Applying the chain formation model to magnetic properties of aggregated ferrofluids

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The magnetization properties of aggregated ferrofluids are calculated by combining the chain formation model developed by Zubarev with the modified mean-field theory. Using moderate assumptions for the inter- and intrachain interactions we obtain expressions for the magnetization and initial susceptibility. When comparing the results of our theory to molecular dynamics simulations of the same model we find that at large dipolar couplings ($\lambda > 3$) the chain formation model appears to give better predictions than other analytical approaches. This supports the idea that chain formation is an important structural ingredient of strongly interacting dipolar particles.

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I. INTRODUCTION

Ferrofluids (dipolar magnetic fluids) are colloidal suspensions of ferromagnetic particles of about 10 nm diameter dispersed in a carrier liquid [1] that are usually stabilized against agglomeration by coating particles with long-chain molecules (sterically) or decorating them with charged groups (electrostatically). The small size of the particles favors magnetic monodomains with a magnetic moment proportional to the volume of the magnetic core. As a result, the particles interact with each other through the long-range anisotropic dipole-dipole potential as well as through short-range symmetric potentials, such as the steric repulsion, the electrostatic repulsion, and the van der Waals attraction. The study of the magnetization properties and the structure are of importance for our fundamental understanding and for potential applications of ferrofluids.

The evaluation of magnetic characteristics of homogeneous ferrofluids faces often the well-known problem of how to adequately account for the interparticle dipole-dipole interaction. The latter is most difficult to treat in concentrated systems since there the mutual correlations of positions and orientations of the magnetic moments of the ferroparticles are particularly strong. The physical properties of dilute ferrofluids with small magnetic moments are well described in the framework of the one-particle model [2], which treats a ferrofluid as an ideal paramagnetic gas of particles, suspended in a liquid carrier. The equilibrium magnetization can be written by applying the Langevin function $L(\alpha) = \coth\alpha - 1/\alpha$ as

$$M_L = nmL(\alpha), \tag{1}$$

where n is the particle concentration, m is the particle's magnetic moment, and $\alpha = mH/k_BT$ is the Langevin parameter, the ratio of the field interaction mH and the thermal energy k_BT. The initial magnetic susceptibility χ_L is called the Langevin susceptibility and is given by

$$\chi_L = nm^2/3k_BT = 2\lambda\varphi/\pi. \tag{2}$$

Here $\varphi = \pi n d^3/6$ is the volume fraction of the ferrofluid, with d being the particle diameter, and $\lambda = m^2/d^3k_BT$ is the dipole-dipole interaction parameter which is the ratio of the interaction energy m^2/d^3 and the thermal energy of two ferroparticle magnetic moments at contact. The Langevin susceptibility represents an effective measure of the dipole-dipole interaction for dilute solutions.

However, experiments [3] and computer simulations [4–6] with concentrated ferrofluids reveal an essential deviation from the Langevin formulas. The initial susceptibility increases faster than expected according to linear dependence $\chi_L \sim \varphi$ of Eq. (2). It is clear that this deviation is primarily due to the interparticle interactions. A number of theoretical models have been developed to adequately treat the dipole-dipole interactions for the evaluation of the magnetic properties. Here we present an application of the chain formation model [7] to strongly interacting ferrofluids, where we look at the magnetic properties and the chain properties. We compare the predictions of the chain formation model with molecular dynamics simulations for a variety of test cases.

The paper is organized as follows. First we review various theoretical approaches that have been developed for concentrated ferrofluids. Then we review the chain formation model [7]. Section IV is devoted to the simulation model used. In Sec. V we present the results and comparisons, and we end in Sec. VI with our conclusion.

II. BEYOND THE LANGEVIN MODEL

A number of theoretical models allow the evaluation of magnetic properties by taking into account the dipole-dipole interactions in various effective ways. These are different variants of the mean-field [8–11], the mean-spherical [12–14], and the thermodynamic perturbation model [15–18]. In the framework of the most popular mean-field model by Weiss [8,10] the dipole-dipole interactions are assumed to be

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equivalent to some increase in the intensity of an external magnetic field, with the amount of its contribution being proportional to the magnetization M of the ferrofluid. The effective field acting on a single-domain particle is expressed as $H_e = H + \kappa M$. The mean-field constant is generally assumed to be equal to the Lorentz value $\kappa = 4\pi/3$. In this case H_e coincides with a field intensity in the spherical cavity formed by a particle in a liquid, provided that the cavity itself exerts no effect on the state of the neighboring particles. Thus, this model yields the Curie-Weiss law for the initial susceptibility $\chi = \chi_L/(1-\kappa\chi_L)$. The Weiss model predicts a magnetic phase transition into a magneto-ordered liquid state; at the transition point the initial susceptibility becomes infinite, that is, $\chi \to \infty$ when $\chi_L \to 3/4\pi$. But a paramagnetic to ferromagnetic second order phase transition is never observed in fluidlike magnetic systems, and hence the validity of the Weiss mean-field theory appears to be questionable.

