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CONDENSED MATTER

Magnetic Properties of Dipolar Chains in Ferrofluids

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Abstract We have investigated the dipole interaction energies per particle and the local dipole field distributions in a frozen-magnetization model of a ferrofluid chain in a saturating magnetic field. A lognormal distribution of particle diameters was assumed. The interaction energies were calculated for one-dimensional arrays of dipoles with moments parallel to the chain. We have computed the energies by various approximations related to the hard sphere particle diameter distribution. A similar approach was followed for the local field distributions. It was found that the energy per particle and mean local field were largely determined by the mean particle diameter, but the distribution of local fields was sensitive to both the mean diameter and the assumptions about spatial correlations between particles of different size. Detailed results are presented for water-soluble Fe_3O_4/PAA (polyacrylic acid).

Keywords Magnetite ferrofluid particles · Dipolar chains · Magnetic dipole interactions · Particle diameter and local field distributions · Polyacrylic acid

1 Introduction

Ferrofluids contain suspended nanosized, single-domain magnetic particles [1] and, as a consequence, have many interesting applications in the medical, optical, and sensor areas [2]. Synthesis of appropriately sized nanoparticles and their homogeneous dispersion in fluids determine their potential applications. Many material properties can be tuned easily by applying external fields. For example, upon application of a modest external magnetic field, the particles form chains. In some cases, a two-dimensional hexagonal arrangement of the particle columns occurs resulting in coloring because of Bragg scattering [3]. The suspension of nanoparticles displays tunable colors in the visible range of the electromagnetic spectrum that depend on particle size and the strength of the applied field. Ferrofluids are often prepared from water-based magnetite Fe_3O_4 nanoparticles. Since the particles must remain suspended in the liquid medium, they are covered with a surfactant so that they do not agglomerate into larger particles. When the size of the particles is on the order of 10 nm, thermal agitation can destroy the agglomerations that results from magnetic interactions.

In a recent study, water-soluble Fe_3O_4/PAA (polyacrylic acid) ferrofluid nanoparticles (NPs) were synthesized using the high-temperature hydrolysis method [4]. The authors measured Faraday rotation (FR) for their synthesized ferrofluid. Their results supported earlier investigations [5, 6] of various ferrofluids where FR enhancement was attributed to magnetic chain formation [7–9]. It is evident that investigating the energies and local fields of magnetic chains can contribute to understanding the physics behind many properties such as FR enhancement and color change. Recently, we investigated excitons in three-dimensional dipolar arrays [10]; we are interested here in applying dipolar theory to ferrofluid chains. We start with a dilute fluid where we consider a situation where the particles are aligned in a field, and the temperature is lowered until the magnetization is 'frozen,' leaving a one-dimensional saturated array with dipolar couplings. The disorder comes from particle sizes and, thus, particle separations and moments. There is ample experimental information from studies of ferrofluids in zero field which show that the particle diameters generally follow the well-known lognormal distribution [11].

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In this paper, we investigate the effect of the distribution of particle diameters on the average energy per particle and the distribution of local fields. We assume that the spherical particles are in chains oriented along the direction of the applied field. The dipole moments are parallel to the field, and the particles are in contact with their nearest neighbors on the chain. The total dipole interaction energy is expressed as

$$E_{\text{dip-dip}} = -2\sum_{i=1}\sum_{j=i+1}\mu_i\mu_j/r_{ij}^3 \tag{1}$$

where μ_i denotes the dipole moment of the ith particle, which is equal to $(\pi/6)D_i^3M$ where M is the magnetization and D_i is the particle diameter (as a first approximation, we assume the saturation magnetization is distributed uniformly throughout the particle). Also, r_{ij} denotes the separation between the centers of particles i and j and is equal to (1/2) (D_i+D_j) if i and j are nearest neighbors and (1/2) $(D_i+D_j)+D_{i+1}+\ldots+D_{j-i}$ if they are more distant neighbors. Our goal is to analyze the interaction energy and the local field distribution when there is a distribution of particle diameters and to compare our results with the corresponding values obtained assuming all particles had the same diameter.

2 Interaction Energy

In the analysis of the interaction energy, we consider three approximations:

Approximation 1. The interaction energy per particle

$$E_{\text{dip-dip}}/N = -(2/N)(\pi M/6)^2\sum_i D_i{}^3\sum_{j=i+1}D_j^3/r_{ij}^3 \tag{2}$$

is evaluated by replacing the diameters (including those contributing to r_{ij}) with the mean value, <D>, which is calculated from the log normal distribution. In this approach, the double summation in (2)

$$\sum_i\sum_{j=i+1}D_i^3D_i^3/r_{ij}^3$$

becomes

$$N\varsigma(3) < D>^3.$$

where ζ denotes the Riemann zeta function. The corresponding expression for the energy is

$$E_{\text{dip-dip}}/N = -2(\pi M/6)^2\varsigma(3)\langle D\rangle^3 \tag{3}$$

Approximation 2. The interaction energy per particle is evaluated numerically for a finite array where the particle diameters are chosen randomly according to the lognormal distribution, with no correlation between sites.

