Magnetization of concentrated polydisperse ferrofluids: Cluster expansion

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The equilibrium magnetization of concentrated ferrofluids described by a system of *polydisperse* dipolar hard spheres is calculated as a function of the internal magnetic field using the Born-Mayer or cluster expansion technique. This paper extends the results of Huke and Lücke [Phys. Rev. E **62**, 6875 (2000)] obtained for *monodisperse* ferrofluids. The magnetization is given as a power series expansion in two parameters related to the volume fraction and the coupling strength of the dipolar interaction, respectively.

I. INTRODUCTION

Ferrofluids [1] are suspensions of ferromagnetic particles of about 10 nm diameter in a carrier fluid. The particles are stabilized against aggregation by coating with polymers or by electrostatic repulsion of charges brought on their surface. As long as the concentration of the particles is low, the equilibrium magnetization of a ferrofluid, is that of an ideal paramagnetic gas. In highly concentrated ferrofluids on the other hand, the magnetization is influenced by effects of particle-particle interactions.

We studied these effects for ferrofluids that are described by a system of identical dipolar hard spheres in Ref. [2], hereafter referred to as paper I. In that paper, we used the technique of the Born-Mayer or cluster expansion technique to evaluate the equilibrium magnetization as a series expansion in terms of the volume fraction $\phi = N\pi D^3/6V$ and a dipolar coupling parameter $\epsilon = m^2/4\pi\mu_0 kT$, with N/V being the particle density, and D and m being the common hard sphere diameter and magnetic moment of the particles, respectively.

However, real ferrofluids are polydisperse, i.e., the particles vary in size and magnetic moment. This property has a strong influence on the equilibrium magnetization, for concentrated as well as for dilute fluids. The goal of this paper is to generalize the findings of paper I to include the effects of polydispersity.

The linear response problem of determining the static initial susceptibility χ of a mixture of dipolar hard spheres was investigated already for the equivalent electric case in the framework of integral theories: The mean spherical model [3] was extended to binary or multicomponent mixtures [4–9]. The reference hypernetted chain method [10] was also applied to bidisperse systems [11,12]. Recently [13], the mean spherical model was used within the algebraic perturbation theory [14], however, without leading to new results for the initial susceptibility. The mean spherical model was also extended to polydisperse ferrofluids in arbitrary high fields [15,16]. Another theory dealing with arbitrary fields is the high temperature approximation [17]. A variant of this theory was proposed in Ref. [18] and extended in Ref. [19].

Our calculation follows closely that of paper I. Therein the application of the cluster expansion technique to a monodisperse system of dipolar hard spheres resulted in an expression for the magnetization M that can be put into the form

$$M = M_{\text{sat}} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \phi^m \epsilon^n L_{m,n}(\alpha), \qquad (1.1)$$

where M_{sat} is the saturation magnetization of the fluid. The functions $L_{m,n}(\alpha)$ were given explicitly in terms of analytic expressions in the dimensionless magnetic field α. We calculated $L_{2,2}(\alpha)$ and some of the $L_{1,n}(\alpha)$. Lower orders vanish, except for the Langevin function $L_{0,0}(\alpha)$.

In the polydisperse case discussed here, the parameters ϕ, ϵ, and α are replaced by more generally defined quantities $\bar{\phi}$, $\bar{\epsilon}$, and $\bar{\alpha}$ (cf. Sec. III). The calculated $L_{m,n}$ transform into onefold, twofold, or threefold sums over all particles, where the individual addends are analytical functions of the magnetic moments, diameters of the involved particles, and of the reduced magnetic field $\bar{\alpha}$.

The paper is organized as follows. In Sec. II, we explain the principles of the cluster expansion technique. The main part of the paper is Sec. III, where we generalize the results of paper I for the equilibrium magnetization in the monodisperse case to polydisperse ferrofluids. The findings are discussed in Sec. IV using sample distributions. In Sec. V, the results are compared to the experimental data. We conclude in Sec. VI.

II. CLUSTER EXPANSION: APPLICATION TO THE SYSTEM OF DIPOLAR HARD SPHERES

Here, we recapitulate briefly the principle of the Born-Mayer or cluster expansion technique: Consider a system of particles $i = 1, \ldots, N$ interacting with an external potential V_i and with each other via a potential V_{ij}. To calculate thermodynamic properties of the system one has to find the canonical partition function

$$Z = \int \exp\left[-\sum_k v_k - \sum_{i<j} v_{ij} \right] d\Gamma. \qquad (2.1)$$

Here, $v_i = V_i/kT$, $v_{ij} = V_{ij}/kT$, and $d\Gamma$ means integration over the configuration space. The kinetic energy of the particles, if important, can be thought to be included in the terms V_i. One now writes

$$Z = \int \prod_k e^{-v_k} \prod_{i<j} (1 + f_{ij}) d\Gamma, \qquad (2.2)$$

where

$$f_{ij}=e^{-v_{ij}}-1. \tag{2.3}$$

If the typical interaction energy is small compared to kT, the f_{ij} can be considered as small parameters for the expansion of the integrand in Eq. (2.2). The leading terms factorize into low-dimensional integrals that can be calculated at least numerically.

In the system of dipolar hard spheres (monodisperse or polydisperse), the interaction potential V_{ij} consists of a dipole-dipole (DD) interaction and a hard core (HC) repulsion part, $V_{ij}=V_{ij}^{DD}+V_{ij}^{HC}$, where the first part is given by

$$V_{ij}^{DD}=-\frac{3(\mathbf{m}_i\cdot\hat{\mathbf{r}}_{ij})(\mathbf{m}_j\cdot\hat{\mathbf{r}}_{ij})-\mathbf{m}_i\cdot\mathbf{m}_j}{4\pi\mu_0 r_{ij}^3} \tag{2.4}$$

for two particles with magnetic moments $\mathbf{m}_i$ and $\mathbf{m}_j$ at a distance $\mathbf{r}_{ij}=\mathbf{x}_i-\mathbf{x}_j$, with $r_{ij}=|\mathbf{r}_{ij}|$ and $\hat{\mathbf{r}}_{ij}=\mathbf{r}_{ij}/r_{ij}$. For particles with diameters D_i and D_j, one has $V_{ij}^{HC}(r_{ij})=\infty$ if $r_{ij}<D_{ij}=(D_i+D_j)/2$, and $V_{ij}^{HC}(r_{ij})=0$ otherwise.

Taking the thermodynamic limit in a system of dipolar particles requires some care because of the long range character of the forces [21]. We circumvented this problem by decomposing the dipolar potentials into a short range and a long range part, and replacing the latter by an effective mean field. Within this approach, a particle experiences the local magnetic field

$$\mathbf{H}_{local}=\mathbf{H}_s+\mathbf{H}_{dipole,near}=\mathbf{H}+\frac{\mathbf{M}}{3}+\mathbf{H}_{dipole,near}. \tag{2.5}$$

It consists of the dipolar near field $\mathbf{H}_{dipole,near}$ that is produced by the other particles within a sphere of radius R_s and of an effective "external" field

$$\mathbf{H}_s=\mathbf{H}+\frac{\mathbf{M}}{3}, \tag{2.6}$$

seen by the particle in question at the center of the sphere. Here, $\mathbf{H}$ is the macroscopic internal magnetic field and $\mathbf{M}$ the sought after equilibrium magnetization. Thus, when evaluating the partition function one has to take

$$V_i=-\mathbf{m}_i\cdot\mathbf{H}_s \tag{2.7}$$

as the external potential. The radius R_s of the sphere has to be taken to be sufficiently large to allow the far-field dipolar contributions to be replaced by those of a continuum—cf. paper I for details. Neither the kinetic energy of the magnetic particles, nor the carrier fluid has to be taken into account in the partition function, since these terms do not contribute to the equilibrium magnetization. The configuration space is thus given by the positions $\mathbf{x}_i$ of all particles and the orientations Ω_i of their magnetic moments: $d\Gamma=d^n\mathbf{x}_i d^n\Omega_i$.

