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# Aggregate formation in ferrofluid monolayers: simulations and theory

Juan J Cerdà<sup>1</sup>, Sofia Kantorovich<sup>1,2,3</sup> and Christian Holm<sup>1,3</sup>

<sup>1</sup> Frankfurt Institute for Advanced Studies, J W Goethe-Universität, Ruth-Moufang Straße 1, D-60438, Frankfurt am Main, Germany

<sup>2</sup> Department of Mathematical Physics, The Urals State University, 51 Lenin Avenue, Ekaterinburg 620083, Russia

<sup>3</sup> Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128, Mainz, Germany

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## Abstract

In order to investigate the peculiarities of the aggregation processes in ferrofluids in a quasi-2D geometry, a combination of density functional theory (DFT) and molecular dynamics (MD) simulations is presented. The microstructure formation in monodisperse ferrofluid monolayers is studied thoroughly through a comparison of the theoretical and computational results.

Theoretical and simulation results show similar trends which renders the theoretical approach a useful tool for getting insight into the microstructure formation in monolayers.

## 1. Introduction

Ferrofluid particles are known to self-assemble into a variety of magnetic equilibrium structures which depend on system geometry, magnetic interactions, particle polydispersity, presence or absence of external fields, etc [1]. The phase behaviour and microstructure of ferrofluid systems in constrained geometries are not necessarily equivalent to those of 3D systems. Recent quasi-2D (Q2D) experiments using cryogenic transmission electron microscopy (cryo-TEM) [2, 3] have provided us with real space images of chain-like and ring-like clusters in ferrofluids based on iron and magnetite nanoparticles. Previously, Wen *et al* [4] had already reported the observation of rings, chains and defects on dry monolayers of microspheres using a CCD camera technique. In turn, several theoretical and simulation approaches have been developed for understanding the nature of the phase behaviour and microstructure formation in such restricted geometries. The existence of the vapour–liquid transition in Q2D Stockmayer fluids has been investigated by Gao *et al* using the Gibbs ensemble Monte Carlo technique [5]. Lomba *et al* [6] have proposed an Ornstein–Zernike integral equation formalism able to describe the structure of Q2D ferrofluid monolayers in good agreement with Monte Carlo simulations. Weis and co-workers (see [7, 8], and references therein) have performed Monte Carlo simulations of monolayers and systems of finite thickness involving dipolar interactions. They have shown that Q2D dipolar systems, alone or in combination with other interactions, present a rich variety of structures,

phases and phase transitions. A comparison of the simulation results with equilibrium polymer theory has shown that the structure of Q2D dipolar fluids in the low density regime is closer to the one observed in 2D equilibrium polymers. The arrangements of Q2D nanoparticles in constrained surfaces has been studied by Ghazali and Lévy [9]. The structure and dynamics in a monolayer of dipolar soft spheres has also been investigated by Duncan and Camp [10] using molecular dynamics simulations. They have shown that it is possible to observe fingerprints of the formation of chains though the structure factor in the form of a power-law scaling at low wavevectors. More recently, Tavares *et al* [11] have performed Monte Carlo simulations of Q2D dipolar hard spheres (DHS). The structure of the fluid at low and intermediate densities has been found to be well described by an ideal mixture of self-assembling clusters. In addition, estimates for the partition function of those clusters have been derived, and results from their work suggest that 2D dipolar fluid undergoes a phase transition from a dilute phase of disconnected clusters to a condensed network phase. In turn, the kinetics of aggregation in monolayers has been studied by Duncan and Camp [12] using stochastic dynamics simulations. Their results suggest that the conditions for defect-driven condensation [13] could be met by kinetic trapping, giving rise to a metastable phase transition between isotropic fluid phases.

Despite the progress obtained in previous studies, the understanding of the phase behaviour and microstructure formation of ferrofluids in constrained geometries is only partial. In the present study we propose a new density functional theory

for monodisperse Q2D ferrofluids in monolayers, which combined with molecular dynamics simulations provides a deeper understanding of the microstructure formation mechanisms in constrained geometries.

