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Structure and magnetic properties of mono- and bi-dispersed ferrofluids as revealed by simulations

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Abstract

Using a Langevin molecular dynamics simulation, we show that the magnetic properties of a mono- and bi-dispersed ferrofluid system depend on the volume fraction and the dipolar coupling parameter. For the bi-dispersed system, most of the chains are formed by the large particles, but the aggregation behavior of the large particles is hindered by the presence of the small particles, which are predominantly attached to the end of the particle chain. To further elucidate the microscopic fluid structure, anisotropic structure factors are calculated.

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Keywords: Polydispersed ferrofluids; Langevin molecular dynamics simulation; Aggregation

1. Introduction

Ferrofluids are colloidal suspensions containing single domain nanosize ferromagnetic particles dispersed in a carrier liquid [1], which possess a wide variety of potential applications [2,3]. Recently, ferrofluids have received much attention in the scientific community [4–15]. Polydispersity of ferrofluids appears naturally since the particles in real ferrofluids possess always a log-normal size distribution [5,6]. Therefore, the magnetization property of a polydisperse system differs from that of a monodisperse system [8,9]. The structure of polydispersed ferrofluids has been discussed theoretically on the basis of a bi-dispersed model in which the fluids consist of two fractions of magnetic particles with significant size differences [10–12,14]. For a bi-dispersed ferrofluid, the small particles are susceptible to Brownian motions and are more or less randomly dispersed. The large magnetic dipole moment of the larger particles leads, however, to a strong interparticle force which dominates the Brownian motion. Thus the salient structure in these systems is proposed to be chain-like aggregates formed by the large particles. Some small particles might be attached to the ends of these aggregates, but most of them remain in the non-aggregated state [11,12,14,15].

In this work, we shall investigate a bi-dispersed ferrofluid system which consists of small particles of magnetic core diameter of 10 nm and large particles of diameter 16 nm. The molecular dynamics simulation method is used to study the structure and magnetization properties of the system at different ratio of the volume fraction of the large and small particles.

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2. Simulation method

Let us consider a ferrofluid system composed of N spherical particles with a diameter of σ_i, and a permanent point dipole moment m_i at its center, distributed in a cubic simulation box of side length L. The dipole–dipole interaction potential between particles i and j is given by

$$U_{\mathrm{dd}} = \frac{1}{4\pi\mu_0}\left[\frac{\vec{m}_i\cdot\vec{m}_j}{r_{ij}^3} - \frac{3(\vec{m}_i\cdot\vec{r}_{ij})(\vec{m}_j\cdot\vec{r}_{ij})}{r_{ij}^5}\right]. \quad (1)$$

Using periodic boundary conditions in all spatial directions, the dipole–dipole interaction is evaluated using the Ewald method with metallic boundary condition [12].

The short-range interactions between the particles are represented by a purely repulsive Lennard–Jones potential. In view of the different sizes of the particles, this potential is determined by

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

with a cutoff radius of $R_{\mathrm{c}} = 2^{-5/6}(\sigma_i+\sigma_j)$. Regarding the detailed simulation method, please refer to Ref. [12].

Based on the simulation data, it is straightforward to calculate the structure factor [16],

$$S(\vec{K}) = \frac{1}{N}\left\langle\left[\sum_{i=1}^{N}\cos(\vec{K}\cdot\vec{r}_i)\right]^2 + \left[\sum_{j=1}^{N}\sin\left(\vec{K}\cdot\vec{r}_j\right)\right]^2\right\rangle, \quad (3)$$

where the wave vectors K were commensurate with the periodic boundary conditions. That is, K is determined by $K = 2\pi/L(l,m,n) \neq (0,0,0)$, with l,m,n integers. In this work, we shall take $2\pi/L \leqslant K \leqslant 9.0$ where $2\pi/L$ is the smallest available value. Since the fluid structure is expected to be rotationally invariant, $S(K)$ is obtained by averaging the contributions from all the wave vectors of magnitude K.