In paper I, we used in addition also an expansion in the dipolar interaction: The f terms were expanded as

$$f_{ij}=e^{-v_{ij}^{HC}}e^{-v_{ij}^{DD}}-1=f_{ij}^{(0)}+f_{ij}^{(1)}+f_{ij}^{(2)}+\cdots, \tag{2.8}$$

with

$$f_{ij}^{(0)}=e^{-v_{ij}^{HC}}-1, \tag{2.9}$$

$$f_{ij}^{(n)}=\frac{(-v_{ij}^{DD})^n}{n!}e^{-v_{ij}^{HC}}, \quad n\geq 1. \tag{2.10}$$

The two expansions concerning the f terms and v_{ij}^{DD} together translate in the monodisperse case into a double power expansion of Z in the the volume fraction ϕ of the particles and the dipolar coupling constant ϵ. We calculated the terms in $O(\phi\epsilon^n)$ and in $O(\phi^2\epsilon^2)$ of Z and from that the equilibrium magnetization in the same order.

III. CALCULATING THE EQUILIBRIUM MAGNETIZATION

A. Notation

Consider a system of N spherical hard particles with diameters $D_1,\ldots,D_N$ carrying permanent magnetic moments $m_1,\ldots,m_N$ contained in a volume V and subjected to a magnetic field $\mathbf{H}$. Let $\bar{D}$ and $\bar{m}$ be some "typical" values for diameters and magnetic moments that are discussed further below. We then define the parameter $\bar{\phi}$ related to the volume fraction of the hard spheres and the dipolar coupling parameter $\bar{\epsilon}$ as

$$\bar{\phi}=\frac{N\pi\bar{D}^3}{6V}, \quad \bar{\epsilon}=\frac{\bar{m}^2}{4\pi\mu_0 kT\bar{D}^3}. \tag{3.1}$$

The equilibrium magnetization is calculated as a power expansion in these two parameters. The dimensionless magnetic fields are defined as

$$\bar{\alpha}=\frac{\bar{m}H}{kT}, \quad \bar{\alpha}_s=\frac{\bar{m}H_s}{kT}. \tag{3.2}$$

Diameters and magnetic moments will be expressed in units of the typical values via

$$\Delta_i=\frac{D_i}{\bar{D}}, \quad \mu_i=\frac{m_i}{\bar{m}}. \tag{3.3}$$

We will also use the minimal possible distance between two hard spheres i and j given by

$$\Delta_{ij}=\frac{1}{2}(\Delta_i+\Delta_j)=\frac{D_{ij}}{\bar{D}}. \tag{3.4}$$

Furthermore, we introduce the reduced magnetic fields for each particle i by

$$\alpha_i=\frac{m_i H}{kT}=\mu_i\bar{\alpha}, \quad \alpha_{si}=\frac{m_i H_s}{kT}=\mu_i\bar{\alpha}_s. \tag{3.5}$$

Our cluster expansion does not depend on how the characteristic values of $\bar{D}$ and $\bar{m}$ are defined in detail. For example, they could be taken as some weighted mean of the D_i and m_i, respectively, or their most probable values. To preserve this freedom of choice in our expansion offers some advantages for the comparison with magnetogranulometric analyses where the distribution of the diameters and magnetic moments is not known *a priori* but on the contrary the goal of the calculations.

Note, however, that $\bar{\phi}$ coincides with the actual volume fraction ϕ of the hard spheres only if one defines $\bar{D}$ via the mean volume of the particles

$$\bar{D}^3 = \frac{1}{N} \sum_i D_i^3 = \int D^3 P(D) dD \equiv \langle D^3 \rangle_P. \quad (3.6)$$

Here, $P(D)$ is the normalized distribution function of the hard sphere diameters.

Similarly $\bar{m}$ is related to the saturation magnetization M_{sat} of the ferrofluid via $M_{\text{sat}} = N\bar{m}/\mu_0 V$ only if $\bar{m}$ is defined by

$$\bar{m} = \frac{1}{N} \sum_i m_i = \int m(D) P(D) dD. \quad (3.7)$$

The second equality of Eq. (3.7) holds when the magnetization of each particle is given by a function of its volume. We assume that this is the case and thus describe in this paper polydispersity effects of the ferrofluid by a distribution function $P(D)$ depending only on the hard sphere diameter D. The generalization to a distribution function $P(D,m)$ of independently varying diameters and moments is straightforward. Averages weighted with the distribution function $P(D)$ of the diameters will mostly appear in the reduced version as integrals over the reduced diameter $\Delta = D/\bar{D}$ with the appropriate weight function $P(\Delta)$.

The thermodynamic mean with respect to the noninteracting system will be denoted by $\langle \cdots \rangle_0$ and the corresponding canonical partition function by Z_0. With this notation integrals over the f terms appearing in Z (2.2) can be written in the form

$$\int \prod_k e^{-v_k} f \cdots d\Gamma = Z_0 \langle f \cdots \rangle_0. \quad (3.8)$$

But in contrast to paper I, we derive here an approximation directly for the free energy $F = -kT \ln Z$. If the particle-particle interaction would depend only on the interparticle distance then F would be given by

$$F = F_0 - kT \left(\frac{1}{2} \sum{}' \langle f_{ij} \rangle_0 + \frac{1}{6} \sum{}' \langle f_{ij} f_{jk} f_{ki} \rangle_0 \right), \quad (3.9)$$

including orders up to $O(\bar{\phi}^2)$, or, more generally speaking, up to terms of second order in the number density. The primed sums are taken over all particle pairs i, j, respectively all triples i, j, k. While Eq. (3.9) does not hold for a system of dipolar particles in a magnetic field in arbitrary order of $\bar{\epsilon}$, it still is correct in the orders we want to calculate.

The polydisperse generalization affects the calculation of the integrals in Eq. (3.9) in the following two ways.

(i) The fact that the individual dimensionless magnetic fields α_i are different leads to more complicated expressions for some resulting functions compared to the monodisperse case—see the definitions of G_n^P and K^P below.

(ii) The dispersion in the hard sphere diameters requires more difficult geometrical considerations concerning the v_{ij}^{HC} terms, especially in the three-particle integral.

B. The leading term: Polydisperse Weiss model

The leading term in Z is the partition function of the (formally) noninteracting paramagnetic gas in the magnetic field H_s,

$$Z_0 = \int \prod_k e^{-v_k} d\Gamma = \prod_k z_k, \quad (3.10)$$

$$z_k = \int e^{-v_k} d\mathbf{x}_k d\Omega_k = 4\pi V \frac{\sinh \alpha_{sk}}{\alpha_{sk}}. \quad (3.11)$$

The equilibrium magnetization $M(\bar{\alpha}_s)$ obtained from

$$M(\bar{\alpha}_s) = -\frac{1}{\mu_0 V} \frac{\partial F}{\partial H_s} = \frac{1}{\mu_0 V} \frac{\partial(kT \ln Z)}{\partial H_s} = \frac{\bar{m}}{\mu_0 V} \frac{\partial \ln Z}{\partial \bar{\alpha}_s} \quad (3.12)$$

reads in leading order

$$M(\bar{\alpha}_s) = \frac{N\bar{m}}{\mu_0 V} \mathcal{L}_{\text{poly}}(\bar{\alpha}_s). \quad (3.13)$$

Here,

$$\mathcal{L}_{\text{poly}}(\bar{\alpha}_s) = \frac{1}{N} \sum_i \mu_i \mathcal{L}(\mu_i \bar{\alpha}_s)$$

$$= \int \mu(\Delta) \mathcal{L}[\mu(\Delta)\bar{\alpha}_s] P(\Delta) d\Delta \quad (3.14)$$

is given by the sum of the Langevin paramagnetic contributions coming from each (reduced) magnetic moment $\mu_i = m_i/\bar{m}$ with $\mathcal{L}$ being the Langevin function. The second equality in Eq. (3.14) is the continuous analog of the sum with $\mu(\Delta) = m(\Delta)/\bar{m}$ and $\Delta = D/\bar{D}$. If one defines $\bar{m}$ via $N\bar{m} = \Sigma_i m_i$, so that $N\bar{m}/\mu_0 V = M_{\text{sat}}$ then $\mathcal{L}_{\text{poly}}(\bar{\alpha}_s \to \infty) = 1$.