The outline of this paper is as follows. In section 2 we present a density functional theory for monolayers (DFTM). The simulation model is presented in section 3, and a comparison and discussion of the results from the simulations and DFTM are given in section 4. In section 5, conclusions are presented.

## 2. Density functional theory for monolayers

Our model system is composed of identical spherical particles. The magnetic cores (with diameter  $\sigma$ ) are covered with a nonmagnetic layer of thickness  $l$ . Each particle possesses a permanent magnetic moment  $\boldsymbol{\mu}$  which can freely rotate in the three-dimensional space, and the centres of the particles are trapped in a plane to mimic quasi-two-dimensional systems which are closer to the description of monolayers than purely two-dimensional systems. We assume two types of inter-particle interactions in our model: magnetic dipole–dipole interaction (1) and steric soft-sphere repulsion (2),

$$U_{ij}^{\text{dip}} = \frac{\mu_0}{4\pi} \left( \frac{\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j}{|\mathbf{r}_{ij}|^3} - \frac{3[\boldsymbol{\mu}_i \cdot \mathbf{r}_{ij}][\boldsymbol{\mu}_j \cdot \mathbf{r}_{ij}]}{|\mathbf{r}_{ij}|^5} \right), \quad (1)$$

where  $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$  is the displacement vector of the two particles, and  $\mu_0 = 4\pi \times 10^{-7} \text{ H m}^{-1}$  is the vacuum permeability. The short-range interactions between pairs of particles are represented by a Weeks–Chandler–Andersen potential [14],

$$U_{ij}^{\text{sr}} = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right] + \epsilon \quad (2)$$

a purely repulsive Lennard-Jones potential with a cut-off radius  $R_c = 2^{1/6}\sigma$ .

Our theoretical approach allows for the existence of ferroparticle flexible chains and quasi-ideal rings. The latter means that the displacement vectors of particles in a ring organize into a regular polygon, the side of which can fluctuate; in other words, the ring can ‘breathe’. In the present formalism, only nearest neighbour interactions are taken into account for particles inside an aggregate. For the cluster definition an entropy criterion is used [15]. A further discussion about the different possible criteria for cluster definition and the entropy criterion is provided in section 4.

We use here a density functional approach to find the equilibrium area fractions of chains  $g(n)$  and rings  $f(n)$ . The comparison of the theoretical and simulation results (see section 4) shows that excluded area interactions play a crucial role in quasi-2D; the constraints imposed by the monolayer geometry change the entropy of clusters. In the present formalism the excluded area interactions are taken into account in the simplest form, as a reduction of the entropy: the factor  $(1 - 8\phi/\pi)$  arises from the excluded area interactions. The free energy density functional (which results from Frenkel’s

heterophase fluctuation theory [16], and can be obtained as a generalization of the free energy functional in [15]) is

$$F(g, f) = k_B T \sum_{n=1}^{\infty} g(n) \left( \ln \frac{g(n)s}{\left[1 - \frac{8\phi}{\pi}\right] e} - \ln Q(n) \right) + k_B T \sum_{n=5}^{\infty} f(n) \left( \ln \frac{f(n)s}{\left[1 - \frac{8\phi}{\pi}\right] e} - \ln W(n) \right), \quad (3)$$

where  $k_B T$  is the thermal energy,  $s$  represents the cross-sectional area of the particle;  $Q(n)$  and  $W(n)$  stand for the chain and the ring partition functions respectively. In the second term of (3) the summation starts at  $n = 5$ , because proper rings are assumed to contain five or more particles. In order to analytically calculate the chain and ring partition functions, special coordinate systems have been used which allow for the factorization of  $Q(n)$  and  $W(n)$ :  $Q(n) = q^{n-1}$ ,  $W(n) = w(n)^n/n$ ; where  $q$  and  $w(n)$  denote the pair effective energies in a chain and ring respectively. Unlike for the chains, where this pair energy does not depend on the chain length, the effective pair energy in a ring is  $n$ -dependent. The factor  $n$  in the denominator in a ring partition function tells that all  $n$  particles in a ring can be chosen to be the first; thus there are  $n$  different configurations for the same ‘macrostate’. For the chain, according to the definition adopted here only one particle can be chosen as the first, because the orientation of its magnetic moment is also taken into account. Finally, the free energy (3) has to be minimized with the help of the Lagrange method under the mass balance condition:

$$\sum_{n=1}^{\infty} n g(n) + \sum_{n=5}^{\infty} n f(n) = \frac{\phi}{s}. \quad (4)$$

This condition means that the total number of particles in the system is limited by the ferroparticle area fraction  $\phi$ .

