

Magnetization of polydisperse colloidal ferrofluids: Effect of magnetostriction

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We exploit magnetostriction in polydisperse ferrofluids in order to generate nonlinear responses and apply a thermodynamical method to derive the desired nonlinear magnetic susceptibility. For an ideal gas, this method has been demonstrated to be in excellent agreement with a statistical method. In the presence of a sinusoidal ac magnetic field, the magnetization of the polydisperse ferrofluid contains higher-order harmonics, which can be extracted analytically by using a perturbation approach. We find that the harmonics are sensitive to the particle distribution and the degree of field-induced anisotropy of the system. In addition, we find that the magnetization is higher in the polydisperse system than in the monodisperse one, as also found by a recent Monte Carlo simulation. Thus, it seems possible to detect the size distribution in a polydisperse ferrofluid by measuring the harmonics of the magnetization under the influence of magnetostriction.

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I. INTRODUCTION

Ferrofluids (magnetic fluids) are colloidal suspensions containing single domain nanosize ferromagnetic particles dispersed in a carrier liquid [1]. These particles are usually stabilized against agglomeration by coating them with long-chain molecules (steric stabilization) or decorating them with charged groups (electrostatic stabilization). Since these particles can easily interact via applied magnetic fields, which in turn can affect the viscosity and structural properties, ferrofluids possess a wide variety of potential applications in many fields ranging from mechanical engineering [2,3] to biomedical applications [4,5]. Thus, ferrofluids have received much attention in the scientific community [6–20].

Polydispersity of ferrofluids emerges naturally since the particles in them always possess a log-normal distribution [8–10]. It has been experimentally observed that different microstructures can spontaneously form in ferrofluids [10]. This has a strong effect on the macroscopic properties of ferrofluids. In this regard, the influence of polydispersity on the magnetization of ferrofluids is of both academic and practical interest. Due to the polydispersity of ferrofluids, their structure and magnetization properties may significantly differ from those of monodisperse systems [11–14].

The structure of polydisperse ferrofluids has been discussed theoretically on the basis of a bidisperse model in which the fluids consist of two fractions of magnetic particles with significant size differences [15,17]. In a bidisperse ferrofluid, the smaller particles are affected by Brownian motion and are therefore more or less randomly dispersed. The larger magnetic dipole moment of the larger particles leads, however, to a strong interparticle force which dominates over Brownian motion. Thus the salient structure in these systems is proposed to be a chainlike aggregate formed by the larger particles. Some small particles may be attached to the ends of these aggregates, but most of them remain in the nonaggregated state [17]. These features have also been observed

in Langevin dynamics simulations [18]. In addition, Wang and Holm [18] found that the smaller particles hinder the aggregation of larger particles. Since then, that effect has been investigated in detail by Zubarev and Iskakova [21], and the influence of polydispersity on the equilibrium properties of ferrofluids was very recently investigated by Kristóf and Szalai using Monte Carlo simulations [19]. Kristóf and Szalai found that magnetization is generally higher in a polydisperse system than in the corresponding monodisperse one.

An inhomogeneous magnetic field \mathbf{H} exerts a translational force \mathbf{F} on a ferromagnetic particle given by

$$\mathbf{F} = \alpha \mathbf{H} \cdot \nabla \mathbf{H} + m_0 \cdot \nabla \mathbf{H}, \quad (1)$$

where m_0 and α are the permanent magnetic dipole moment and the magnetizability of the particle, respectively. Thus, if the permanent moment points in the direction of \mathbf{H} , the particles will be displaced towards the regions of higher field strength. In a macroscopic sample the average moment is in the direction of the field; i.e., the particles favor orientations where their permanent magnetic dipole moments are directed along the field. Thus, an inhomogeneous field acting on a macroscopic sample causes a concentration gradient with high concentrations at high field strengths. If a sample is situated partially in a field and held at constant pressure, the particle density in the field region will increase, leading to an increase of the permeability. This effect is called magnetostriction or, in general, a response of the solution to an inhomogeneous magnetic field. Magnetostriction has been extensively studied—e.g., in dipolar fluids [22], single crystals of the high- T_c cuprate $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [23], polycrystalline Fe films [24], and cylindrical type-II superconductors [25]. Unfortunately, to the best of our knowledge, so far there is neither theory nor experiments dealing with the important problem of the magnetostriction of ferrofluids. The only notable exception is ferrogels [26] which are chemically cross-linked polymer networks swollen with a ferrofluid.

