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Study of the structure factor anisotropy and long range correlations of ferrofluids in the dilute low-coupling regime

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ABSTRACT

Dipolar soft-sphere (DSS) fluids in the dilute low-coupling regime are studied via Molecular Dynamic simulations and the extension of a theoretical formalism previously used for dipolar hard spheres in which new terms for the virial expansion of the radial distribution function corresponding to the three-particle contribution are presented and tested for the zero and non-zero magnetic field case. A thorough comparison with simulations shows that the extended formalism is able to account for the structure factors of DSS with and without externally applied magnetic fields in the dilute low-coupling regime: quantitative agreement between theory and simulations is found for dipolar coupling parameters $\lambda \lesssim 2$, and volume fraction $\varphi \lesssim 0.25$. When $\lambda > 1$ the new added term to the virial expansion is observed to play a crucial role in order to match quantitatively theory and simulations at zero field. In the presence of an external magnetic field our tests show that further improvements are needed and only new terms with Langevin function dependences can significatively contribute to improve the predictions for the dilute low-coupling regime. Numerical simulations show that despite that the ferrofluids considered here are in the dilute low-coupling regime, when an external field is applied, important correlations along the parallel direction to the field and depletion phenomena along the perpendicular direction are observed in the averaged density surrounding a particle.

1. Introduction

Ferrofluids are colloidal suspensions of monodomain ferromagnetic nanoparticles stabilized against aggregation by steric coatings (in non-electrolyte solutions) or by electrical double layers (in aqueous solutions). Despite the differences in sizes and magnetic materials that can be used to make ferrofluid particles [1,2], the behavior of a monodisperse ferrofluid system can be characterized by two dimensionless parameters: the volume fraction of particles $\varphi = Nv_p/V$ (where N is the number of particles, v_p is the volume of a particle and V the total volume of the system), and the dipolar coupling parameter $\lambda = 0.5U_{dd}/k_BT$, where U_{dd} is the interaction energy of two particles in head-to-tail contact. Typical ferrofluids have a volume fraction of suspended magnetic material about 7% in volume, raising to a 23% when their surfactant is included [3]. The value of λ strongly depends on the material and size [2]: conventional maghemite ($\gamma-Fe_2O_3$) or magnetite (Fe_3O_4) ferrofluids with particle size 5–10 nm have a value of $\lambda < 1$, $\varepsilon-$Co particles and iron ($Fe_{0.75}Co_{0.25}$) dispersions have been reported to have typical values of $\lambda \approx 2.5$. More recently magnetite and Co particles of larger size with λ up to 7 and 14, respectively, has been synthesized [2]. Magnetite colloids extracted from magnetotactic bacteria have been reported to have even larger dipole strengths ($\lambda \approx 70$) [2]. When a uniform stationary magnetic field $\boldsymbol{H}$ is introduced, a third dimensionless parameter, the Langevin parameter $\alpha \equiv \mu H/(k_BT)$ (where μ is the typical magnetic dipole of the particles) is needed to characterize the system. The use of φ, λ and α allows a generalized description of ferrofluid systems.

In the non-aggregating regime $\lambda < 2$, the physical properties of very dilute systems ($\varphi \to 0$) are well described using the framework of the one-particle model [4], which treats the ferrofluid as an ideal paramagnetic gas of particles suspended in a liquid carrier. However, this model breaks down when either the particle concentration or the strength of the dipole–dipole interaction are increased. Although in this regime the number of aggregates is negligible, correlations among particles exist. Several theoretical models have been proposed in order to explain the magnetic properties of ferrofluids in this

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regime which are based on adapted versions of the mean-field [5,6], and mean-spherical [7–12] models, as well as the thermodynamic perturbation model [13,14]. In the non-aggregating regime, structure factors determined experimentally are a valuable source of information [15–18], but it is difficult to extract from them a detailed knowledge about the correlations of the ferrofluid particles. Thus, theoretical methods that can relate the observed structure factors to the interparticle correlations in the ferrofluid are desirable. In order to get insight about the observed radial distribution functions and structure factors a theoretical framework has been recently proposed [19] for the case of dipolar hard spheres (DHS) at zero-field in the low-coupling regime $\lambda<2$. However, that model has not been stringently tested against numerical results.

In this work we aim to study in depth the low-coupling regime via a combination of numerical simulations and an extension of the theoretical formalism of Elfimova et al. [19] to the case of dipolar soft-spheres (DSS) at zero and non-zero field. The soft-core interaction here considered is a cut-shifted Lennard-Jones potential, also called Weeks–Chander–Andersen (WCA) potential [20], of the form

$$U_{ss}(r_{ij})=\begin{cases}\varepsilon\left[1-2\left(\dfrac{\sigma}{r_{ij}}\right)^6\right]^2, & r_{ij}<2^{1/6}\sigma\\ 0, & r_{ij}>2^{1/6}\sigma\end{cases}\tag{1}$$

where r_{ij} is a distance between i and j ferroparticles, σ is an effective ferroparticle diameter including steric shell, and the energy parameter ε describes the shell hardness, $U_{ss}(r_{ij}=\sigma)=\varepsilon$. The point dipole–dipole interaction potential is

$$U_d(ij)=-\left[3\frac{(\boldsymbol{m}_i\cdot\boldsymbol{r}_{ij})(\boldsymbol{m}_j\cdot\boldsymbol{r}_{ij})}{r_{ij}^5}-\frac{(\boldsymbol{m}_i\cdot\boldsymbol{m}_j)}{r_{ij}^3}\right],\quad \boldsymbol{r}_{ij}=\boldsymbol{r}_i-\boldsymbol{r}_j\tag{2}$$

The extension of the theory for DHS to DSS systems is done by using an effective hard-sphere diameter mapping. The predictions of the theoretical model are then thoroughly compared to the results of molecular dynamics (MD) simulations. Special emphasis is given to the study of the observed anisotropy of the structure factor in the presence of magnetic fields.