Approximation 3. In the third approximation, it is assumed that there are strong correlations in the diameters of neighboring particles such that particles of approximately the same size cluster together so that we have $D_i \approx D_{i+1}$. Since the sum in the definition of $\zeta(3)$ falls off rapidly with distance if the correlations in D extend over a range on the order of 3–4 neighbor separations, one can approximate the interaction energy by adding up the contributions of different regions of D with the contributions weighted by the particle diameter distribution, $P_{\log N}(D)$. One can think of this approach as a continuum approximation to a discrete distribution of diameters. We assume all particles with the same diameter are in one region. If the number of particles with the same diameter is >>1, we can neglect 'edge effects' where regions of different diameters are in contact and sum the contributions of each region weighted by $P_{\log N}(D)$. In this case, the sum that appears in the expression for the interaction energy is approximated by

$$N\varsigma(3)\langle D^3\rangle$$

and the interaction energy takes the form

$$E_{\text{dip-dip}}/N = -2(\pi M/6)^2\varsigma(3)\langle D^3\rangle \tag{4}$$

which is to be compared with Eq. (3).

In Section 4, we will compare the numerical values of the interaction energy obtained with the three approximations.

3 Local Field Distribution

Another important property is the distribution of the local dipole field, which is the field acting on moment on site i due to dipolar interactions with all of the other particles in the chain. The distribution of local fields determines the spin resonance lineshape (provided the resonance line is inhomogeneously broadened). If one can measure the lineshape in an ESR or NMR experiment by assuming a lognormal distribution, one can work backwards and determine the parameters of the distribution. The local field at site i can be written as

$$\partial E_{\text{dip-dip}}/\partial\mu_i = H_i^{loc} = -2\sum_{j\neq i}\mu_j/r_{ij}^3. \tag{5}$$

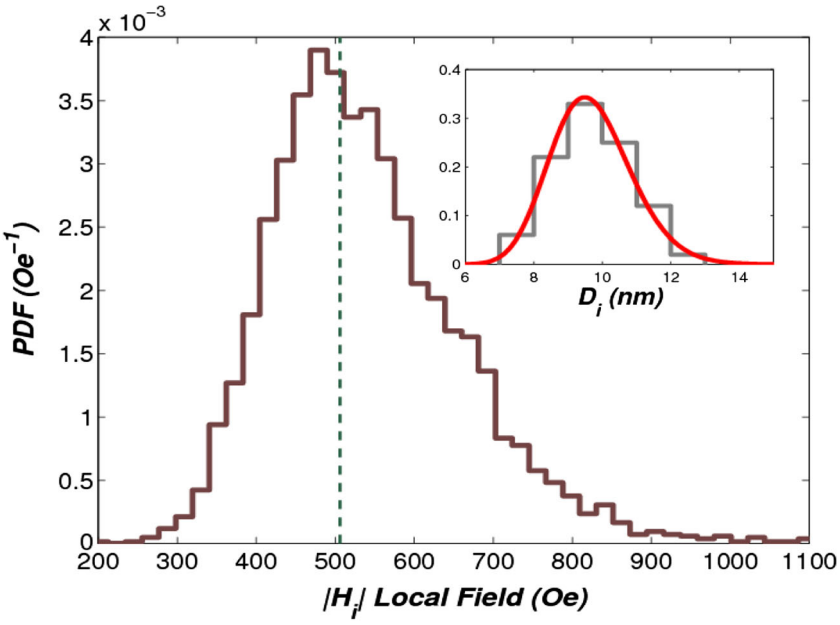

Fig. 1 Probability distribution for the local field, *PDF*, in units of Oe^{-1} calculated from Eq. (7). Magnetic moments and r_{ij} are obtained from the lognormal distribution of particle diameters with parameters appropriate to Fe_3O_4/PAA[4] and no correlation between sites. The *inset* shows the measured particle diameter distribution and the corresponding lognormal fit (see text). The *dashed line* denotes the value of the local field given by Eq. (6)

We can also study the local field distributions using the three approximations that were employed in the dipolar energy calculation. In approximation (1), we can easily obtain results for the local field, H^{loc}, since all moments $\langle\mu\rangle$ and all nearest neighbor distances $\langle D\rangle$ are the same

$$H^{loc} = -\varsigma(3)(2\pi M/3)\langle D\rangle^3/\langle D\rangle^3 = -\frac{2\pi}{3}M\,\varsigma(3). \tag{6}$$

Equation (6) is also the result obtained with third approximation.