To model ferrofluids we use a thermodynamical method to derive the magnetostriction-induced effective third-order nonlinear magnetic susceptibility ξ . As a sinusoidal ac magnetic field is applied, the magnetization will, in general, con-

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sist of ac fields at frequencies of the higher-order harmonics. We derive the harmonics analytically by using a perturbation approach. The aim of the present paper is to exploit magnetostriction in ferrofluids in order to generate a nonlinear response and thus a harmonic response. In experiments, measurements of the harmonic responses of magnetization have been used to obtain information of the anisotropy distribution in a ferromagnetic amorphous alloy [27].

This paper is organized as follows. In Sec. II, the nonlinear magnetic susceptibility arising from the magnetostriction is derived and the harmonics of the magnetization are extracted analytically. In Sec. III, we numerically calculate the harmonics of the magnetization under various conditions. We finish with a discussion and conclusions in Sec. IV.

II. FORMALISM

A. Nonlinear characteristic arising from magnetostriction

Let us assume that a ferrofluid is placed in an inhomogeneous magnetic field and kept at constant pressure. Then, the density of the particles in the field regions will increase due to the interaction between the permanent magnetic moments of the particles and the field leading to an increase in the permeability. This effect is called magnetostriction.

The experimental situation is the following: There is a field-affected volume with volume V_c , in which the magnetic field and the magnetic induction are denoted by H_c and B_c , respectively. Both of them should satisfy the usual magneto-static equations [28]

$$\nabla \cdot \mathbf{B}_c = 0, \quad (2)$$

$$\nabla \times \mathbf{H}_c = 0. \quad (3)$$

Here Eq. (3) implies that the magnetic field \mathbf{H}_c can be expressed as the gradient of a magnetic scalar potential Φ such that

$$\mathbf{H}_c = -\nabla \Phi. \quad (4)$$

Under appropriate boundary conditions, the inhomogeneous ferrofluid inside the field-affected volume can be represented as a region of volume V_c , surrounded by a surface S' . Such boundary conditions can be written as

$$\Phi = -\mathbf{H} \cdot \mathbf{X} \text{ on } S', \quad (5)$$

which, if the ferrofluid within V_c were uniform, would give rise to a magnetic field which is identical to \mathbf{H} (external field) everywhere within V_c . In fact, this boundary condition guarantees that even in an inhomogeneous ferrofluid the volume average of the magnetic field $\langle \mathbf{H}_c \rangle$ within V_c still equals that of the external field, $\langle \mathbf{H} \rangle$ —namely,

$$\langle \mathbf{H}_c \rangle = \frac{1}{V_c} \int \mathbf{H}_c(\mathbf{X}) d^3x = \langle \mathbf{H} \rangle. \quad (6)$$

In this case there is no external field outside the field-affected volume and (or, in practice, the external field in other areas is weak enough to be neglected). The ferrofluid with volume V is situated such that it has regions both inside and outside the

field-affected volume at a constant pressure p .

In the presence of an inhomogeneous external magnetic field \mathbf{H} , the effective linear permeability μ_e and the effective third-order nonlinear magnetic susceptibility ξ for the ferrofluid inside the field-affected volume are defined as

$$\langle \mathbf{B}_c \rangle = (\mu_e + 4\pi\xi\langle \mathbf{H} \rangle^2)\langle \mathbf{H} \rangle, \quad (7)$$

where $\langle \dots \rangle$ denotes the volume average. Equation (7) implies that there is a nonlinear relation between the magnetization M and the magnetic field $\langle \mathbf{H} \rangle$. This will be explicitly shown later in Eq. (31). Further, it is worth noting that the nonlinear term ξ of the magnetic susceptibility is actually an effective quantity. It appears due to the fact that the particles can receive a translational force which drives them into the field-affected volume in the presence of an inhomogeneous field. In this regard, rather than \mathbf{H} , we should use $\langle \mathbf{H} \rangle$ in Eq. (7) in order to derive the (effective) nonlinear term ξ .

Alternatively, based on thermodynamics, the permeability μ_H including the incremental part due to the magnetostriction can be defined as

$$\begin{aligned} \mu_H &= \left(\frac{\partial \langle \mathbf{B}_c \rangle}{\partial \langle \mathbf{H} \rangle} \right)_{T,p} = \left(\frac{\partial \langle \mathbf{B}_c \rangle}{\partial \langle \mathbf{H} \rangle} \right)_{T,p} + \int_{d_{\min}}^{d_{\max}} f(d) \left(\frac{\partial \langle \mathbf{B}_c \rangle}{\partial \rho(d)} \right)_{T,\langle \mathbf{H} \rangle} \\ &\quad \times \left(\frac{\partial \rho(d)}{\partial \langle \mathbf{H} \rangle} \right)_{T,p} dd, \end{aligned} \quad (8)$$

where ρ stands for the density of the part of the ferrofluid inside the field-affected volume and d_{\min} (or d_{\max}) denotes the minimum (or maximum) particle diameter. Here the size distribution of particles $f(d)$ satisfies the known log-normal law [9,29]

$$f(d) = \frac{1}{\sqrt{2\pi\sigma d}} \exp\left[-\frac{\ln^2(d/\delta)}{2\sigma^2}\right], \quad (9)$$

where σ is the standard deviation of $\ln d$ and δ the median diameter.

