Phi$  smaller than 1% only dimers are observed, for the Hamaker constant and the grafting number considered in our simulations. Although the surface–surface particle distance and the fraction of monomers are found to be in excellent agreement with the experimental data for concentrations up to 4%, the same level of agreement is not found for higher particle concentrations. We understand that this might be related to a phase

separation phenomenon not correctly described in the present simulation. In addition, the importance of polydispersity is accessed by means of comparison with monodisperse simulations and experimental data.

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