Structure factor of colloidal magnetic fluid

R Peredo-Ortíz and M Hernández-Contreras
Departamento de Física, Centro de Investigación y Estudios Avanzados del Instituto Politécnico Nacional, Apartado Postal 14-740, México Distrito Federal, México
E-mail: marther@fis.cinvestav.mx

Abstract. We determined with Langevin dynamics simulations the structure factor of a monodisperse ferrofluid as a function of the density of the suspension, and dipole strength in the particles valid for hard ferrofluids. The structure factor shows the transition from a liquid-like ordering of the particles at low density and dipole moment up to the formations of chain structures at high dipole strength. The collective diffusion coefficient shows a decaying dependence on the dipole moment magnitude for low density of colloid, however, at a high density, such a dependence gets reversed, and the diffusion increases with the dipole moment.

1. Introduction
Colloidal magnetic fluids consist of nanometer size ferromagnetic particles dispersed in organic or aqueous solvents [1]. The spatial arrangements of the particles inside of the fluid are measured with small angle neutron scattering experiments providing the structure factor of their microstructure [2]. This static property yields information on the effective interaction of a pair of particles in the concentrated suspension [2], and also on the collective dynamics of the particles [3, 4]. There are still few comprehensive studies of the effect of the particle’s chaining and their dispersion regarding the particle’s strength of interaction, and variation in concentration, on the collective diffusion in the fluid. Magnetic fluids made of particles of sizes larger than $10\,\text{nm}$ develop self-assembled amorphous structures, clusters, or chains [1]. In ferrofluids, chaining arises due to the constant value of the magnetic moment anisotropy on each particle, and head to tail configurations that lower the electrostatic energy. Due to a surfactant layer that provides a shell to the core of the particles, the suspension gets stabilized against the attractive Van der Waals short-range attraction, resulting in an effective diameter for the particles about $d = 12\,\text{nm}$ [5]. Ferrofluids look dark. Thus visualizations of the ordering of the particles can be made with neutrons at a small angle of their scattering which provides an accurate determination of the structure factor $S(k)$ [2]. The real space inversion of this static microstructural property yields the pair correlation function which gives the probability of spatial configurations of a pair of particles separated by the most probable distance $d_{np}$ related to the scattering vector dependence of the first principal peak of the structure factor as $k_{\text{max}} \approx 2\pi / d_{np}$. Many thermodynamics properties can be determined from the knowledge of the pair correlation function. One of the most important is the compressibility modulus $\chi_T = S(k = 0) / \rho k_b T$ and the collective diffusion coefficient of the ferroparticles at zero wave vector $D_c = D_0 / S(k = 0)$, with $D_0$ the free diffusion coefficient of one particle in the solvent and $k_b T$ the thermal energy [6-10]. We used Langevin dynamics simulations to
determine the pair correlation function using the material parameters of the maghemite ferrofluid in an organic solvent without the presence of an external magnetic field [11]. The resulting $S(k)$ shows that at the dilute suspension, a set of the particles cluster without defined shape at moderate concentration and low dipole strength, however when the dipole moment per particle increases there appears formation of chains. If the concentration is further increased the particles, do not cluster, they make, however, a more dense fluid where their average distance of separation is reduced. Also, we noticed that the mean distance between particles $d_{\text{mean}} = \rho^{-1/3} \neq d_{\text{mp}}$, where $\rho$ is the suspension density.

2. Monodisperse ferrofluid

Our model suspension is made of spherical particles with a permanent magnetic moment of magnitude $\mu$. We represent a particle as a hard sphere (HS) of diameter $\sigma = 12 nm$ modeled by a Lennard-Jones short range (sr) repulsive interaction energy of depth $\varepsilon_0$ which magnitude have been measured for maghemite [5]. Thus there is a certain attraction given by the depth of the potential. The total pair direct interaction is,

$$u_{sr} = 4\varepsilon_0 \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6}, r < 2.5\sigma$$

plus the dipolar interaction energy $\phi_{di} = -\mu_0 \mu^2 D_2(\Omega_1,\Omega_2,\Omega_r) / 4\pi r^3$. $\mu_0$ is the magnetic permeability of vacuum. $D_2(\Omega_1,\Omega_2,\Omega_r) = \hat{3}(\hat{r}_{12} \cdot \mathbf{u}) (\hat{r}_{12} \cdot \mathbf{u}) - (\mathbf{u} \cdot \mathbf{u})$, Where $\hat{r} = r / r$ is a unitary vector along the vector $r$ joining two particles, and with orientation $\Omega_r$. $\mathbf{u} = (\theta, \phi)$ is a unitary vector of dipole’s orientation.

At equilibrium, the bulk profile concentration of particles around the tracer $n_{eq}^r = \rho g(r,\Omega_1,\Omega_2)$. Here $\rho = N / V$ is the number density of particles and the anisotropic correlation function $g(r,\Omega_1,\Omega_2)$. We determined the isotropic structure factor $S(k) = 1 + \rho \int d^3 r e^{i\mathbf{k} \cdot \mathbf{r}} \left[ g(r) - 1 \right]$ with $k$ the magnitude of the wave vector, $i = \sqrt{-1}$. Positional configurations of all particles at equilibrium were generated from the Langevin dynamics simulation [11]. We used the generated configurations to obtain the pair correlation function $g(r) = \langle \sum_{i,j,(i \neq j)} \delta(r - |r_{ij}|) \rangle / N 4\pi \rho r^3$. We determined structure factors for a dimensionless number density $\rho^* = \rho \sigma^3$ and reduced dipolar strength $\mu^2 = \mu^2 \mu_0 / 4\pi k_B T \sigma^3$. Here $\beta = 1 / k_B T$, $k_B$ is Boltzmann constant and $T = 300 K$ the room temperature.