In Eq. (8), $(\partial \langle \mathbf{B}_c \rangle / \partial \langle \mathbf{H} \rangle)_{T,p}$ represents the effective permeability including all nonlinear effects at a constant density. As a matter of fact, regarding both Eqs. (7) and (8), the total effective third-order nonlinear susceptibility generally contains two contributions. The first is the magnetostriction-induced one considered in this work, and the other is the normal-saturation contribution. At large field intensities, the higher terms of the Langevin function should be taken into account. This contribution is negative and is called normal saturation. In contrast, the magnetostriction has a positive contribution. In this work, we assume that the field is moderate such that the normal-saturation contribution is weak enough to be neglected. It should be noted that the argument of the Langevin function can become large for a very small number of large particles in the tail of the size distribution. Further, we shall also neglect the normal-saturation contribution resulting from the very small amount of the large particles since this contribution might be expected to have a very weak effect on the total effective third-order susceptibility. To summarize the above, throughout this work, only the magnetostriction-induced contribution is considered.

Using the above assumptions $(\partial\langle\mathbf{B}_c\rangle/\partial\langle\mathbf{H}\rangle)_{T,p}\equiv\mu_e$ can be given by the anisotropic Clausius-Mossotti equation—namely [30],

$$\frac{g_L(\mu_e - \mu_2)}{\mu_2 + g_L(\mu_e - \mu_2)} = \frac{4\pi}{3} \int_{d_{\min}}^{d_{\max}} f(d)N(d) \left(\alpha(d) + \frac{m_0(d)^2}{3k_B T} \right) dd, \quad (10)$$

where μ_2 denotes the permeability of the carrier liquid, $m_0(d)$ [or $\alpha(d)$] the permanent magnetic dipole moment [or magnetizability] of a particle with diameter d , $N(d)$ is the number density of particles with diameter d , k_B the Boltzmann constant, and T the temperature. Regarding Eq. (10), more issues should be remarked on. It is known that the usual (isotropic) Clausius-Mossotti equation does not include the particle-particle interaction. When Lo and Yu [30] studied the field-induced structure transformation in electrorheological solids, they succeeded in developing a generalized Clausius-Mossotti equation by introducing a local-field factor β' which reflects the particle-particle interaction between the particles in an anisotropic lattice. This generalized Clausius-Mossotti approach [Eq. (10)] is a self-consistent determination of the local field due to a lattice of dipole moments. In other words, Eq. (10) should be expected to include particle-particle interactions (at least to some extent) and the degree of the particle-particle interactions depends on how much g_L deviates from $1/3$ (note that here $g_L = \beta'/3$), where g_L represents the demagnetizing factor in the longitudinal field case. In particular, the case when $1/g_L = 3$ (or $g_L = 1/3$) corresponds to the isotropic case, which yields the well-known (isotropic) Clausius-Mossotti equation. It is worth noting that there is a sum rule $g_L + 2g_T = 1$ [31], where g_T is the demagnetizing factor in the transverse field case. For electrorheological fluids, similar factors were measured in simulations [32,33].

In Eq. (10), the term $m_0(d)^2/3k_B T$ results from the average contribution of the permanent magnetic dipole moment to the average value of the work required to bring a particle with diameter d into the field $\langle\mathbf{H}\rangle$. More precisely, the mean value of the component of the dipole moment in the direction of the field is given by

$$m_0(d)L(\gamma) = \frac{m_0(d)^2}{3k_B T} \langle H \rangle, \quad (11)$$

with $\gamma = m_0(d)\langle H \rangle/k_B T$. That is, we set the Langevin function to $L(\gamma) = \gamma/3$. Regarding this relation, the following issues should be noted. In the present work, we shall adopt a perturbation approach [34] [see Sec. II C], which is suitable for a weak nonlinearity. In the perturbation approach, it is well established that the effective third-order nonlinear susceptibility can be calculated from the linear field [35], while the effective higher-order nonlinearity must depend on the nonlinear field [34]. In fact, we could have adopted a self-consistent mean-field approach [36], but the perturbation approach appears to be more convenient for analytic expressions [36]. Thus, to be able to focus on (weak) third-order nonlinearity, it suffices to use the Clausius-Mossotti equation [Eq. (10)] by taking into account the linear relation

only—i.e., $L(\gamma) = \gamma/3$. Due to the same reason, in what follows we shall omit the contribution from the nonlinear field, too.