Thus equilibrium chain and ring area fractions have the following form:

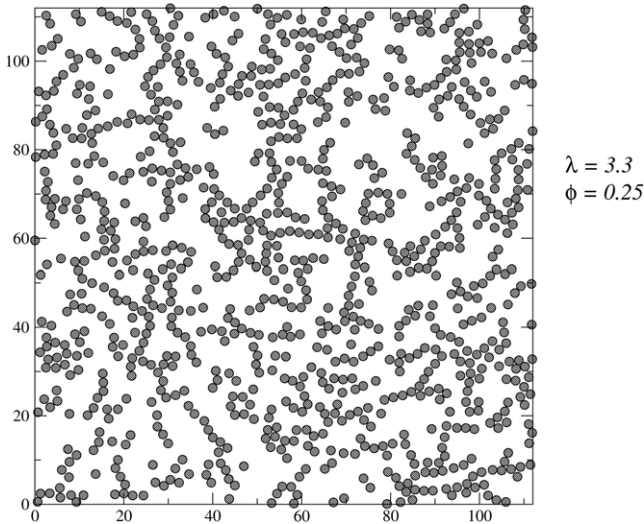
$$g(n) = \frac{1}{s} \left[ 1 - \frac{8\phi}{\pi} \right] q^{n-1} \exp(pn) \quad (5)$$

$$f(n) = \frac{1}{sn} \left[ 1 - \frac{8\phi}{\pi} \right] w(n)^n \exp(pn),$$

where  $p$  has the meaning of a Lagrange multiplier.

## 3. Simulation model

We model the ferrofluids in our equilibrium molecular dynamic simulations as systems consisting of  $N$  spherical particles of diameter  $\sigma$ , distributed in a square simulation area of side length  $L$ . Like in the theory, we assume particles to be monodisperse, and exhibit a permanent point dipole moment  $\boldsymbol{\mu}$  at its centre, which can freely rotate in 3D, and interact through equation (1). For the particle movements, periodic boundary conditions are applied along  $X$ – $Y$  directions. The long-range dipole–dipole interactions are calculated in a first step by using a recently developed dipolar P<sup>3</sup>M algorithm (dP<sup>3</sup>M) on the basis of the Coulomb P<sup>3</sup>M [17, 18]; in a second step, a dipolar



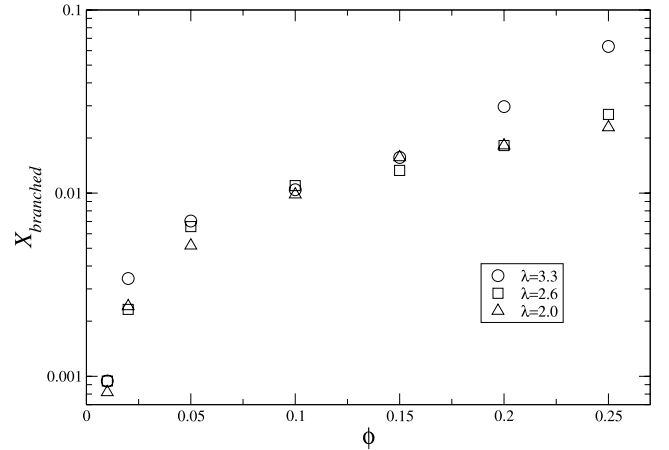
**Figure 1.** A typical snapshot for a system with area fraction  $\phi = 0.25$  and dipolar coupling parameter  $\lambda = 3.3$ . The fraction of particles in branched structures is still low enough for the theoretical ansatz to be valid since there only ring-like and chain-like aggregates are considered. In agreement with DFT, in the range of  $\lambda$  s under study, stable ring-like structures that represent a small fraction of the whole set of clusters are observed.