The result (3.13) reduces to the well-known expression for the magnetization of a polydisperse ideal paramagnetic gas as a superposition of Langevin functions, if one replaces $\bar{\alpha}_s$ by $\bar{\alpha}$ (see, e.g., Ref. [16]). However, the dipolar far-field contributions enter via Eq. (2.6) as a mean field into

$$\bar{\alpha}_s = \bar{\alpha} + \bar{m} M / 3kT. \quad (3.15)$$

Thus, the lowest-order result (3.13) for $M(\bar{\alpha})$,

$$M = \frac{N\bar{m}}{\mu_0 V} \mathcal{L}_{\text{poly}}\left(\bar{\alpha} + \frac{\bar{m}M}{3kT}\right), \quad (3.16)$$

already contains corrections from the particle-particle interaction in the mean field approximation and Eq. (3.16) is the polydisperse generalization of the Weiss model [20].

By replacing M on the right hand side of Eq. (3.16) by the expression for the ideal paramagnetic gas, one arrives at the equation proposed in Ref. [18].

C. The magnetization in $O(\bar{\phi})$

To calculate the canonical partition function in linear order of $\bar{\phi}$, we follow the lines of paper I, Sec. IV. One needs to include only the linear f terms in the expansion (3.9). Thus, we write

$$F = F_0 - kT \frac{1}{2} \sum{}' \langle f_{ij}\rangle_0. \quad (3.17)$$

For the second term in Eq. (3.17), the trivial integrations over the degrees of freedom of all particles except i and j are performed first. This gives

$$\frac{1}{2} \sum{}' \langle f_{ij}\rangle_0 = \frac{1}{2Z_0} \sum{}' \int \prod_k e^{-v_k} f_{ij} d\Gamma$$

$$= \sum{}' \frac{1}{2z_i z_j} \int e^{-v_i - v_j} f_{ij} d\mathbf{x}_i d\mathbf{x}_j d\Omega_i d\Omega_j. \quad (3.18)$$

Now we expand f_{ij}. Let

$$A_{n,ij} = \int e^{-v_i - v_j} f_{ij}^{(n)} d\mathbf{x}_i d\mathbf{x}_j d\Omega_i d\Omega_j, \quad (3.19)$$

such that

$$F = F_0 - \sum{}' \frac{kT}{2z_i z_j} \sum_{n=0}^{\infty} A_{n,ij}. \quad (3.20)$$

We need not calculate A_0, since this term does not contribute to the equilibrium magnetization. Furthermore, $A_1 = 0$, because a dipolar magnetic field vanishes when averaged over a spherical surface. This is explained in more detail in paper I. Using the definition (2.10) of $f_{ij}^{(n)}$, and the dipolar potential (2.4), we can write

$$A_n = \frac{V}{n!} \int e^{\alpha_{si}\cos\vartheta_i + \alpha_{sj}\cos\vartheta_j}$$

$$\times \left(\frac{\bar{m}^2 \mu_i \mu_j}{4\pi\mu_0 kT r_{ij}^3}\right)^n P^n(\varphi_i, \vartheta_i, \varphi_j, \vartheta_j, \varphi, \vartheta)$$

$$\times e^{-v_{12}^{HC}} r_{ij}^2 dr_{ij} d\omega_{ij} d\Omega_i d\Omega_j. \quad (3.21)$$

Here, we have integrated over $\mathbf{x}_i$ and decomposed $\mathbf{r}_{ij}$ into the distance r_{ij} and a spherical angle ω_{ij}. The angles (φ_i, ϑ_i), (φ_j, ϑ_j), and (φ, ϑ) represent the spherical angles Ω_i, Ω_j, and ω_{ij}, respectively. The function

$$P(\varphi_i, \vartheta_i, \varphi_j, \vartheta_j, \varphi, \vartheta) = 3(\hat{\mathbf{m}}_i \cdot \hat{\mathbf{r}}_{ij})(\hat{\mathbf{m}}_j \cdot \hat{\mathbf{r}}_{ij}) - \hat{\mathbf{m}}_i \cdot \hat{\mathbf{m}}_j \quad (3.22)$$

comes from the dipolar interaction. The integration over the directions of $\mathbf{r}_{ij}$, $\mathbf{m}_i$, and $\mathbf{m}_j$ can still be done analytically. But in contrast to the monodisperse calculation, the result is now a function of two parameters α_{si} and α_{sj}. We define

$$G_n^P(\alpha_{si}, \alpha_{sj}) = \frac{V^2}{n!(n-1)\pi z_i z_j} \times \int e^{\alpha_{si}\cos\vartheta_i + \alpha_{sj}\cos\vartheta_j}$$

$$\times P^n(\varphi_i, \vartheta_i, \varphi_i, \vartheta_j, \varphi, \vartheta) d\Omega_i d\Omega_j d\omega_{ij}. \quad (3.23)$$

$G_n^P(\alpha_{si}, \alpha_{sj})$ is symmetric in its two arguments and a polydisperse counterpart to the function $G_n(\alpha_s)$ defined in paper I. It is $G_n^P(\alpha_s, \alpha_s) = G_n(\alpha_s)$. Some of the G_n^P are given in the Appendix.

Inserting Eq. (3.23) into Eq. (3.21), integrating over r_{ij} between the minimal distance D_{ij} and ∞, and introducing $\bar{\phi}$ and $\bar{\epsilon}$ yields

$$A_n = \frac{2}{N} z_i z_j \bar{\phi} \bar{\epsilon}^n (\mu_i \mu_j)^n \Delta_{ij}^{3-3n} G_n^P(\alpha_{si}, \alpha_{sj}), \quad (3.24)$$

and together with Eq. (3.20) the free energy

$$F = F_0 + \cdots - \frac{kT}{N} \sum_{n=2}^{\infty} \bar{\phi} \bar{\epsilon}^n \sum{}' (\mu_i \mu_j)^n \Delta_{ij}^{3-3n} G_n^P(\alpha_{si}, \alpha_{sj}). \quad (3.25)$$

Here the dots represent the contribution from A_0 that was not calculated. It can easily be shown that F does not depend on a particular definition of $\bar{m}$ or $\bar{D}$.

Now, the equilibrium magnetization $M(\bar{\alpha}_s)$ is given in $O(\bar{\phi})$ by

$$M(\bar{\alpha}_s) = \frac{N\bar{m}}{\mu_0 V}\left[\mathcal{L}_{\text{poly}}(\bar{\alpha}_s) + \sum_{n=2}^{\infty} \bar{\phi} \bar{\epsilon}^n G'_{\text{poly},n}(\bar{\alpha}_s)\right]. \quad (3.26)$$

The function $G'_{\text{poly},n}$ is the derivative of

$$G_{\text{poly},n}(\bar{\alpha}_s) = \frac{1}{N^2} \sum{}' (\mu_i \mu_j)^n \Delta_{ij}^{3-3n} G_n^P(\alpha_{si}, \alpha_{sj})$$

$$= \int [\mu(\Delta_i)\mu(\Delta_j)]^n \Delta_{ij}^{3-3n}$$

$$\times G_n^P(\alpha_{si}, \alpha_{sj}) P(\Delta_i) P(\Delta_j) d\Delta_i d\Delta_j, \quad (3.27)$$

which is a generalization of G_n [2] and reduces to the latter in the monodisperse case $D_i = \bar{D} = D$ and $m_i = \bar{m} = m$.

In a last step, we convert the expression for M as a function of $\bar{\alpha}_s$ into a function of $\bar{\alpha}$ using the definition of H_s in Eq. (2.6). By expanding and iterating in a way that is analogous to the procedure in paper I, Sec. IV C, we obtain the final result for M up to the order of $\bar{\phi}$:

$$M(\bar{\alpha}) = \frac{N\bar{m}}{\mu_0 V} \left[\mathcal{L}_{\text{poly}}(\bar{\alpha}) + 8\bar{\phi}\bar{\epsilon}\mathcal{L}_{\text{poly}}(\bar{\alpha})\mathcal{L}'_{\text{poly}}(\bar{\alpha}) \right.$$
$$\left. + \sum_{n=2}^{\infty} \bar{\phi}\bar{\epsilon}^n G'_{\text{poly},n}(\bar{\alpha}) \right]. \qquad (3.28)$$

The two leading terms can be seen as the polydisperse extension of the high temperature approximation derived in Ref. [17] for monodisperse systems.

