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Bidisperse Monolayers: Theory and Computer Simulations

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Abstract

We try to elucidate the microstructure formation in a bidisperse ferrofluid monolayer and understand in detail the difference brought by the geometrical constrains. The system under study consists of soft-sphere magnetic dipolar particles confined to a thin fluid layer. The positions of the particles are constraint to a 2D geometry, whereas the particle magnetic dipole moments are not fixed to the body systems, and are free to rotate in 3 dimensions, hence forming in what we call a quasi-2D geometry (q2D). Unlike the q2D monodisperse case studied in [1] we discover that the presence of small particles inhibit ring formation. Unlike the bidisperse system in bulk thoroughly investigated in [2], small particles can form clusters and can appear in various amounts in the clusters formed by large particles. Finally we come to the conclusion, that geometrical constraints play a crucial role in determining the ferrofluid microstructure, and thus, the direct extrapolation of experimental results obtained for q2D systems to the bulk magnetic fluids might be misleading.

Keywords: Ferrofluid; microstructure; monolayer; polydispersity

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. The phase behaviour and microstructure of ferrofluid systems in constrained geometries is not necessarily equivalent to that of 3D systems. Recent quasi-2D (q2D) experiments using cryogenic transmission electron microscopy (cyro-TEM) [3] have provided with sound evidence of the existence of chain-like, and ring-like clusters in ferrofluids based in iron and magnetite nanoparticles.

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 bidisperse q2D-ferrofluids in monolayers, which combined with molecular dynamics

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simulations provides a deeper inside on the understanding of the microstructure formation mechanisms in constrained geometries.

2. Computer simulations

We model the ferrofluids in our equilibrium molecular dynamic simulations as systems consisting of N spherical particles of diameter σ_l, and M spherical particles of diameter σ_s distributed in a square simulation area of side length L. We assume $\sigma_s < \sigma_l$. Each particle has a permanent 3D point dipole moment $\vec{\mu}_{s(l)}$ at its centre, dipoles interact through magnetic dipole-dipole interaction. 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 $dipolar-P^3M$ algorithm (dP^3M); in a second step, a dipolar layer correction (DLC) is applied which discounts the effect of the excess of infinite replicas added in the first step along the Z direction. The use of dP^3M plus DLC method allows a much faster calculation of the dipolar long-range correlations that the traditional two-dimensional dipolar Ewald summation. The level of accuracy of the algorithm for computing dipolar forces and torques is set to $\delta \sim 10^{-4}$.

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 Γ_T, and Γ_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 time step $\Delta t^* = 15 \cdot 10^{-4}$ 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 systems is first equilibrated for a period of $2 \cdot 10^6$ time steps to ensure results to be totally independent of the starting conditions. Analysis of the autocorrelation 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, measures are taken at intervals of $2 \cdot 10^4 \Delta t^*$ for another period of $8 \cdot 10^6$ time steps. The number of particles per system was $N = 1000$ 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 $ESPResSo$[4] has been used to do the simulations.

3. Theory

Our model system is composed by two types (small and large) of spherical particles, the magnetic cores (with the diameter σ_s (small) and σ_l (large)) of which are covered by nonmagnetic layer (the thickness l). Each particle possesses a permanent magnetic moment $\vec{\mu}_{(s)l}$ which can rotate in 3D space; the centers of all particles are trapped in one plain. Thus we are dealing with quasi-two dimensional systems which are closer to the description of monolayers than purely two-dimensional systems. We assume two types of interparticle interactions in our model: magnetic dipole-dipole interaction (1) and steric soft-sphere repulsion (2).

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

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ is the displacement vector of the two particles and $\mu_0 = 4\pi \times 10^{-7} H/m$ is the vacuum permeability. The short-range interactions between pairs of particles are represented by the WCA potential

$$U_{ij}^{sr} = 4\varepsilon\left[\left(\frac{\sigma_i+\sigma_j}{2r_{ij}}\right)^{12} - \left(\frac{\sigma_i+\sigma_j}{2r_{ij}}\right)^{6}\right] + \varepsilon, \quad (2)$$

a purely repulsive Lennard-Jones potential with a cutoff radius $R_c = 2^{-5/6}(\sigma_i+\sigma_j)$.

Our theoretical approach allows for the existence of ferroparticle flexible chains made of large and small particles and rings. We use here the density functional approach to find the equilibrium area fractions of chains $g(n,m,i)$ and rings $f(n,m,i)$ (the density of chains and rings respectively, composed by n large particles, m small particles and having a certain structure i). It turned out that an excluded area plays a crucial role in quasi 2D. We introduce it into the free energy density functional in the simplest form as a reduction of the entropy. Finally, the free energy has to be minimized with the help of Lagrange method under the mass balance condition.