layer correction (DLC) [19] is applied which discounts the effect of the excess of infinite replicas added in the first step along the  $Z$  direction. The use of the dP<sup>3</sup>M plus DLC method allows a much faster calculation of the dipolar long-range correlations than the traditional dipolar Ewald summation [20]. The correctness and exactitude of the algorithm used in this work have been tested against both the dipolar Ewald sum and the dipolar direct sum. The level of accuracy of the algorithm for computing dipolar forces and torques is set to  $\delta \sim 10^{-4}$  in this study.

In our simulations, the short-range interactions between pairs of particles are represented by equation (2); translational and rotational Langevin equations of motion of particle  $i$  are given by [21]

$$M_i \frac{d\mathbf{v}_i}{dt} = \mathbf{F}_i - \Gamma_T \mathbf{v}_i + \boldsymbol{\xi}_i^T, \quad \mathbf{I}_i \cdot \frac{d\boldsymbol{\omega}_i}{dt} = \boldsymbol{\tau}_i - \Gamma_R \boldsymbol{\omega}_i + \boldsymbol{\xi}_i^R, \quad (6)$$

where  $\mathbf{F}_i$  and  $\boldsymbol{\tau}_i$  are the resulting force and torque acting on the particle  $i$ , respectively.  $M_i$  and  $\mathbf{I}_i$  are the mass and the inertia tensor of the particle.  $\Gamma_T$  and  $\Gamma_R$  are the translational and rotational friction constants, respectively.  $\boldsymbol{\xi}_i^T$  and  $\boldsymbol{\xi}_i^R$  are the Gaussian random force and torque with mean zero, and satisfying usual fluctuation-dissipation relations. The variables can be given in dimensionless form as length  $r^* = r/\sigma$ , dipole moment  $(\mu^*)^2 = \mu^2/(\epsilon/\sigma^3)$ , time  $t^* = t(\epsilon/(M\sigma^2))^{(1/2)}$ , and temperature  $T^* = k_B T/\epsilon$ . The simulations are performed at constant temperature  $T^* = 1$ . In doing equilibrium simulations, the values of the mass, the inertia tensor, as well as friction constants  $\Gamma_T$ , and  $\Gamma_R$  are somewhat arbitrary. The particle mass is chosen to be  $M = 1$ , and the inertia tensor  $\mathbf{I} = \mathbf{1}$ , the identity matrix, to ensure isotropic rotations. We adopted  $\Gamma_T = 1$ , and  $\Gamma_R = 3/4$  which are observed in our systems to give a fast relaxation towards the equilibrium. A reduced

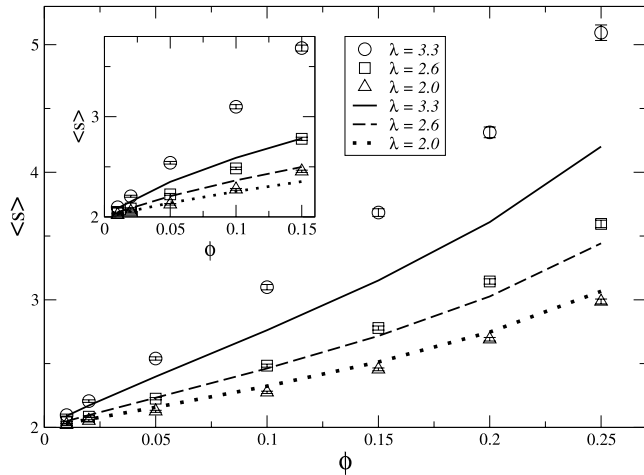


**Figure 2.** Fraction of particles in the system that are embedded into branched clusters (i.e. neither chains nor rings). The plot shows that the omission of branched structures is admissible in the range of surface fractions and dipolar couplings under study.