D. The contribution in $O(\bar{\phi}^2\bar{\epsilon}^2)$

For the monodisperse system, the magnetization contribution in $O(\bar{\phi}^2\bar{\epsilon}^2)$ was calculated in Sec. V and Appendix B of paper I. The cluster integrals needed in that order are shown in Fig. 3 of paper I. Some of them vanish for the same reason as the contribution A_1 in $O(\bar{\phi}\bar{\epsilon})$; they involve the averaging of a dipolar field over a spherical surface. Most of the remaining integrals cancel when the free energy $F = -kT \ln Z$ is calculated. Up to $O(\bar{\epsilon}^2)$, we can write the remaining term in Eq. (3.9) as

$$\langle f_{ij}f_{ik}f_{jk}\rangle_0 = \langle f^{(0)}_{ij}f^{(0)}_{ik}f^{(0)}_{jk}\rangle_0 + 3\langle f^{(2)}_{ij}f^{(0)}_{ik}f^{(0)}_{jk}\rangle_0$$
$$+ 3\langle f^{(1)}_{ij}f^{(1)}_{ik}f^{(0)}_{jk}\rangle_0. \qquad (3.29)$$

These three terms correspond to the graphs E, G, and H in paper I. The first one is an $O(\bar{\phi}^2\bar{\epsilon}^0)$ term that does not contribute to the magnetization.

1. Graph G

Here, we give an outline of the polydisperse generalization of the calculation pertaining to graph G (Appendix B.7 of paper I). The quantity Z_G calculated in paper I is given by the sum

$$Z_G = Z_0 \frac{1}{2} \sum{}' \langle f^{(2)}_{ij}f^{(0)}_{jk}f^{(0)}_{ki}\rangle_0 \qquad (3.30)$$

over distinct particles i,j,k. For calculating $\langle f^{(2)}_{ij}f^{(0)}_{jk}f^{(0)}_{ki}\rangle_0$ one starts with the trivial integrations: the degrees of freedom of all particles except i, j, and k, the position of the center of mass of the three remaining particles, and the orientation of $\mathbf{m}_k$, since particle k is not involved in dipolar interactions in this cluster. Then, for a fixed distance r_{ij} the integrations over ω_{ij}, Ω_i, and Ω_j, defined as in Sec. III C are carried out. This introduces the function G^P_2 into the result

$$\langle f^{(2)}_{ij}f^{(0)}_{ik}f^{(0)}_{jk}\rangle_0 = \frac{36}{\pi N^2}(\mu_i\mu_j)^2\bar{\phi}^2\bar{\epsilon}^2 G^P_2(\alpha_{si},\alpha_{sj})$$

$$\times \int r_{ij}^{-4} e^{-v^{HC}_{ij}} f^{(0)}_{ik}f^{(0)}_{jk} dr_{ij}d\mathbf{r}_{ik}. \qquad (3.31)$$

The integral over $\mathbf{r}_{ik}$ can be described by the following geometrical considerations: The volume of possible positions of particle k has to be found such that this particle overlaps with both particles i (i.e., $r_{ik} < D_{ik}$) and j ($r_{jk} < D_{jk}$). Otherwise the integral would vanish because of the factor $f^{(0)}_{ik}f^{(0)}_{jk}$. This is only possible, if $r_{ij} < D_{ik} + D_{jk}$.

In a final step the integration over r_{ij} between D_{ij} and $D_{ik} + D_{jk}$ is carried out. The final result is

$$\langle f^{(2)}_{ij}f^{(0)}_{ik}f^{(0)}_{jk}\rangle_0 = \frac{3}{N^2}(\mu_i\mu_j)^2\bar{\phi}^2\bar{\epsilon}^2 G^P_n(\alpha_{si},\alpha_{sj})$$

$$\times f^G(\Delta_{ij},\Delta_{ik},\Delta_{jk}). \qquad (3.32)$$

The function $f^G(\Delta_{ij},\Delta_{ik},\Delta_{jk})$ is given in the Appendix. The contribution to the free energy is according to Eqs. (3.9) and (3.29) given by

$$-kT\frac{1}{6}\sum{}' 3\langle f^{(2)}_{ij}f^{(0)}_{jk}f^{(0)}_{ki}\rangle_0$$

$$= -NkT\bar{\phi}^2\bar{\epsilon}^2 \frac{1+6\ln 2}{4}\widetilde{G}_{\text{poly},2}(\bar{\alpha}_s). \qquad (3.33)$$

The function

$$\widetilde{G}_{\text{poly},2}(\bar{\alpha}_s) = \frac{6}{1+6\ln 2} \times \frac{1}{N^3}\sum{}' (\mu_i\mu_j)^2 G^P_n(\alpha_{si},\alpha_{sj})$$

$$\times f^G(\Delta_{ij},\Delta_{ik},\Delta_{jk}), \qquad (3.34)$$

was defined in such a way that it reduces to $G_2(\alpha_s)$ in the monodisperse case. Finally, introducing the diameter distribution function $P(\Delta)$ requires the replacement

$$\frac{1}{N^3}\sum{}' \rightarrow \int P(\Delta_i)d\Delta_i P(\Delta_j)d\Delta_j P(\Delta_k)d\Delta_k \qquad (3.35)$$

in Eqs. (3.33) and (3.34).

2. Graph H

The integrations to calculate $\langle f^{(1)}_{ij}f^{(1)}_{jk}f^{(0)}_{ki}\rangle_0$ are performed as follows (compare to Appendix B.8 in paper I). After doing the trivial integrations (concerning the possible configurations of the particles except i, j, and k, and the center of mass of the cluster), the possible orientations of the cluster are integrated out. Then, the integrations over the orientations of $\mathbf{m}_i$, $\mathbf{m}_j$, and $\mathbf{m}_k$ are performed. One arrives at

$$\langle f_{ij}^{(1)} f_{ik}^{(1)} f_{jk}^{(0)} \rangle_0 = \mu_i^2 \mu_j \mu_k \bar{\epsilon}^2 \frac{4\pi^2}{15V^2} K^P(\alpha_{si}, \alpha_{sj}, \alpha_{sk})$$

$$\times \int \frac{\bar{D}^6}{r_{ij} r_{ik}} (3\cos^2\vartheta_{jk} - 1) e^{-v_{ij}^{HC}} e^{-v_{ik}^{HC}} f_{jk}^{(0)}$$

$$\times dr_{ij} dr_{ik} \sin\vartheta_{jk} d\vartheta_{jk}. \quad (3.36)$$

This is, up to a factor of $N^2 Z_0 / 2$, a polydisperse generalization of Eq. (B21) of paper I. The remaining integrations concern the distances r_{ij} and r_{ik}, and the angle ϑ_{jk} between $\mathbf{r}_{ij}$ and $\mathbf{r}_{ik}$. The function K^P is defined by

$$K^P(\alpha_{si}, \alpha_{sj}, \alpha_{sk}) = \frac{3}{8} \frac{(4\pi V)^3}{z_i z_j z_k}$$

$$\times \int_{-1}^{1} \int_{-1}^{1} \int_{-1}^{1} e^{(\alpha_{si} u_i + \alpha_{sj} u_j + \alpha_{sk} u_k)}$$

$$\times (3 + u_i^2) u_j u_k du_i du_j du_k \quad (3.37)$$

[compare to Eq. (B22) of paper I]. An expression for the monodisperse counterpart $K(\alpha_s)$ was given in Appendix A of paper I. Here, we express K^P via Langevin functions,

$$K^P(\alpha_{si}, \alpha_{sj}, \alpha_{sk}) = 3\mathcal{L}(\alpha_{sj}) \mathcal{L}(\alpha_{sk})[3 + \mathcal{L}'(\alpha_{si}) + \mathcal{L}(\alpha_{si})^2]. \quad (3.38)$$