Regarding the incremental permeability due to the magnetostriction, namely, the last term in Eq. (8)

$$\int_{d_{\min}}^{d_{\max}} f(d) \left(\frac{\partial\langle\mathbf{B}_c\rangle}{\partial\rho(d)} \right)_{T,\langle\mathbf{H}\rangle} \left(\frac{\partial\rho(d)}{\partial\langle\mathbf{H}\rangle} \right)_{T,p} dd \equiv 12\pi\xi\langle\mathbf{H}\rangle^2,$$

we obtain

$$12\pi\xi\langle\mathbf{H}\rangle^2 = \int_{d_{\min}}^{d_{\max}} f(d)\langle\mathbf{H}\rangle \left(\frac{\partial\mu_e}{\partial\rho(d)} \right)_{T,\langle\mathbf{H}\rangle} \left(\frac{\partial\rho(d)}{\partial\langle\mathbf{H}\rangle} \right)_{T,p} dd. \quad (12)$$

This equation is valid for the lowest-order perturbation. The differential increase of the density inside the field-affected volume $d\rho(d)$ corresponds to an increase in mass given by $V_c d\rho(d)$. This increase is equal to the decrease in mass outside the field-affected volume given by $-\rho(d)d(V-V_c) = -\rho(d)dV$, so that $d\rho(d) = -[\rho(d)/V_c]dV$. Thus, we may rewrite Eq. (12) as

$$12\pi\xi\langle\mathbf{H}\rangle^2 = - \int_{d_{\min}}^{d_{\max}} f(d)\langle\mathbf{H}\rangle \left(\frac{\partial\mu_e}{\partial\rho(d)} \right)_{T,\langle\mathbf{H}\rangle} \frac{\rho(d)}{V_c} \left(\frac{\partial V}{\partial\langle\mathbf{H}\rangle} \right)_{T,p} dd. \quad (13)$$

Next, we can obtain $(\partial V/\partial\langle\mathbf{H}\rangle)_{T,p}$ based on the differential of the free energy dF :

$$dF = -SdT - p dV + \frac{V_c}{4\pi} \langle\mathbf{H}\rangle d\langle\mathbf{B}_c\rangle, \quad (14)$$

where S denotes the entropy. Introducing the transformed free enthalpy \bar{G} ,

$$\bar{G} = F + pV - \frac{V_c}{4\pi} \langle\mathbf{H}\rangle \langle\mathbf{B}_c\rangle, \quad (15)$$

we obtain the following expression for its differential:

$$d\bar{G} = -SdT + V dp - \frac{V_c}{4\pi} \langle\mathbf{B}_c\rangle d\langle\mathbf{H}\rangle. \quad (16)$$

From this equation, we find

$$\left(\frac{\partial V}{\partial\langle\mathbf{H}\rangle} \right)_{T,p} = - \frac{V_c}{4\pi} \left(\frac{\partial\langle\mathbf{B}_c\rangle}{\partial p} \right)_{T,\langle\mathbf{H}\rangle} = - \frac{V_c\langle\mathbf{H}\rangle}{4\pi} \left(\frac{\partial\mu_e}{\partial p} \right)_{T,\langle\mathbf{H}\rangle}. \quad (17)$$

Then, the substitution of this into Eq. (13) leads to

$$12\pi\xi\langle\mathbf{H}\rangle^2 = \int_{d_{\min}}^{d_{\max}} f(d) \frac{\langle\mathbf{H}\rangle^2}{4\pi} \rho(d) \left(\frac{\partial\mu_e}{\partial\rho(d)} \right)_{T,\langle\mathbf{H}\rangle} \left(\frac{\partial\mu_e}{\partial p} \right)_{T,\langle\mathbf{H}\rangle} dd. \quad (18)$$

We now use

$$\left(\frac{\partial \mu_e}{\partial p}\right)_{T, \langle \mathbf{H} \rangle} = \left(\frac{\partial \mu_e}{\partial \rho(d)}\right)_{T, \langle \mathbf{H} \rangle} \left(\frac{\partial \rho(d)}{\partial p}\right)_{T, \langle \mathbf{H} \rangle} = \beta \rho(d) \left(\frac{\partial \mu_e}{\partial \rho(d)}\right)_T, \quad (19)$$

$$\left(\frac{\partial \mu_e}{\partial \rho}\right)_T = \frac{4\pi}{m_m} \left(\alpha + \frac{m_0^2}{3k_B T}\right), \quad (25)$$