3. Simulation results

When the volume fraction of particles is low enough, the ferrofluid system behaves as an ideal paramagnetic gas. In this case, its physical properties are well described by the one-particle model [17]. Then, the equilibrium magnetization of this kind of system is expressed in terms of the Langevin function. As the volume fraction of the particles increases, the interparticle interaction is expected to play a role. In this case, the corresponding expression for the magnetization M is given by the modified mean-field model [8,12,18], see Eq. (10) of Ref. [12].

Since the total volume fraction of the particles is fixed, the saturation magnetization M_{s} is the same for all these cases discussed in Fig. 1. Fig. 1 shows the magnetization as a function of the field strength which is reflected by the dimensionless Langevin parameter α of the small particle, for different volume fraction of large particles ϕ_{L}, at fixed total volume fraction $\phi = 0.07$ in comparison with the theoretical result. In Fig. 1, the volume fraction of the larger particles is varied from $\phi_{\mathrm{L}} = 0.0$ to 0.07. In other words, we go from the monodispersed small particle system through the bidispersed cases, and finally to the monodispersed large particle system. The initial susceptibility χ and magnetization curves of the system show a strong dependence on the value of ϕ_{L}. With the increase of ϕ_{L}, the magnetization M of the system has a much faster increment at weak field, and thus leads to a larger χ. The simulation results show good agreement with the theoretical predictions up to $\phi_{\mathrm{L}} = 0.02$. However, significant discrepancy occurs at larger values of ϕ_{L}. A cluster analysis indicates that this is due to the aggregation of the large particles in the system. The average length $\langle n_{\mathrm{L}}\rangle$ of the clusters formed by the large particles increases as ϕ_{L} increases, which results in an enhancement of the magnetization of the system. The average size of clusters formed by the large particles $\langle n_{\mathrm{L}}\rangle$ is investigated in Fig. 2 as a function of the volume fraction of the small particles ϕ_{S} at zero field ($\alpha = 0$). In this case, we fixed the volume fraction of the larger particles to 0.05 and added more and more small particles (by changing ϕ_{S}) in order to study how the presence of small particles affect the chain formation of the large particles. We found a decrease of the average

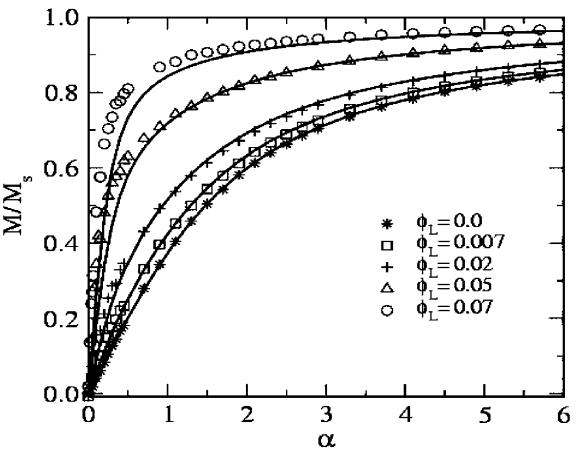

Fig. 1. Magnetization for different volume fraction of large particles ϕ_{L}, at fixed total volume fraction $\phi = 0.07$. Symbols: Simulation results. Solid lines: Corresponding theoretical predictions obtained from Eq. (10) of Ref. [12].

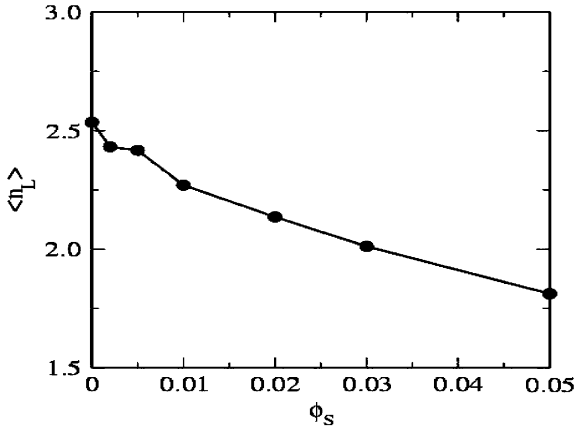

Fig. 2. Average size of clusters formed by the large particles $\langle n_L \rangle$ as a function of the volume fraction of the small particles ϕ_S at zero field ($\alpha = 0$). Line is a guide for the eye.