Note that $r_{ij} > D_{ij}$ and $r_{ik} > D_{ik}$ is required, otherwise the integral (3.36) vanishes. The requirement that particles j and k have to overlap imposes the additional restrictions $|r_{ij} - r_{ik}| < D_{jk}$ and

$$\vartheta_{jk} < \vartheta_{jk}^{\max} = \arccos \frac{r_{ij}^2 + r_{ik}^2 - D_{jk}^2}{2 r_{ij} r_{ik}}. \quad (3.39)$$

After performing the remaining integrations within these limits, the result is

$$\langle f_{ij}^{(1)} f_{ik}^{(1)} f_{jk}^{(0)} \rangle_0 = \mu_i^2 \mu_j \mu_k \bar{\phi}^2 \bar{\epsilon}^2 \frac{48}{5N^2}$$

$$\times K^P(\alpha_{si}, \alpha_{sj}, \alpha_{sk}) f^K(\Delta_{ij}, \Delta_{ik}, \Delta_{jk}). \quad (3.40)$$

The function $f^K(\Delta_{ij}, \Delta_{ik}, \Delta_{jk})$ is given in the Appendix. The contribution to the free energy is

$$-kT \frac{1}{6} \sum' 3 \langle f_{ij}^{(1)} f_{jk}^{(1)} f_{ki}^{(0)} \rangle_0 = NkT \bar{\phi}^2 \bar{\epsilon}^2 K_{\text{poly}}(\bar{\alpha}_s), \quad (3.41)$$

with

$$K_{\text{poly}}(\bar{\alpha}_s) = -\frac{24}{5} \frac{1}{N^3} \sum' \mu_i^2 \mu_j \mu_k$$

$$\times K^P(\alpha_{si}, \alpha_{sj}, \alpha_{sk}) f^K(\Delta_{ij}, \Delta_{ik}, \Delta_{jk}). \quad (3.42)$$

3. The magnetization contribution

Inserting Eqs. (3.33) and (3.41) in Eq. (3.9) and calculating the equilibrium magnetization results in an additional $O(\bar{\phi}^2 \bar{\epsilon}^2)$ term in Eq. (3.26):

$$\frac{N\bar{m}}{\mu_0 V} \bar{\phi}^2 \bar{\epsilon}^2 \left[\frac{1 + 6\ln 2}{4} \tilde{G}'_{\text{poly},2}(\bar{\alpha}_s) - K'_{\text{poly}}(\bar{\alpha}_s) \right]. \quad (3.43)$$

The expansion and iteration procedure to switch from $\bar{\alpha}_s$ to $\bar{\alpha}$ is identical to the monodisperse case in paper I. The full expression for the magnetization containing all calculated terms reads

$$M = \frac{N\bar{m}}{\mu_0 V} \left[\mathcal{L}_{\text{poly}}(\bar{\alpha}) + 8\bar{\phi}\bar{\epsilon} \mathcal{L}_{\text{poly}}(\bar{\alpha}) \mathcal{L}'_{\text{poly}}(\bar{\alpha}) \right.$$

$$+ \sum_{n=2}^{\infty} \bar{\phi}\bar{\epsilon}^n G'_{\text{poly},n}(\bar{\alpha}) + 64\bar{\phi}^2\bar{\epsilon}^2 \mathcal{L}_{\text{poly}}(\bar{\alpha}) \mathcal{L}'_{\text{poly}}(\bar{\alpha})^2$$

$$+ 32\bar{\phi}^2\bar{\epsilon}^2 \mathcal{L}_{\text{poly}}(\bar{\alpha})^2 \mathcal{L}''_{\text{poly}}(\bar{\alpha}) + \bar{\phi}^2\bar{\epsilon}^2 \frac{1 + 6\ln 2}{4} \tilde{G}'_{\text{poly},2}(\bar{\alpha})$$

$$\left. - \bar{\phi}^2\bar{\epsilon}^2 K'_{\text{poly}}(\bar{\alpha}) \right]. \quad (3.44)$$

IV. SELECTED RESULTS FOR THE MAGNETIZATION

The Figs. 1 and 2 showing separate contributions to $M(\bar{\alpha})$ in polydisperse systems were obtained by using log-normal distributions

$$P(D) = \frac{1}{\sqrt{2\pi}\sigma D_0} e^{-\sigma^2/2} e^{-\ln^2(D/D_0)/(2\sigma^2)}, \quad (4.1)$$

for the particle diameters as a representative and often used example for size distibutions of model polydisperse systems. Using similar distributions, e.g., Γ distributions, however, would not qualitatively modify the results. In Sec. V, we use also an experimentally determined size distribution. Here, the quantity $\bar{D}$ was taken to be defined via the mean volume (3.6), i.e., $\bar{D}^3 = \langle D^3 \rangle_P = D_0^3 e^{15\sigma^2/2}$, so that $\bar{\phi}$ is the volume fraction ϕ. The magnetic moments of the particles were taken to scale with their volumes, $m \sim D^3$, allowing to set $\mu(\Delta) = \Delta^3$ such that $\bar{m} = \langle m \rangle_P$.

Figures 1 and 2 show the contributions

$$L_{1,1}(\bar{\alpha}) = 8\mathcal{L}_{\text{poly}}(\bar{\alpha}) \mathcal{L}'_{\text{poly}}(\bar{\alpha}), \quad (4.2a)$$

$$L_{2,2}(\bar{\alpha}) = 64\mathcal{L}_{\text{poly}}(\bar{\alpha}) \mathcal{L}'_{\text{poly}}(\bar{\alpha})^2 + 32\mathcal{L}_{\text{poly}}(\bar{\alpha})^2 \mathcal{L}''_{\text{poly}}(\bar{\alpha})$$

$$+ \frac{1 + 6\ln 2}{4} \tilde{G}'_{\text{poly},2}(\bar{\alpha}) - K'_{\text{poly}}(\bar{\alpha}), \quad (4.2b)$$

$$L_{1,2}(\bar{\alpha}) = G'_{\text{poly},2}(\bar{\alpha}), \quad (4.2c)$$

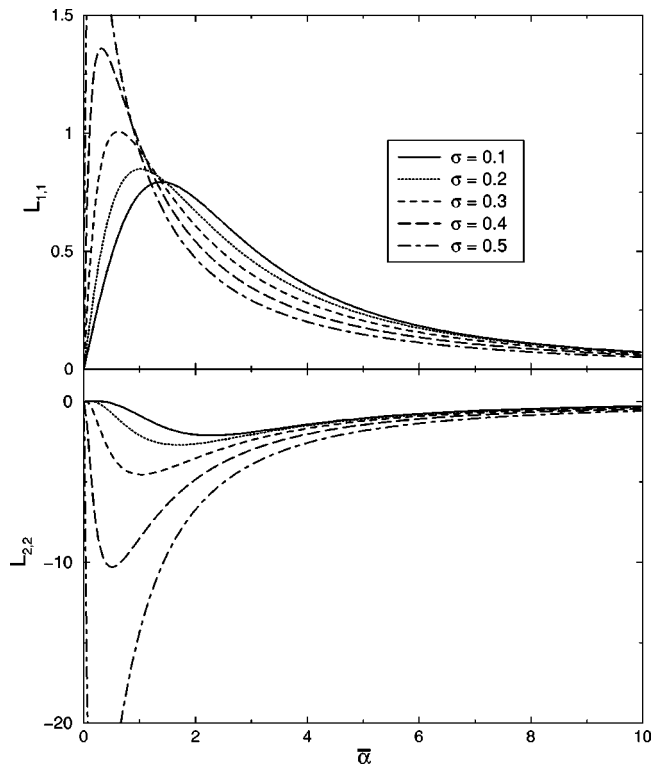$$L_{1,3}(\bar{\alpha}) = G'_{\text{poly},3}(\bar{\alpha}) \quad (4.2d)$$

FIG. 1. The contributions $L_{1,1}$ and $L_{2,2}$ as functions of $\bar{\alpha}$ for lognormal distributions with different widths σ. Here, $\langle\Delta^3\rangle_P = 1$ and $\mu(\Delta) = \Delta^3$.