3. Results

In figure 1 it is plotted the structure factor versus wave number using the parameters of the ferrofluid $Fe_2O_3$ reported in Ref. [5]. The magnetic dipolar moment is varied $\mu = \mu^* \mu_{\text{exp}}$ according to the experimental value $\mu_{\text{exp}} = 2.335210^{-19} Am^2$. For the dilute case of $\rho^* = 0.1$ and dipole moment per particle, $\mu^* = 1.31$, the particles are dispersed in the liquid. However, for the significant value of dipole magnitude $\mu^* = 6.17$ there occurs formation of chains as can be seen in the inset. A further increase of the concentration up to $\rho^* = 0.9$ produces the particles to return to a liquid like distribution and forming few pairs of particle’s dimers and a less amount of chains composed of three particles. It was not possible to compare these results with those of other authors for the same ferrofluid and conditions we studied here. However, in Ref. [2] it was determined the phase diagram of an ionic ferrofluid stabilized electrostatically: their results show that as the concentration of particles is increased the colloid evolve
from a fluid to a solid phase. On the other hand, experimentally they found that for low ionic salt systems, the most probable interparticle distance $d_{mp}$ is equal to the mean interparticle distance $d_{mp}$ in contrast to our simulation results for a sterically stabilized ferrofluid.

Figure 1 Simulation results of the structure factor versus wave number. The contact values at $k=0$ yield the compressibility modulus. The material parameters of maghemite colloid were used. At low values of density and magnetic moment per particle there is liquid order, For higher dipole moments there appears formation of chains.

Figure 2 displays the effect of successively increasing the density of the suspension $\rho^{*} = 0.1, 0.2, 0.4, 0.9$ for two values of the dipole moment $\mu^{*} = 6.17, 1.31$ respectively. The main effect observed is the presence of monomers, then a less populated set of dimers, and finally some chains in a liquid-like distribution in the available volume. For increasing density, the pair’s particle average distance of separation is lowered from $d_{\text{mean}} = 2.15\sigma$ down to the value $d_{\text{mean}} = 1.7\sigma$.

Figure 2 Same data used as in figure 1. Effect of increasing colloid density for fixed dipole moment per particle. At high density and dipole strength, the particles are tightly packed in close contact in the available volume. The largest population is made of monomers then are found dimers of particles, next trimers which are connected forming chains.
In figure 3 are plotted the collective diffusion coefficient \( D_c \) normalized to the free diffusion of a single particle \( D_0 \) in the hydrodynamic limit of zero wave number. It is given as \( D_c = D_0 / S(k = 0) \). In the left-hand side of figure 3, it is observed that the collective diffusion coefficient increases as the magnitude of dipole moment increase at high-density limit of \( \rho^* = 0.9 \) (plot with symbol ○). We are not aware of previous reports of the observation of this effect in the literature. However, a reverse behavior is shown by this collective diffusion property when the density is very low \( \rho^* = 0.1 \) (plot with symbol ●). We should note that in the former case there occurs the formation of chains, and at the highest concentration, the particles are dispersed mainly as monomer as the largest population (see figure 2).

![Figure 3](image)

**Figure 3** Calculated collective diffusion coefficient at the hydrodynamic limit of shortwave number \( k=0 \). Notice that at high density \( \rho^* = 0.9 \) this property increases (symbol ○).

From the right-hand side of figure 3, we find that our calculated \( D_c \) yields an increasing collective diffusion of particles as a function of concentration confirming the same behavior as it was observed in the experiments of Refs. [3,4] for ionic ferrofluids.

4. Conclusions
With Langevin dynamics simulations we characterized the formation of structures inside of a ferrofluid through the structure factor. In figure 3 we showed that the formation of such structures has an important effect on the collective diffusion of the particles in the hydrodynamic limit of zero wave vector dependence. In the case of the low reduced density of 0.1, the diffusion coefficient lowers for increasing dipole moment per particle. However, at the large density 0.9 of magnetic colloid, the diffusion increases for increasing dipole moment (left side of this plot). For our model of a sterically stabilized ferrofluid, we found that the collective diffusion coefficient increases with the concentration of colloid particles (see figure 3 right-hand side) and qualitatively confirms the observations made in Refs. [3,4] for ionically stabilized ferrofluids. This fact is also well known in the context of highly charged but dilute suspensions of latex colloids in electrolytes solutions, and it has been documented before for instance in Refs. [12,13]. Knowledge of the collective diffusion constant is relevant for the determination of diameters of particles but also as experimental model systems for testing statistical mechanics models of diffusion in colloidal magnetic fluids [14]. It is expected that experimental studies assisted in their interpretation by model theories of diffusion will pave the way to a better understanding and control in the manufacture of applications based on magnetic colloidal fluids. A further interesting study to be
performed will be the inclusion of the effect of the external magnetic field and the hydrodynamic interactions among particles on the collective diffusion property.

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