2. Theoretical model

The radial distribution function can be written in terms of a virial expansion of the ferroparticle volume concentration φ [21]

$$g(r_{12})=\left\langle\exp\left[-\frac{U_{hs}(r_{12})}{k_BT}-\frac{U_d(12)}{k_BT}\right]\left(1+\sum_{p=3}^{\infty}\beta_p(12)\varphi^{p-2}\right)\right\rangle_{12}\tag{3}$$

where U_{hs} is the DHS potential. The coefficients $\beta_p(12)$ describe the influence of the other $p-2$ particles on the probability density of the two first ones and are defined by the p-particle cluster integrals based on a diagrammatic expansion method [21]. For typical ferroparticle sizes $d\sim10$ nm, the dipolar coupling constant is close to $\lambda\sim1$ and therefore Eq. (3) can be written as a power series over λ:

$$g(r)=\exp\left[-\frac{U_{hs}(r)}{k_BT}\right]\left[\left(1+\frac{\lambda^2}{3r^6}\right)[1+h_{hs}(r,\varphi)]+\lambda^2\varphi\beta_3^d(r)+\lambda^2\varphi^2\beta_4^d(r)+\lambda^3\varphi\beta_{3^*}^d(r)\right]\tag{4}$$

where distances are measured in particle diameter units $r=r_{12}/d$, and $[1+h_{hs}(r,\varphi)]$ is the hard-sphere radial distribution function, which can be found, for instance, with the help of the Perkus–Yevick approximation [21–23] or the virial expansion [24]. The $\beta_3^d(r)$ and $\beta_4^d(r)$ contributions were first calculated in Ref. [19]. A previously non-tested three-particle contribution $\lambda^3\varphi\beta_{3*}^d(r)$ which is the next term in importance in the virial expansion has been taken into account in this work. That term can be calculated in a similar way as described in [19] leading to the following expression:

$$\beta_{3*}^d(r)=\begin{cases}0, & 0<r<1\\ (r^2-6)/(18r^2), & 1\le r<2\\ -\dfrac{16}{9r^6}, & r\ge2\end{cases}\tag{5}$$

When an externally magnetic field is applied, it can be proved that the radial distribution function can be written as

$$g(r,\theta)=\exp\left[-\frac{U_{hs}(r)}{k_BT}\right]\left[\left(1+\lambda L^2(\alpha)\frac{3\cos^2\theta-1}{r^3}+\frac{\lambda^2}{3r^6}\right)[1+h_{hs}(r,\varphi)]+\lambda\varphi L^2(\alpha)\frac{3\cos^2\theta-1}{r^3}\beta_3^{df}(r)+\lambda^2\varphi\beta_3^d(r)+\lambda^2\varphi^2\beta_4^d(r)+\lambda^3\varphi\beta_{3^*}^d(r)\right],\quad\theta\equiv\theta_{12}\tag{5'}$$

where $L(\alpha)=\coth\alpha-1/\alpha$ is the squared Langevin function, θ is the angle between vector $\mathbf{r}$ and the direction of the magnetic field. The $\beta_3^{df}(r)$ coefficient is already known from a previous work by Ivanov et al. [25].

Although previous results with the three- and four-contributions calculated by the Ivanov and co-workers [19,25] strictly hold only for DHS, it is very interesting to test if such theory can be or not easily extended to dipolar soft spheres (DSS) using a simple and naive effective hard-sphere diameter d_e:

$$d_e=\int_0^{\infty}\left[1-\exp\left(-\frac{U_{ss}}{k_BT}\right)\right]dr.\tag{6}$$

The effective repulsive energy is set equal to the thermal energy during the simulations, that is $\varepsilon=k_BT$. This yields an effective hard-sphere diameter d_e quite close to σ: $d_e=1.016\sigma$.

In order to test such extension of the theory to DSS and get further insight about the dilute low-coupling regime of ferrofluids, equilibrium MD simulations are performed using the simulation package ESPResSo [26]. The simulated systems consist of $N=1000$ point-dipole particles in a cubic simulation box of side length L where periodic boundary conditions are assumed in all three-directions. The calculation of long-range dipole–dipole interactions has been substantially sped up with the help of a recently developed dipolar P^{3}M algorithm [27].

3. Simulation details

Ferrofluids are modeled as systems consisting of N spherical particles of diameter σ, distributed in a cubic simulation box of side length L. Similarly to the theory, we assume particles to be monodisperse, and exhibit a permanent point dipole moment $\boldsymbol{m}$ at its center, which can freely rotate in 3D. The interaction energy between two particles is the sum of the short range interaction equation (1) and the dipolar interaction equation (2). Periodic boundary conditions are assumed along all directions. The long-range dipole–dipole interactions are calculated using a recently developed dipolar P^{3}M algorithm [27]. The use of the dipolar P^{3}M method allows a much faster calculation of the dipolar long-range correlations than the traditional three-dimensional dipolar Ewald summation. The level of accuracy of the algorithm for computing dipolar forces and torques is set to $\delta\sim10^{-4}$ in reduced units of force $f^*=f\sigma/\varepsilon$ and torque $\tau^*=\tau/\varepsilon$.