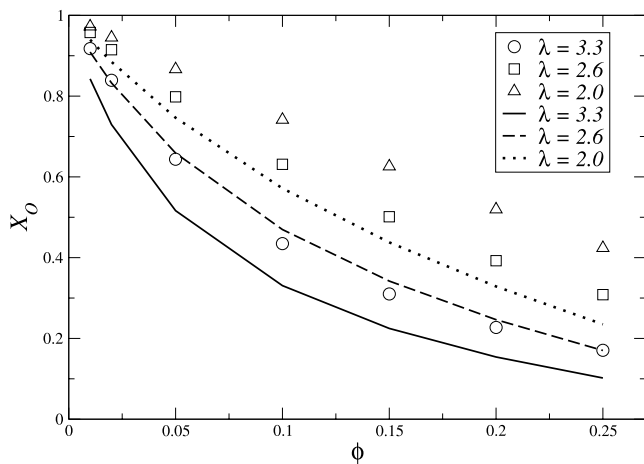
time step  $\Delta t^* = 15 \times 10^{-4}$  is used. The runs are started from initial configurations with random particle positions over the simulation area, and 3D random orientation for the dipole moments of the particles. Each system is first equilibrated for a period of  $2 \times 10^6$  time steps to ensure results to be totally independent of the starting conditions. Analysis of the auto-correlation function of the energy indicates correlation times smaller than  $10^4 \Delta t^*$  even in the worst cases. In order to ensure a proper and almost uncorrelated sampling, measurements are taken at intervals of  $2 \times 10^4 \Delta t^*$  for another period of  $8 \times 10^6$  time steps. The number of particles per system is  $N = 1000$  in regular simulations, although several extra runs (up to  $N = 10000$ ) have been performed in order to ensure independence of results from finite-size effects. The simulation package ESPResSo [22] has been used to do the simulations.

## 4. Results and discussion

The behaviour of ferrofluid monolayers can be characterized through the use of two main parameters: the area fraction  $\phi = N\pi(\sigma/2)^2/L^2$  and the dipolar coupling parameter  $\lambda = 0.5U_{dd}/k_B T$ , where  $U_{dd}$  is the interaction energy of two particles when they centres are at a distance  $\sigma$ , and their dipoles are perfectly aligned. In the present work we study the behaviour of systems  $\lambda = 2.0, 2.6, 3.3$  for area fractions ranging from  $\phi = 0.01$  to  $0.25$ . In our particle model we assume the magnetic core to be surrounded by a nonmagnetic layer of surfactants with thickness  $l = 2$  nm; the total particle diameters associated with the previous dipolar coupling parameters  $\lambda$  are  $\sigma = 18, 19, 20$  nm. The values of  $\lambda$ ,  $\sigma$  and  $\phi$  under study have been chosen for a twofold reason: they roughly correspond to the values found in typical experimental systems; and they provide the most adequate scenario for testing the theory because the types of aggregates that we basically observe in these ranges of parameters are chain-like and ring-like clusters; see figures 1 and 2. Figure 2 shows that in the range of area fractions and dipolar coupling



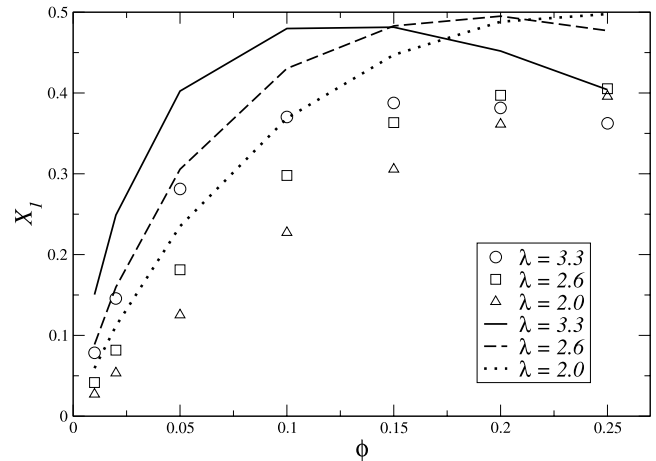
**Figure 3.** Shown is the average cluster size  $\langle s \rangle$  as a function of surface fraction  $\phi$  for various dipolar couplings  $\lambda$ . The theoretical predictions are shown by the various lines, and are in reasonable agreement with the data points that were obtained using molecular dynamic simulations. To stress the importance of the excluded volume interaction we show in the inset a similar comparison in which the excluded area interactions are not taken into account in the DFT theory.