In the second approximation, the magnetic moments are random as are the distances between them. In this case, the local field at the *i*th site takes this form

$$H_i^{\text{loc}} = -(\pi M/3)\sum_{j\neq i} D_j^3/r_{ij}^3, \tag{7}$$

where r_{ij} denotes the separation between the centers of particles as given previously. We will provide numerical results for the distributions in the next section.

4 Results

Particle diameters for Fe_3O_4/PAA are obtained from random numbers distributed in lognormal fashion. The parameters of the lognormal distribution are inferred from the data displayed in [4]: dynamic light scattering (DLS) experiments for the distribution in diameters and vibrating sample magnetometer (VSM) results for the saturation magnetization. A log normal fit of the DLS results gave the mean diameter D=9.7 nm and the variance S^2=1.4nm^2. Thus, the lognormal distribution is expressed by

$$P_{\text{Log}N}(D_i) = \frac{1}{\sqrt{2\pi}D_i\sigma}e^{-\frac{\left(\ln\left(D_i/m\right)\right)^2}{2\sigma^2}} \tag{8}$$

where the lognormal distribution parameters are $m = D^2/\sqrt{D^2+S^2} = 9.62$ and $\sigma = \sqrt{\ln((S/D)^2+1)} = 0.121$ (see inset in Fig. 1). For the saturated magnetization of the ferrofluid in [4], we have M=201 emu/cc (corresponding to M=38.8 emu/g taking the mass density of the particles to be that of Fe_3O_4). The lognormal distribution enables us to

Table 1 Dipolar interaction energy per particle (EPP) and mean local field (MLF)

	First approximation	Second approximation	Third approximation
EPP (meV)	−15.2	−15.4	−15.9
MLF (Oe)	−506	−519	−506

EPP is calculated using approximations given in the text. First, second, and third columns are obtained from Eqs. (3), (2), and (4), respectively. The MLFs are calculated using Eq. (6), first and third columns, and Eq. (7), second column. All data are obtained assuming a lognormal distribution for particle diameters with parameters appropriate to Fe_3O_4/PAA[4], and in the case of the second column, no correlation between sites. Parameters for the lognormal distribution are given in Section 3

calculate the averages of any power of the particle diameter which can be written [12] as

$$\langle D^k \rangle_{\mathrm{Log}N} = m^k e^{k^2\sigma^2/2} \tag{9}$$

We can calculate the needed average values for the formulas developed in the previous section. After evaluating Eqs. (2), (3), and (4) for the energy per particle (EPP), we obtain the numerical values shown in Table 1. The results in Table 1 are analogous to those of the kinetic theory of gases where one has the root mean square velocity, most probable velocity and the average velocity. The results for the mean local dipole field (MLF) are also shown in Table 1 for the three approaches followed in the analysis of the energy per particle.

Figure 1 displays results for the local field distribution for Fe_3O_4/PAA calculated numerically for a finite array of dipoles with diameters following the lognormal distribution. The inset in Fig. 1 shows the particle diameter distribution for Fe_3O_4/PAA taken from [4] (histogram) along with the corresponding lognormal fit (solid curve).

5 Summary and Discussion

We have calculated dipolar interaction energies and local field distributions for nanoparticle chains in saturated ferrofluids. We considered three approximations for the dipole interaction energy. Approximation (1) where the diameters are replaced by the mean value, $<D>$, is the simplest approximation. In approximation (2), where we used direct numerical evaluation, it is assumed that there is no correlation between the values of D_i in neighboring sites. In other words, D_i is not correlated with D_{i+1}, etc. In approximation (3), it is assumed that particles of approximately the same diameter cluster together so that $D_i \approx D_{i+1}$.

The results shown in Table 1 indicate that the dipole energy per particle and the mean local field depend mainly on the mean particle diameter. On the other hand, from Fig. 1, it is evident that the local field distribution is sensitive to both particle diameter and near-neighbor particle correlations since approach (3), where the particle diameters are highly correlated, leads to a delta-function distribution for the local field. Because of this, it would be interesting to investigate particle-diameter distributions in ferrofluid chains to see if there are correlations between diameters of neighboring particles, which may be present since the dipolar interaction energy for the correlated array given by approach (3) is somewhat lower than the dipolar energy of an array of particles having a lognormal diameter distribution (see Table 1).

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