chain length $\langle n_L \rangle$ when ϕ_S is increased from 0.0 to 0.05. A topological analysis of the structure reveals that the majority of the small particles remain nonaggregated. Only a small number of them are attracted to the ends of the chains formed by large particles. The attachment of the small particles at the ends may prevent the further aggregation of the shorter clusters into longer chains, because the chains with small particles inside are relatively unstable. On the other hand, the addition of small particles will increase the effective magnetic permeability of the background for the large particles, and thus weaken the effective dipole–dipole interaction between them.

In Fig. 3, we display the anisotropic structure factors (a,b) $S(K_{xy})$ and (c,d) $S(K_{xz})$ as a function of the volume fraction of large particles ϕ_L, at (a,c) zero field and (b,d) non-zero field. Here we attempt to study the influence of polydispersity in the particle size and subsequently in the dipole moment. In this case, the total volume fraction of the large and small particles is again fixed to $\phi = 0.07$. In fact, at zero field ($\alpha = 0$), the system of interest behaves as an isotropic system, and therefore Fig. 3(a) [$S(K_{xy})$] displays the same behavior as Fig. 3(c) [$S(K_{xz})$]. In particular, at zero field or non-zero field, increasing ϕ_L always causes $S(K_{xy})$ to increase in the low-K_{xy} region [see Figs. 3(a) and (b)]. However, at non-zero field, increasing ϕ_L causes $S(K_{xz})$ to decrease in the low-K_{xz} region [see Fig. 3(d)]. Moreover, increasing the magnetic field leads to increasing $S(K_{xy})$ in the low-K_{xy} region again, but decreasing $S(K_{xz})$ in the low-K_{xz} region. Also, it is found that $S(K_{xz})$ increases in the high-K_{xz} region as the magnetic field increases. Our results can be used to interpret experimental observations as obtained in a recent work [19] on the anisotropic structure of colloidal ferrofluids.

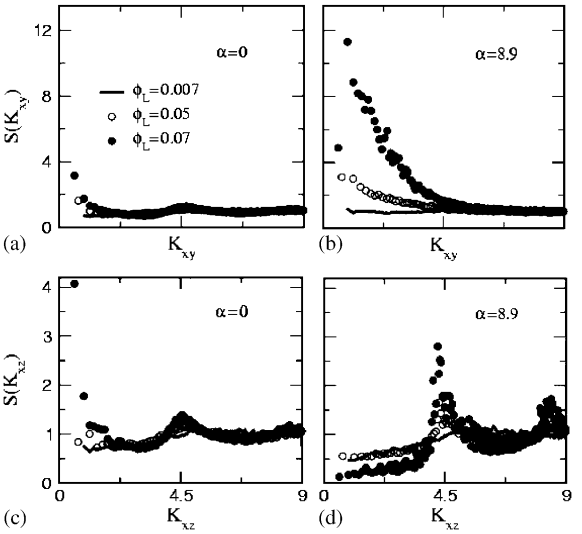

Fig. 3. Structure factor (a,b) $S(K_{xy})$ and (c,d) $S(K_{xz})$ as a function of the volume fraction of large particles ϕ_L at (a,c) zero field and (b,d) non-zero field. The total volume fraction of the large and small particles is fixed to $\phi = 0.07$.

4. Discussion and conclusion

To sum up, using a Langevin molecular dynamics simulation, we have found that the magnetic properties of the bi-dispersed ferrofluid systems depend on both the volume fraction and aggregation of the large particles. Most of the chains are formed by the large particles, but the aggregation behavior of the large particles is hindered by the presence of the small particles, which are predominantly attached to the end of the particle chain. Moreover, the difference between the XY- and XZ-plane structure factors is of value in comparing with experimental observations.

Acknowledgments

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