FIG. 2. The contributions $L_{1,2}$ and $L_{1,3}$ as a function of $\bar{\alpha}$ for lognormal distributions with different widths σ. Δ and $\mu(\Delta)$ as in Fig. 1.

to $M(\bar{\alpha})$ (3.44) for different values of the width σ of the distribution (4.1). The contributions of higher-order terms increase with growing σ. This is so because they depend on higher moments of the distribution $P(\Delta)$ that grow with the width of the distribution, even if the third moment $\langle\Delta^3\rangle_P$ is kept fixed. The shift of the maxima of the curves to the right has a similar reason: Bigger particles, that react to smaller fields become more and more important when the width of the distribution grows.

The assumption $\mu(\Delta) = \Delta^3$ that the magnetic moments in our ferrofluid model scale $\sim D^3$ with the total volume of its hard sphere constituents is somewhat too simple for particles in real ferrofluids for two reasons. First, in the common case of steric stabilization by polymers, surfactants providing the repulsion the surfactant layer of about $1-3$ nm do not contribute to the magnetic moment. Second, an outer layer of the magnetic material might be magnetically dead so that it does not contribute to the magnetic moment either. For magnetite particles a dead layer depth of ≈ 0.8 nm has been reported [22]. To account for the sum of these two effects, we have introduced in our calculation for M an effective magnetic diameter D_{mag} via the relation $D = D_{\mathrm{mag}} + 5.6$ nm. It ascribes to every particle that has a magnetically effective core of diameter D_{mag}, a hard sphere with a magnetically inert layer of depth 2.8 nm. The magnetic moment of each particle was then taken to scale with is magnetically effective volume, i.e., $\mu = (D_{\mathrm{mag}}/\bar{D})^3$.

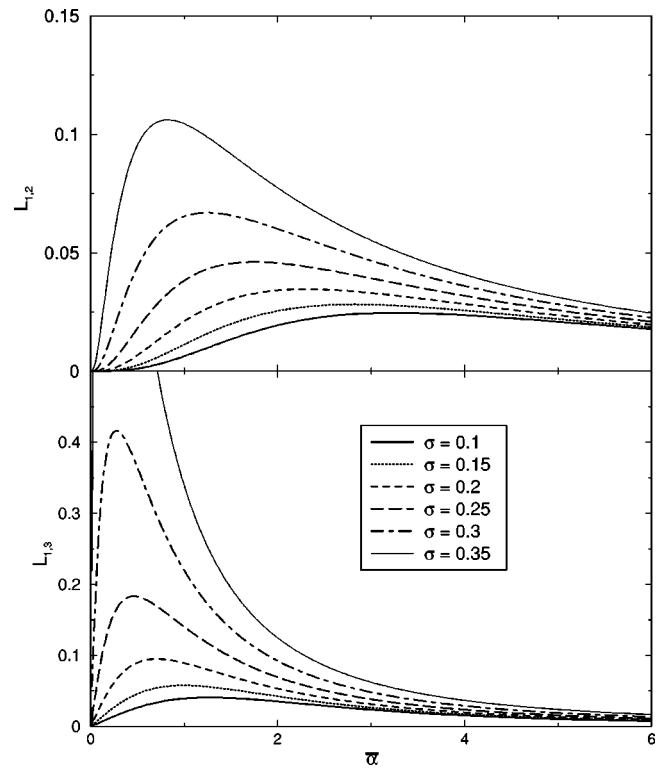The full line in Fig. 3 shows the reduced equilibrium magnetization of an interacting polydisperse ferrofluid as a function of $\bar{\alpha}$. Here, each particle has a total magnetic inactive layer of 2.8 nm and the diameters D_{mag} of the magnetic cores are log-normally distributed with $\sigma = 0.25$ and $\langle D_{\mathrm{mag}}^3\rangle_P^{1/3} = 10$ nm. The latter is taken as the reference diameter $\bar{D}$ in the calculation. The particle density is chosen in such a way that $\bar{\phi} = 0.05$. Note that here $\bar{\phi} = \phi_{\mathrm{mag}}$, the volume fraction of the magnetically active material. The mag-
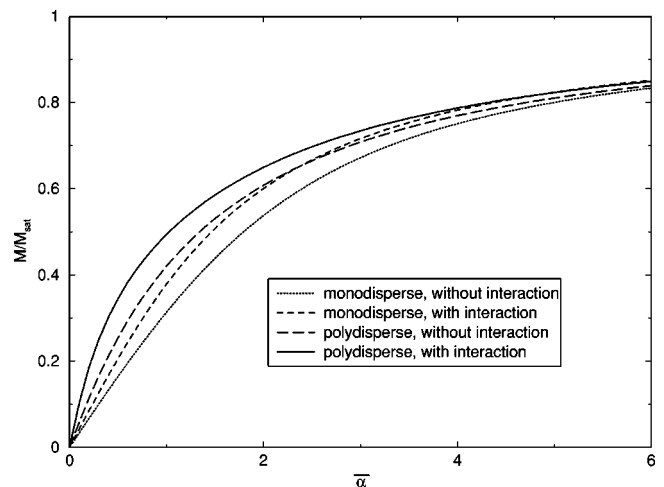

FIG. 3. Equilibrium magnetization of a polydisperse ferrofluid $[\langle D_{\mathrm{mag}}^3\rangle_P^{1/3} = 10$ nm, $\sigma = 0.25$, $\mu = (D_{\mathrm{mag}}/\bar{D})^3]$ and a comparable monodisperse ferrofluid, both with and without taking into account the particle interaction. See text for further details.

netic moment $\bar{m}$ for $D_{\mathrm{mag}} = 10$ nm is chosen such that $\bar{\epsilon}$ $= 2$. The magnetization of the core is then about 550 kA/m at room temperature, which is a little bit larger than that of magnetite.

Expansion terms of the order of $\bar{\phi}\bar{\epsilon}^n$ are taken into account up to order $n = 5$ for the magnetization curves in Fig. 3. Higher $O(\bar{\phi}\bar{\epsilon}^n)$ terms have only a small effect on the magnetization. Here, $\bar{\epsilon}$ is by definition of $\bar{m}$ and $\bar{D}$ a typical interaction energy divided by kT for particles at a distance of $\bar{D} = 10$ nm. But with the two additional dead layers of total size 5.6 nm in between the particles of our model ferrofluid the real typical dipolar energies at contact are smaller.

The magnetization is compared to that of a polydisperse fluid without particle-particle interaction (long dashed line), and to a monodisperse ferrofluid, both with and without taking into account the particle-particle interaction (short dashed and dotted line, respectively). The monodisperse system consists of particles with $D_{\mathrm{mag}} = 10$ nm with the same nonmagnetic layer thickness, bulk magnetization, and ϕ_{mag} as before.

One sees that taking into account polydispersity or particle interaction alone strengthens the magnetization and especially the initial susceptibility. Both effects are comparable for the given parameters. Together, they result in an even higher equilibrium magnetization.

Figure 4 shows magnetization curves for magnetite-based ferrofluids with a bulk magnetization of 480 kA/m for distributions of different widths. D_{mag} is taken to be lognormally distributed with $\langle D_{\mathrm{mag}}^3 \rangle_P = (8 \text{ nm})^3$ and $\sigma = 0.2$, 0.3, and 0.4. The volume fraction of the magnetic material is $\phi_{\mathrm{mag}} = 0.1$. The particles are again assumed to carry a nonmagnetic layer of 2.8 nm thickness.

The increase in σ causes an increase of the initial susceptibility already in the noninteracting case (long dashed lines). Including the $O(\bar{\phi}\bar{\epsilon})$ terms (short dashed lines) has a positive effect on the magnetization. The relative increase is maximal for small $\bar{\alpha}$. The magnetization decreases again at higher $\bar{\alpha}$, if higher-order terms are taken into account (solid lines). For the considered ferrofluids the $O(\bar{\phi}^2\bar{\epsilon}^2)$ term that is negative for higher $\bar{\alpha}$ (see Fig. 1) is almost solely responsible for this decrease. The positive contributions from the higher $O(\bar{\phi}\bar{\epsilon}^n)$ terms ($n \geq 2$) are again negligible, except for $\sigma = 0.4$ and small $\bar{\alpha}$, where they cause a further increase of the initial susceptibility. For small $\bar{\alpha}$ the $O(\bar{\phi}^2\bar{\epsilon}^2)$ term also has a positive effect, but this effect is too small to be visible. The plots show again that the influence of higher-order terms is larger for broad distributions.