**Figure 4.** A comparison of the theoretical predictions, and the simulation results for the fraction of monomers  $X_0$  as a function of the area fraction  $\phi$ .

parameter considered, the fraction of particles in branched clusters, i.e. those which cannot be considered either chains or rings, is to a good approximation, negligible. Nonetheless, the assumption that systems are only composed of chain-like and ring-like clusters is at present one of the main constraints of the theory.

In order to study the formation of cluster aggregates we have adopted the so-called entropy criterion [15], in which two particles  $i$  and  $j$  are considered to be bonded when the following three conditions are satisfied:  $\mathbf{r}_{ij} \leq r_c$ ,  $\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j \geq 0$  and  $(\boldsymbol{\mu}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\mu}_j \cdot \mathbf{r}_{ij}) \geq 0$ . In our cluster analysis we have set the cut-off radius  $r_c = 1.35\sigma$ . The entropy criterion provides a better resolution of the neighbouring clusters than energy or



**Figure 5.** Shown is a comparison of the fraction of particles forming dimers and chain ends,  $X_1$ , versus the surface fraction  $\phi$ . The legend is the same as in figure 4 for  $X_0$ .

distance criteria. The entropy criterion is advantageous with respect to the distance criterion because it takes into account that not only must two particles be close to be considered as bonded, but also their dipolar moments must be correlated. Despite dipole correlations being implicitly taken into account in energy criteria, we have observed that the entropy criterion is more tolerant to the thermal fluctuations that artificially split isolated chains and rings into small pieces when an energy criterion is used, and allows for a direct comparison with DFT calculations.

Figure 3 shows a comparison of the theoretical and simulation results for the evolution of the size of the aggregates with the area fraction. Despite a lack of perfect quantitative agreement, we observe that theory and simulation show similar predictions. We can observe that the inclusion of the excluded area term in the theory is crucial for getting a correct description of the systems at large area fractions. The inset in figure 3 shows a comparison of the results obtained when excluded area interactions are not taken into account in the theory. The mismatch between simulation and theoretical results is larger in that case. In fact, the observed trends between theory and simulation are quite different when excluded area effects are disregarded. As a further test of the usefulness of the theory, figures 4 and 5 show a comparison of the evolution with the area fraction of the fractions of monomers  $X_0$ , and particles with a single neighbour  $X_1$ , respectively. It is important to notice that the value of  $X_1$  accounts not only for the number of dimers, but also for the number of chain ends present in the system, and therefore gives supplementary information about the system. In both figures 4 and 5, we observe again that theoretical predictions show trends similar to the values obtained in simulations. Despite the constraints implicit in the theory, we observe that once the excluded area term is taken into account, the theoretical formalism that we present is able to capture the main essence of the problem, and therefore it constitutes an excellent tool for doing a further analysis of the microstructure formation in constrained geometries.

## 5. Conclusions

In the present work we have described a new density functional theory for quasi-two-dimensional monolayers of dipolar particles. Ring and chain aggregates can be treated in this way. A thorough comparison of the predictions of the theory with the values obtained through equilibrium molecular dynamic simulations has shown that in the range of the space of parameters ( $\lambda$ ,  $\phi$ ) in which the theory could be expected to be valid, the theory is able to closely predict the simulation results. For higher densities and larger couplings, however, we see an increase in branched structures. These might play a crucial role for discussing any possible phase transitions which could occur in this system, and whose investigation will be left for a future study. An improvement of the present theory by dropping several of the limiting constraints will be the object of forthcoming work.

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