where $\beta = -(1/V)(\partial V/\partial p)_T$ is the compressibility in the absence of the field. In the last term of Eq. (19), terms depending on $\langle \mathbf{H} \rangle$ have been neglected since they lead to terms in powers of $\langle \mathbf{H} \rangle$ higher than the second term in Eq. (18). In the same approximation, after substitution of Eq. (19) into Eq. (18) we obtain

$$12\pi\xi\langle \mathbf{H} \rangle^2 = \int_{d_{\min}}^{d_{\max}} f(d) \frac{\langle \mathbf{H} \rangle^2}{4\pi} \beta \rho(d)^2 \left(\frac{\partial \mu_e}{\partial \rho(d)}\right)_T^2 dd. \quad (20)$$

Thus, we have

$$\xi = \frac{\beta}{48\pi^2} \int_{d_{\min}}^{d_{\max}} f(d) \rho(d)^2 \left(\frac{\partial \mu_e}{\partial \rho(d)}\right)_T^2 dd. \quad (21)$$

So far, the effective third-order nonlinear magnetic susceptibility ξ has been derived in terms of the compressibility, size distribution function, and the differential of effective linear permeability with respect to the density.

B. Comparison with a statistical method

The increase of the density $\Delta\rho$ due to magnetostriction can be calculated from $(\partial V/\partial \langle \mathbf{H} \rangle)_{T,p}$. Details are as follows:

$$\begin{aligned} \Delta\rho &= \int_{d_{\min}}^{d_{\max}} \int_0^{\langle \mathbf{H} \rangle} f(d) \left(\frac{\partial \rho(d)}{\partial \langle \mathbf{H} \rangle}\right)_{T,p} d\langle \mathbf{H} \rangle dd \\ &= \int_{d_{\min}}^{d_{\max}} \int_0^{\langle \mathbf{H} \rangle} -f(d) \frac{\rho(d)}{V_c} \left(\frac{\partial V}{\partial \langle \mathbf{H} \rangle}\right)_{T,p} d\langle \mathbf{H} \rangle dd \\ &= \int_{d_{\min}}^{d_{\max}} \int_0^{\langle \mathbf{H} \rangle} \frac{\langle \mathbf{H} \rangle \rho(d)}{4\pi} \left(\frac{\partial \mu_e}{\partial p}\right)_{T, \langle \mathbf{H} \rangle} d\langle \mathbf{H} \rangle dd \\ &= \int_{d_{\min}}^{d_{\max}} \int_0^{\langle \mathbf{H} \rangle} \frac{\langle \mathbf{H} \rangle \beta \rho(d)^2}{4\pi} \left(\frac{\partial \mu_e}{\partial \rho(d)}\right)_T d\langle \mathbf{H} \rangle dd. \quad (22) \end{aligned}$$

To obtain this equation, Eq. (19) has been used, which means that in the expression for $\Delta\rho$ terms in powers of $\langle \mathbf{H} \rangle$ higher than the second have been neglected. Then, the integration can be performed, and we obtain

$$\Delta\rho = \int_{d_{\min}}^{d_{\max}} \frac{\langle \mathbf{H} \rangle^2}{8\pi} \beta \rho(d)^2 \left(\frac{\partial \mu_e}{\partial \rho(d)}\right)_T dd. \quad (23)$$

For comparing with a statistical method, let us apply our formalism to a (monodisperse) ideal gas [22]. For its effective permeability, in view of $g_L = 1/3$, Eq. (10) can be rewritten as

$$\frac{\mu_e - 1}{\mu_e + 2} = \frac{4\pi}{3} N \left(\alpha + \frac{m_0^2}{3k_B T}\right). \quad (24)$$

For the ideal gas, $\mu_e \sim 1$, and hence we obtain

where m_m denotes the mass of a single molecule, $m_m = M/N_A$. Here M is the molecular weight and N_A the Avogadro constant. For this case, using $\beta = M/\rho RT$, Eq. (23) predicts

$$\Delta\rho = \frac{N_A \langle \mathbf{H} \rangle^2 \rho}{2RT} \left(\alpha + \frac{m_0^2}{3k_B T}\right). \quad (26)$$

Here R represents the molar gas constant.