V. COMPARISON TO EXPERIMENTS

We compared our theorerical predictions for the magnetization curves with experimental results of two different magnetite-based ferrofluids. Odenbach (ZARM, Bremen) provided data on the equilibrium magnetization of the ferrofluid EMC 905 produced by FerroTec. We fitted our theoretical result (3.44) taking into account the terms in $O(\phi\epsilon^n)$ up
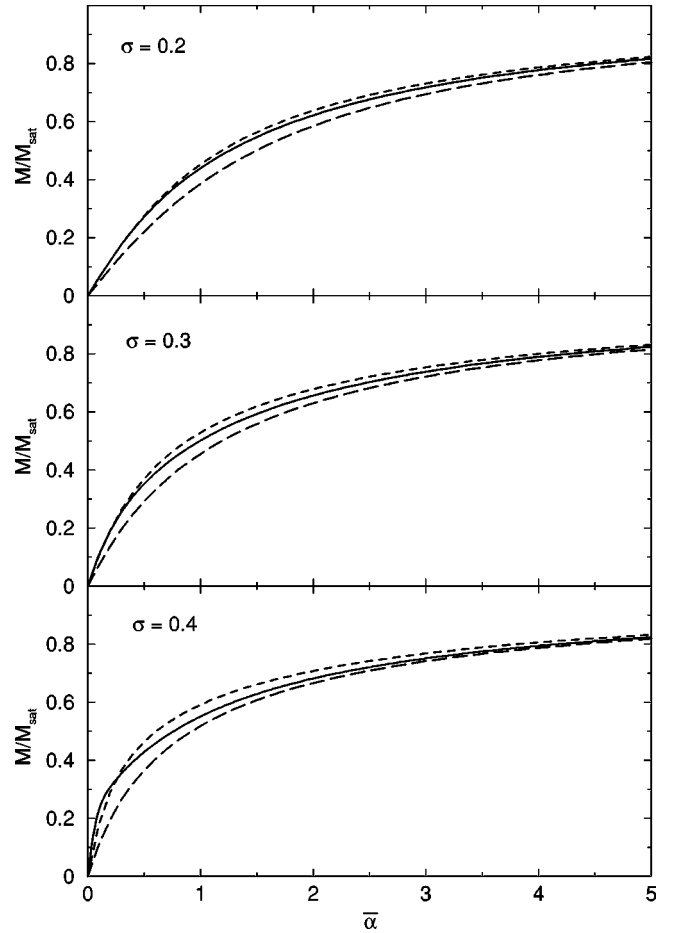

FIG. 4. Equilibrium magnetization as a function of $\bar{\alpha}$ for log-normal distributions with $\langle D_{\mathrm{mag}}^3 \rangle_P^{1/3} = 8$ nm and different widths σ. Long dashed: without particle interaction; dashed: particle interaction only in $O(\bar{\phi}\bar{\epsilon})$; solid lines: all calculated terms.

to $n = 5$ to the data assuming log-normally distributed D_{mag} and a nonmagnetic layer of depth 2.8 nm. The bulk magnetization of magnetite was taken to be 480 kA/m. The result is shown in Fig. 5. According to the fit, the saturation magnetization of the ferrofluid is $M_{\mathrm{sat}} = 37.4$ kA/m. The parameters defining the distribution turn out to be $D_0 = 8.3$ nm and $\sigma = 0.28$. There are small differences between the data and the fit curve that are, in our opinion, due to deviations of the real diameter distribution curve from the idealized log-normal form.

Embs [23] measured the equilibrium magnetization curve of the ferrofluid APG 933 of FerroTec. In addition, he determined the diameter distribution of the particles by transmission electron microscopy (TEM) that was then used in our theoretical analysis. Diameters found in TEM measurements are those of the magnetite particles. We assumed the magnetically effective diameters D_{mag} to be 2×0.8 nm $= 1.6$ nm smaller and to be zero for particles smaller than 1.6 nm. The hard core diameters D were taken to be 2×2 nm $= 4$ nm larger than the diameters obtained from the TEM measurements. As above, we took into account terms up to $O(\phi\epsilon^5)$ and set the bulk magnetization of magnetite to 480 kA/m. Figure 6 shows the TEM data and the experimental magne-
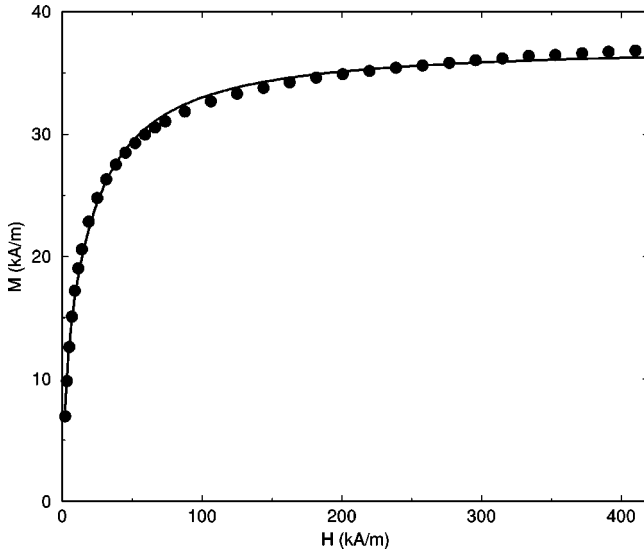
FIG. 5. Equilibrium magnetization of the ferrofluid EMC 905. Dots: experimental; solid line: the theoretical magnetization curve assuming lognormally distributed D_{mag}, cf. text.
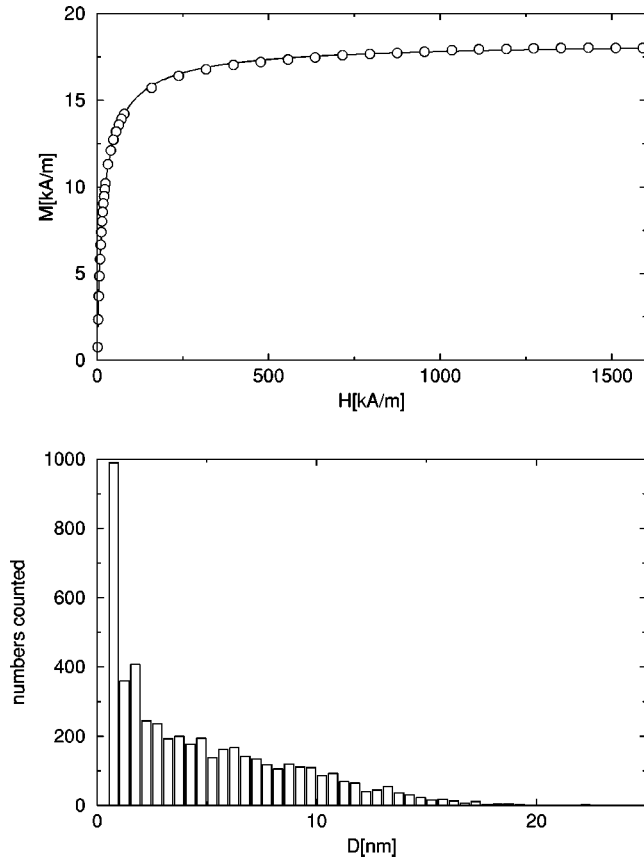

FIG. 6. Top: equilibrium magnetization of the ferrofluid APG 933. Dots: experiment; solid line: the theoretical magnetization curve. Bottom: diameter distribution according to TEM measurements.

tization curve together with the results of our theory. Both agree very well.

