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On the self-assembly of net-like nanostructures in ferrofluids

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HIGHLIGHTS

- The internal structures in ferrofluids in the absence of magnetic field are studied.
- Nanoparticles form linear chains when their concentration and magnetic interaction are low.
- Increasing these parameters leads to formation of the Y-forks and net-like structures.
- A bottom-up approach for constructing hierarchical nano-architectures of viable applications is introduced.

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ABSTRACT

Understanding the physical forces that govern nanoparticles self-assembly is central to the ability to engineer super-nanostructures for advanced nanotechnology applications. Magnetic force represents one of such important forces that is responsible for structural transformations and condensation in ferrofluids (FF). In this work, we study internal structural transformations in FF in the absence of external magnetic field by introducing the first direct statistical model that takes into account formation of linear chains, Y-forks and net-like nanostructures. The results show that, in agreement with experiments, when the concentration of the magnetic nanoparticles and their magnetic interaction energy are small enough, majority of the particles are united in individual linear chains. But, when these parameters exceed some threshold magnitude, the main particles population switches to net-like nanostructures. These results highlight the importance of magnetic dipole interactions in the absence of external magnetic field, and their essential role in the bottom-up construction of hierarchical nano-architectures of viable fundamental and practical implications.

1. Introduction

Ferrofluids (FF), being colloidal suspensions of single-domain magnetic nanoparticles, has been a fascinating system for scientists and engineers for long time. The fascination stems from the fact that FF combine physical properties of more than one state of condensed matter, and from their ability to change phases with the application of a magnetic field. This allowed for several biomedical and technological applications, as well as fundamental findings [1,2]. The typical size of particles in a FF is about 10–20 nm. In order to prevent their irreversible agglomeration under the action of central disperse attraction, the particles are covered by special surfactant or ionic layers, which screen this attraction.

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Ferrofluid nanoparticles can form various heterogeneous structures—linear chains, bulk drops, closed rings and branched structures [3–6]. The typical size of the drops is several microns and they can be observed using optical microscopy. Since size of the particles is less than the wavelength of visual light, the linear chains cannot be detected by optical microscopy. However, they have been observed on the nanoparticle level recently by using electron microscopy [5–7]. At the same time the chains have been detected in many computer simulations (see, for example, Refs. [8–13]).

In systems of individual dipole particles, the formation of FF drops have been treated and modeled as a Van-der-Waals "gas–liquid" phase transition [14–17]. Formation of chains has not been considered in these models. However, the fact that the particles at the pre-transition state can form linear chains, rings and branched structures is firmly ascertained now (see results of experiments and computer simulations [5–13]). A model for the particle phase condensation in FF, taking into account formation of linear chains has been suggested in Ref. [18]. Two limiting cases of zero and infinitely strong external magnetic field were considered in this model. Analysis of Ref. [18] shows that when the energy of magnetic interaction between particles increases, linear chains appear and then they condense into bulk dense phases. For the case of strong magnetic field, a dense phase of closely situated chains has been detected in laboratory experiments [5,6] and computer simulations [11].

Experiments [5,6,19–21] and simulations [13,22–26] show that the increase of the interparticle magnetic interaction energy leads to the formation of rings and branched structures. The question, whether pure magnetic interaction, without central attraction and external magnetic field, can induce the "gas–liquid" condensation in the systems of ferroparticles; or leads to the formation of branched and net-like structures is disputable in literature. For example, the "gas–liquid" phase separation has been detected in the simulations [27]; whereas authors of Refs. [10,13] emphasized on the absence of any signals of such separation in their simulations.

Thus, so far the fundamental details of the scenario of colloidal magnetic nanoparticles condensation in FF are unknown. It should be noted that study of the details of the condensation phenomenon and its associated structural transformations in FF presents not only fundamental interest, but it is important for various applications as well. For example, recently magnetopolymer nanocomposites (ferrogels and ferroelastomers) consisting of the magnetic nanoparticles imbedded into polymer matrix, have been synthesized and intensively studied. After matrix curing, the structures formed by the particles in the liquid polymer are fixed. The macroscopic mechanical properties and other physical properties of these compositions are very sensitive to details of the internal structure [19,20,28]. The other reason for the interest in the details of the internal structural transformations in FF is their biomedical applications. For example, the effectiveness of hypethermia and thermoablation methods for cancer therapy is determined by the mesostructures that are formed by the particles in a tissue [1,29].

The first model of a FF with particles united in linear chains and Y-forks has been suggested in Ref. [30]. A first type phase transition from the dilute gas-like to the dense liquid-like phase was predicted in this model. The dense phase was treated as a dense system of the forks. It should be noted that the statistical distributions over the number of particles in these chains and forks had not been considered in Ref. [30]. However, these statistics play an important role in the scenario of internal structural transformations [18], and their associated macroscopic properties [31]. Besides, though extensive studies have been dedicated for studying structural transformations in FF systems under the effect of external magnetic field, yet there are very little detailed studies concerning the self-assembly of branched and net-like structures in the absence of magnetic field, which was also a motivation for the present study.

In the present work, we study the internal structural transformations in ferrofluids in the absence of external magnetic field. We propose a direct statistical model of a FF, taking into account formation of linear chains, Y-forks and net-like structures. Only steric and magnetic dipole–dipole interaction between particles is taken into account. In other words, we assume that the disperse interparticle forces are screened by the surface layers on the particles. The results show that when the concentration of particles and/or energy of their magnetic interaction are small enough, only linear chains appear in the system. When these parameters exceed some threshold magnitudes, the particles self-assemble into net-like nanostructures.

2. Physical model and main approximations

Let us consider a system of monodisperse spherical magnetic nanoparticles, each has permanent magnetic dipole moment m. The main assumption of the model is that the particles can self-assemble to form linear chains, Y-like forks and larger branched networks, observed in the experiments [5,6,19–21].

It should be noted that at very low temperatures the particles of ferrofluids can form individual closed rings [13]. However, experiments show that the linear and branched structures prevalence in these systems is at typical room temperatures [5,6,19–21]. Besides, computer simulations demonstrate that appearance of the rings leads to nonmonotonic temperature dependence of the ferrofluid magnetic susceptibility at rather low temperature and density [22]. To the best of our knowledge, this nonmonotonic dependence has not been observed in experiments at room temperature. That is why here, for simplicity, we will not consider the rings and focus on the linear and branched structures.

The structures under consideration are schematically illustrated in Fig. 1. It is impossible, in framework of one model, to consider all physically possible topologies for the formed nets. In order to simplify analysis and to get physically reasonable estimates, we will suppose that the Y-forks are composed of linear chain segments linked through three particles-ties. The