This result [Eq. (26)] can also be achieved by using a statistical method. Because of Boltzmann's distribution law, $n^{\langle \mathbf{H} \rangle}$, the number of moles per cm^3 of the gas at a point with field strength $\langle \mathbf{H} \rangle$, is given by

$$n^{\langle \mathbf{H} \rangle} = n^{(0)} \exp(-W/k_B T), \quad (27)$$

where $n^{(0)}$ is the number of moles per cm^3 of the gas at a point with zero field and W the average value of the work required to bring a molecule into the field $\langle \mathbf{H} \rangle$:

$$W = -\frac{1}{2} \left(\alpha + \frac{m_0^2}{3k_B T}\right) \langle \mathbf{H} \rangle^2. \quad (28)$$

Thus, we have

$$n^{\langle \mathbf{H} \rangle} = n^{(0)} \exp\left[\frac{1}{2} \left(\alpha + \frac{m_0^2}{3k_B T}\right) \langle \mathbf{H} \rangle^2 / k_B T\right]. \quad (29)$$

Let us neglect the terms in higher than second powers of $\langle \mathbf{H} \rangle$, and we have

$$\Delta\rho = M(n^{\langle \mathbf{H} \rangle} - n^{(0)}) = \frac{N_A \langle \mathbf{H} \rangle^2 \rho}{2RT} \left(\alpha + \frac{m_0^2}{3k_B T}\right). \quad (30)$$

For an ideal gas, Eq. (30) yields exactly the same result as Eq. (26), albeit derived using a different approach. This shows the consistency of our arguments.

C. Magnetization and high-order harmonics

The orientational magnetization (z axis) has the general form

$$\mathbf{M} = \frac{\mu_e - \mu_2}{4\pi} \langle \mathbf{H} \rangle + \xi \langle \mathbf{H} \rangle^3. \quad (31)$$

Here, the higher-order terms have been omitted. We use an inhomogeneous sinusoidal ac field $\mathbf{H} = (l_z/L_z) H_{ac}(t) \hat{\mathbf{z}} = (l_z/L_z) H_{ac} \hat{\mathbf{z}} \sin(\omega t)$, where $0 < l_z \leq L_z$, with L_z being the length of the field-affected volume along the z axis. Without loss of generality, we set $L_z = 1$ in the following. We now obtain

$$M = \frac{\mu_e - \mu_2}{8\pi} H_{ac}(t) + \frac{\xi}{8} H_{ac}(t)^3. \quad (32)$$

In view of $H_{ac}(t) = H_{ac} \sin(\omega t)$, the magnetization M can be expressed in terms of the odd-order harmonics such that

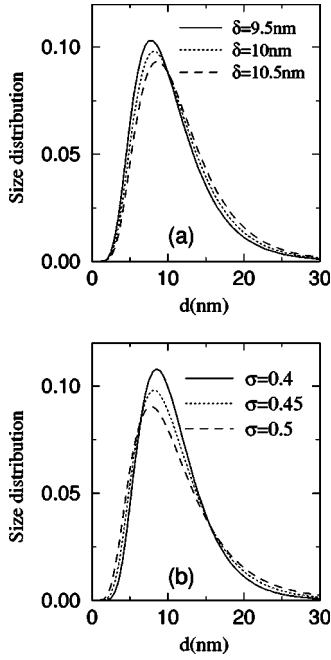


FIG. 1. Lognormal distribution of particles for different (a) median diameter δ and (b) standard deviation σ . Parameters: (a) $\sigma = 0.45$ and (b) $\delta = 10$ nm.

$$M = M_{\omega} \sin(\omega t) + M_{3\omega} \sin(3\omega t), \quad (33)$$

where the fundamental and third-order harmonics are given by

$$M_{\omega} = \frac{\mu_e - \mu_2}{8\pi} H_{ac} + \frac{3\xi}{32} H_{ac}^3, \quad (34)$$

$$M_{3\omega} = -\frac{\xi}{32} H_{ac}^3. \quad (35)$$

In the above derivation, we have used the identity $\sin^3(\omega t) = (3/4)\sin(\omega t) - (1/4)\sin(3\omega t)$.

III. NUMERICAL RESULTS

Without any loss of generality, we choose the following parameters for our numerical calculations: $\mu_2 = 1$ (nonmagnetic carrier fluid), density of the bulk material of the particles 7 g/cm^3 , $H_{ac} = 20 \text{ Oe}$, $\beta = 0.62 \times 10^{-10} \text{ cm s}^2/\text{g}$, $\alpha(d) = 0$ (due to the small size of the particles), and $T = 298 \text{ K}$. In addition, the volume fraction of the particles is set to be 0.08, and the saturation magnetization of the bulk material of the particles is 450 emu. Finally, setting $d_{\min} = 1 \text{ nm}$ and $d_{\max} = 30 \text{ nm}$ ensures

$$\int_{d_{\min}}^{d_{\max}} f(d) dd \approx 1,$$

as expected.