VI. CONCLUSION

In this paper, we used the technique of cluster expansion to derive an approximation to the equilibrium magnetization for the system of dipolar hard spheres in a magnetic field with diameter and/or magnetic moment dispersion as a model system for a polydisperse ferrofluid. The calculation results in an expression for the magnetization M in form of a twofold series expansion in the parameters $\bar{\phi}$, closely related to the volume fraction ϕ, and $\bar{\epsilon}$, a coupling parameter measuring the strength of the dipolar interaction:

$$M = \frac{N\bar{m}}{\mu_0 V} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \bar{\phi}^m \bar{\epsilon}^n L_{m,n}(\bar{\alpha}). \tag{6.1}$$

$\bar{\phi}$, $\bar{\epsilon}$, and the dimensionless magnetic field $\bar{\alpha}$ are defined for some typical values $\bar{D}$ and $\bar{m}$ for the hard sphere diameters and magnetic moments, respectively. $\bar{m}$ can be chosen in such a way that the prefactor $N\bar{m}/\mu_0 V$ reduces to the saturation magnetization of the system. We gave expressions for $L_{1,n}$ ($n \leq 5$) and $L_{2,2}$. Lower-orders vanish, except for $L_{0,0}$ reducing to the Langevin function in the monodisperse case. The calculated $L_{m,n}$ can be written as multiple sums over all particles whose addends are analytical expressions.

The influence of particle-particle interaction grows with increasing width of the considered diameter distribution. Taking into account only the $L_{1,1}$ term results in an increase of the magnetization relative to the non interacting system, whereas the $L_{2,2}$ term leads again to somewhat smaller values at higher $\bar{\alpha}$. Only at very small $\bar{\alpha}$ is its contribution positive. The $L_{1,n}$ terms have little effect for realistic, magnetite-based ferrofluids, except for broad distributions, where they increase the initial magnetization.

ACKNOWLEDGMENTS

APPENDIX: THE FUNCTIONS G_n^P, f^G, f^K

The functions $G_n^P(x_1, x_2)$ are symmetric in their arguments and have the form

$$G_n^P(x_1, x_2) = G_n^{P(0)}(1/x_1, 1/x_2) + \coth(x_1) G_n^{P(1)}(1/x_1, 1/x_2)$$

$$+ \coth(x_2) G_n^{P(1)}(1/x_2, 1/x_1)$$

$$+ \coth(x_1)\coth(x_2) G_n^{P(2)}(1/x_1, 1/x_2). \tag{A1}$$

The $G_n^{P(i)}$ are polynomials and read for $n \leq 5$

$$G_2^{P(0)}(y_1,y_2) = \frac{8}{5} + \frac{4}{5}y_1^2 + \frac{4}{5}y_2^2 + \frac{12}{5}y_1^2y_2^2,$$

$$G_2^{P(1)}(y_1,y_2) = -\frac{4}{5}y_1 - \frac{12}{5}y_1y_2^2, \qquad \text{(A2)}$$

$$G_2^{P(2)}(y_1,y_2) = \frac{12}{5}.$$

$$G_3^{P(0)}(y_1,y_2) = -\frac{4}{35}y_1y_2 - \frac{24}{35}y_1^3y_2 - \frac{24}{35}y_1y_2^3 - \frac{12}{7}y_1^3y_2^3,$$

$$G_3^{P(1)}(y_1,y_2) = -\frac{4}{35}y_2 + \frac{24}{35}y_1^2y_2 + \frac{4}{35}y_2^3 + \frac{12}{7}y_1^2y_2^3, \qquad \text{(A3)}$$

$$G_3^{P(2)}(y_1,y_2) = \frac{16}{105} - \frac{4}{35}y_1^2 - \frac{4}{35}y_2^2 - \frac{12}{7}y_1^2y_2^2.$$

$$G_4^{P(0)}(y_1,y_2) = \frac{8}{105} + \frac{4}{35}y_1^2 + \frac{4}{35}y_1^4 + \frac{4}{35}y_2^2 + \frac{12}{5}y_1^2y_2^2$$
$$+ \frac{36}{7}y_1^4y_2^2 + \frac{4}{35}y_2^4 + \frac{36}{7}y_1^2y_2^4 + 12y_1^4y_2^4,$$

$$G_4^{P(1)}(y_1,y_2) = -\frac{8}{105}y_1 - \frac{4}{35}y_1^3 - \frac{24}{35}y_1y_2^2 - \frac{36}{7}y_1^3y_2^2$$
$$- \frac{8}{7}y_1y_2^4 - 12y_1^3y_2^4, \qquad \text{(A4)}$$

$$G_4^{P(2)}(y_1,y_2) = \frac{32}{105}y_1y_2 + \frac{8}{7}y_1^3y_2 + \frac{8}{7}y_1y_2^3 + 12y_1^3y_2^3.$$

$$G_5^{P(0)}(y_1,y_2) = \frac{12}{385}y_1y_2 - \frac{104}{385}y_1^3y_2 - \frac{60}{77}y_1^5y_2 - \frac{104}{385}y_1y_2^3$$
$$- \frac{732}{77}y_1^3y_2^3 - \frac{240}{11}y_1^5y_2^3 - \frac{60}{77}y_1y_2^5 - \frac{240}{11}y_1^3y_2^5$$
$$- \frac{540}{11}y_1^5y_2^5,$$

$$G_5^{P(1)}(y_1,y_2) = -\frac{4}{231}y_2 + \frac{4}{385}y_1^2y_2 + \frac{60}{77}y_1^4y_2 + \frac{4}{385}y_2^3$$
$$+ \frac{172}{77}y_1^2y_2^3 + \frac{240}{11}y_1^4y_2^3 + \frac{4}{77}y_2^5 + \frac{60}{11}y_1^2y_2^5$$
$$+ \frac{540}{11}y_1^4y_2^5, \qquad \text{(A5)}$$

$$G_5^{P(2)}(y_1,y_2) = \frac{16}{1155} + \frac{8}{1155}y_1^2 - \frac{4}{77}y_1^4 + \frac{8}{1155}y_2^2 - \frac{32}{77}y_1^2y_2^2$$
$$- \frac{60}{11}y_1^4y_2^2 - \frac{4}{77}y_2^4 - \frac{60}{11}y_1^2y_2^4 - \frac{540}{11}y_1^4y_2^4.$$

It is

$$f^G(\Delta_{ij},\Delta_{ik},\Delta_{jk}) = \ln\left(\frac{\Delta_{ik}+\Delta_{jk}}{\Delta_{ij}}\right) - \frac{3(\Delta_{ik}^2-\Delta_{jk}^2)^2}{4\Delta_{ij}^4}$$
$$+ \frac{8(\Delta_{ik}^3+\Delta_{jk}^3)}{3\Delta_{ij}^3} - \frac{3(\Delta_{ik}^2+\Delta_{jk}^2)}{\Delta_{ij}^2}$$
$$+ \frac{13\Delta_{ik}^2+14\Delta_{ik}\Delta_{jk}+13\Delta_{jk}^2}{12(\Delta_{ik}+\Delta_{jk})^2}, \quad \text{(A6)}$$

and

$$f^K(\Delta_{ij},\Delta_{ik},\Delta_{jk}) = -\frac{2}{9} - \frac{5}{36}\frac{\Delta_{ij}^6+\Delta_{ik}^6+\Delta_{jk}^6}{\Delta_{ij}^3\Delta_{ik}^3} - \frac{\Delta_{jk}^2}{4\Delta_{ij}\Delta_{ik}}$$
$$- \frac{2\Delta_{jk}^3}{9\Delta_{ij}^3} - \frac{2\Delta_{jk}^3}{9\Delta_{ik}^3}$$
$$+ \frac{(\Delta_{ij}^4+\Delta_{ik}^4+\Delta_{jk}^4)(\Delta_{ij}^2+\Delta_{ik}^2+\Delta_{jk}^2)}{8\Delta_{ij}^3\Delta_{ik}^3}. \qquad \text{(A7)}$$

When all diameters are equal, these functions reduce to

$$f^G(\Delta,\Delta,\Delta) = \frac{1}{6} + \ln 2, \qquad \text{(A8)}$$

$$f^K(\Delta,\Delta,\Delta) = -\frac{5}{24}. \qquad \text{(A9)}$$

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