4. Results and Discussion

The behaviour of ferrofluid monolayers can be characterised through the use of two main parameters: the area fraction, and the dipolar coupling parameter $\lambda = 0.5U_{dd}/k_BT$ (in bidisperse case we have three of them), where U_{dd} is the interacting energy of two particles at close contact, and their dipoles are perfectly aligned. In the present work we study the behaviour of the following systems $\sigma_l = 14,16,18$nm, $\sigma_s = 7,9,11$nm. Corresponding values of coupling constants for large-large particle differ from 2 to 5, for small particles are always less than unity. The area fraction of large particles was fixed at 0.05. The range of small particle area fractions under study if fairly broad: from 0 to 0.1. In our particle model we assume the magnetic core to be surrounded by a non magnetic layer of surfactants with thickness 2 nm, the total particle diameters associated with the previous dipolar coupling parameters λ_l are $\sigma = 18,20,22nm$. The values of λ, σ and ϕ under study have been chosen for a two-fold reason: they roughly correspond to the values found in typical experimental systems; and they provide the most adequate scenario for testing the theory.

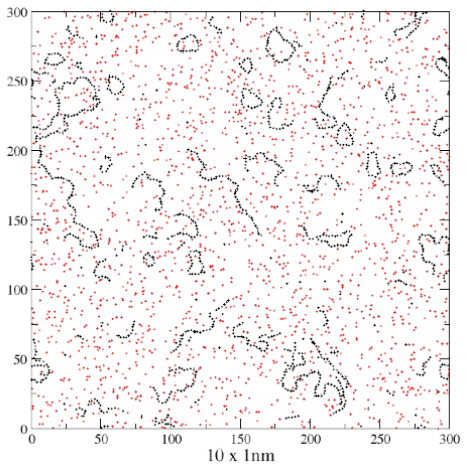

Figure 1: This figure illustrates the simulation snapshot. The large particles (22 nm) are black, small ones (15 nm) are red, area fraction of large particles is 0.05, area fraction of small particles is 0.1.

In Fig. 1 we present a typical simulation snapshot of a bidisperse system. It can be seen that chains and ring of ferroparticles are formed. It is worth saying, that the rings become more rare and have smaller size in the bidisperse case in comparison to monodisperse monolayers. The ring appears to be a ground state for monodisperse system,

however, gives a sufficient decrease in entropy. For bidisperse systems the groundstate structure is more complicated and rings become less probable.

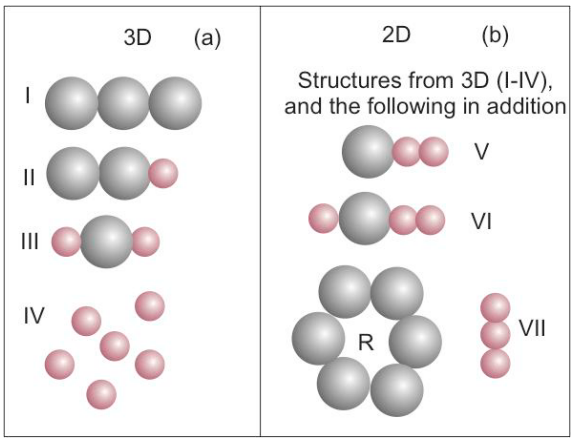

Figure 2: Cluster structure in 3D (Fig. 2a) and 2D (Fig. 2b)

In Fig. 2 we present new cluster structures which appear in a bidisperse monolayer in addition to those observed in bulk. Interesting enough, small particles do aggregate in monolayers, when in 3D they remain in majority nonaggregated. So, we have to include in theory many more additional topological classes. The aggregation of small particles is related to entropy changes and to the excluded area interactions. Besides that, the rings were not observed in bulk simulations. Even though, as mentioned above, the presence of small particles really inhibit the ring formation, one cannot totally neglect their presence.

5. Conclusion and Outlook

We have developed a theoretical model for calculating the microstructure of bidisperse ferrofluid monolayers in the absence of an applied magnetic field. Our method is based on density functional minimization. An extensive comparison of the theoretical model to the results of molecular dynamics simulation demonstrated a very good agreement. We showed that polydispersity changes the microstructure of a monolayer noticeably, and even more important, we observed qualitative changes in the microstructure driven by the influence of the geometry. The latter means one has to be careful when extrapolating experimental results directly to bulk magnetic fluids, as any conclusion in this case might be misleading.

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