Based on the model parameters, we calculated the dipolar coupling constant [37] $\lambda(\delta) = m_0(\delta)^2 / \mu_0 k_B T \delta^3$ and found $\lambda(9.5 \text{ nm}) = 1.16$, $\lambda(10 \text{ nm}) = 1.35$, and $\lambda(10.5 \text{ nm}) = 1.56$,

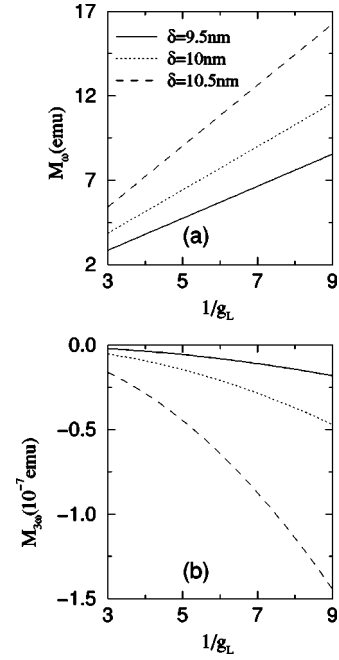


FIG. 2. Polydisperse case. (a) Fundamental and (b) third-order harmonics of the magnetization against the degree of anisotropy $1/g_L$ for different median diameter δ . Parameter: $\sigma = 0.45$.

which ensures the assumption that the particle interaction in our system is weak.

In Fig. 1, we display the size distribution of the particles in the lognormal law for different (a) median diameter δ and (b) standard deviation σ . Figure 2 shows the fundamental [Fig. 2(a)] and third-order [Fig. 2(c)] harmonics of the magnetization as a function of the degree of anisotropy $1/g_L$ for different median diameters δ . The size distribution of the particles is shown in Fig. 1(a). It is found that increasing the degree of anisotropy $1/g_L$ causes both the fundamental and third-order harmonics to increase. Also, a higher median diameter δ leads to larger harmonics.

In Fig. 3, the fundamental [Fig. 2(b)] and third-order [Fig. 2(c)] harmonics of the magnetization are plotted as a function of $1/g_L$ for different standard deviations σ . The lognormal size distribution of the particles is shown in Fig. 1(b). Again, it is shown that the harmonics increase with increasing median diameter δ .

Finally, to compare the above polydisperse case with the corresponding monodisperse one, we study the monodisperse case in Fig. 4 for three different diameters which have the same values as the median diameters used in Fig. 2. In the monodisperse case, it is also evident that increasing the degree of anisotropy $1/g_L$ causes both the fundamental and third-order harmonics to increase. In addition, larger diameter leads to larger harmonics. It is worth noting that both the fundamental and third-order harmonics of the magnetization are higher in the polydisperse system than in the monodisperse one when comparing Fig. 2 with Fig. 4. In particular, the third-order harmonics of the polydisperse system can be of two orders of magnitude larger than those of the monodisperse system. In other words, the magnetization is higher in the polydisperse system than in the monodisperse one, due

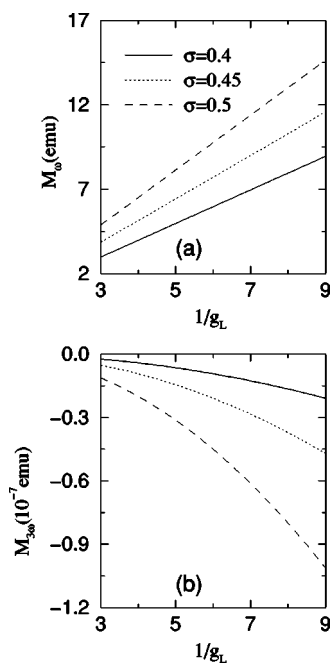


FIG. 3. Polydisperse case. (a) Fundamental and (b) third-order harmonics of the magnetization against the degree of anisotropy $1/g_L$ for different standard deviation σ . Parameter: $\delta=10$ nm.

to the fact that for this comparison the volume fraction of the particles is fixed. This is in agreement with the findings of Ref. [19] where a Monte Carlo simulation was used to study the influence of polydispersity on the equilibrium properties of ferrofluids.

IV. DISCUSSION AND CONCLUSION

Here some comments are in order. In the present paper, we have exploited magnetostriction in ferrofluids in order to generate nonlinear responses. The proposed mechanism should work for dc magnetic fields. It will also work for ac fields with frequency $\nu=\omega/(2\pi)$ if the size of the sample is not greater than c_s/ν , where c_s is the sound velocity. Thus, ν can be up to kHz or so. Otherwise the required mass density oscillations will not be able to keep up with the rapid changes in the magnetic field.

To obtain the lowest-order (i.e., cubic) nonlinearity, we have assumed that material properties such as permeability of the polydisperse system can be calculated as a linear superposition of the corresponding values in the monodisperse systems; see Eqs. (8), (10), and (22). For Eq. (8), the linear superposition should hold since the nonlinear term ξ is actually an effective quantity which results from all the monodisperse systems. For Eq. (10), we used the linear superposition again. The reason is that the right-hand side of Eq. (10) actually represents the effective contribution from two parts: the induced magnetization (which has been assumed to disappear due to the small size of the particles in our numerical calculations) and the permanent-moment-related magnetization. In addition, once the inhomogeneous field is applied, the particles with different sizes are able to move into the field-affected volume, thus yielding an increasing particle

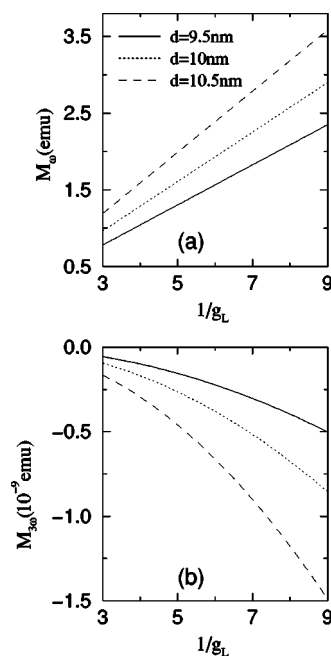


FIG. 4. Monodisperse case. (a) Fundamental and (b) third-order harmonics of the magnetization against the degree of anisotropy $1/g_L$ for different diameter d .

density. In this regard, for Eq. (22), the linear superposition should be used naturally.

Nonlinear optical materials with large values of (effective) third-order nonlinear dielectric susceptibilities [38] are in great need in industrial applications such as nonlinear optical switching devices for use in photonics, and real-time coherent optical signal processors, and so on. Due to the similarity between magnetics and dielectrics, the present (effective) third-order nonlinear magnetic susceptibilities are expected to have some potential applications in nonlinear magnetic devices.

Throughout the paper, only odd-order harmonics are induced to appear. As a matter of fact, if one applies an ac magnetic field superimposed onto a dc field, the even-order harmonics should appear [27]. That is due to the coupling between the two kinds of fields. On the other hand, since the second-order harmonics are often of several orders of magnitude larger than the corresponding third-order harmonics, the second-order harmonics are more attractive for the experimental measurements [27].

We have considered the fundamental and third-order harmonics. In fact, we can consider much higher-order harmonics [36,39], such as fifth-order, seventh-order, etc. In doing so, we need to keep more terms in powers of $\langle \mathbf{H} \rangle$ higher than the second in Eq. (18). Accordingly, more terms should be included in Eq. (31). However, such higher-order harmonics are often of several orders of magnitude smaller than the third-order and, thus, less attractive.

In the numerical calculations, we have omitted the magnetizability of the particles due to the fact that the sizes of the particles are very small in ferrofluids. For these particles, the permanent magnetic dipole moments play the main role. However, in the case of a magnetorheological fluid, the magnetizability of the particles should be taken into account

since the particle sizes range from 2 to 20 μm —about three orders of magnitude larger than in ferrofluids. Fortunately, for treating magnetorheological fluids, the present theory holds as well.

In this paper, we have investigated a log-normal distribution [see Eq. (9)]. Our theory could be extended to treat other particle distributions as well. For instance, for a Γ distribution [40], we should replace Eq. (9) with

$$f(d) = \frac{1}{d_0} \left(\frac{d}{d_0} \right)^a \frac{e^{-d/d_0}}{\Gamma(a+1)},$$

where d_0 and a are the parameters of the distribution and Γ denotes the gamma function.

In view of the existing theory which deals with the influence of polydispersity on the magnetization of ferrofluids, such as a perturbation theoretical study [12] and a cluster expansion study [14], it is instructive to compare the present theory with these methods.

To sum up, we have used a thermodynamical method to derive the nonlinear magnetic susceptibility resulting from magnetostriction, which further yields the harmonics of magnetization in response to an applied ac magnetic field. For an ideal gas, this method has been shown to be in excellent agreement with a statistical method. It has been shown that

the harmonics are sensitive to the particle distribution (namely, median diameters and standard deviations) and degree of field-induced anisotropy of the system. In addition, we also find that the magnetization is higher in the polydisperse system than in the corresponding monodisperse one, which is in agreement with previous findings. Thus, it seems possible to detect the size distribution in the polydisperse ferrofluids by measuring the harmonics of the magnetization of colloidal ferrofluids under the influence of magnetostriction. In detail, the size distribution might be achieved by using Eq. (21) and choosing a suitable distribution for $f(d)$ to fit experimental data.

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