The mean-field Onsager model [9] is based on the assumption that the cavity formed by a particle in a ferrofluid influences the orientation of the magnetic moments of the neighboring particles. The initial susceptibility remains finite for any finite temperature and concentration, but experimental and computer studies have shown that the Onsager model greatly underestimates the values of the initial susceptibility of concentrated ferrofluids (as well as the dielectric constant of polar fluids) [3,15,19–21].

Attempts to use the mean-spherical model [13,14] and the first order thermodynamic perturbation method [15,16] proved far more successful. These models are appropriate to describe experimental data on magnetostatic properties of real magnetic fluids. These models yield similar results and are valid for ferrofluids with low or moderate volume concentrations of magnetic cores ~ 10–$12\,\%$ under the presence of an arbitrary valued uniform magnetic field.

The most precise description of the magnetization curves of moderately concentrated ferrofluids is given by the so-called ''modified mean-field model'' [11]. This approach is based on the assumption that the effective field acting on a ferroparticle is proportional to the Langevin magnetization M_L, that is, $H_e = H + (4\pi/3)M_L$:

$$M = M_L(H_e) = nmL(\alpha_e), \quad \alpha_e = \frac{m}{k_B T}\left[H + \frac{4\pi}{3}M_L(H)\right], \tag{3}$$

$$\chi = \chi_L\left(1 + \frac{4\pi}{3}\chi_L\right).$$

The resulting expressions for the initial susceptibility and for the magnetization under saturation conditions coincide with the predictions of the thermodynamic perturbation model [15,16]. But the ''modified mean-field model'' gives a more accurate description of the magnetization curves under arbitrary applied external field strengths.

All the last mentioned models are valid in those cases when the intensity of the interparticle dipole-dipole interaction does not grow much more strongly than the thermal energy $k_B T$. This means that the dipole-dipole interaction parameter λ has the order of unity or less, that is $\lambda \lesssim 1$. For dense ferrofluids with a magnetic volume concentration larger than 15–$18\,\%$, or ferrofluids with a large value of λ, this is insufficient. The temperature dependencies of the initial susceptibility of these systems show large deviations [3,19] between the theoretical predictions and the experimental data. At low temperatures the models [11,13,15] underestimate the values of the initial susceptibility by 15–20 %. It is clear that this deviation is due to the dipole-dipole interactions in concentrated magnetic fluids.

A further extension of the theory for the case of dense ferrofluids is based on second-order perturbation methods [17,18]. Both approaches give the same expression for the initial magnetic susceptibility in the form of an expansion like (3), but include the next term of the higher order over χ_L:

$$\chi = \chi_L\left(1 + \frac{4\pi}{3}\chi_L + \frac{(4\pi)^2}{144}\chi_L^2\right). \tag{4}$$

This expression describes well the initial susceptibility temperature dependence for ferrofluids with a maximum allowable magnetic volume concentration $\sim 18\%$ [18] at low temperatures $(4\pi\chi \sim 60$–$80)$. The ferrofluid magnetization is obtained in a form of a complicated series over different combinations of the Langevin magnetization. In Ref. [18] it was shown that the ferrofluid magnetization should be presented by using the ''modified mean-field approach'' (2), and the mean field H_e for dense systems can be written as

$$H_e = H + \frac{4\pi}{3}M_L(H) + \frac{(4\pi)^2}{144}M_L(H)\frac{dM_L(H)}{dH}, \tag{5}$$

$$M = nmL(\alpha_e), \quad \alpha_e = mH_e/k_B T.$$

This expression describes very accurately the magnetization curves of dense ferrofluids with a saturation magnetization of about 80–90 kA/m and allows us to obtain the particle size distribution with the help of a magnetogranulometric analysis [18].

Naturally, for low and moderately concentrated ferrofluids the expressions (3)–(5) give very close results, and deviations appear only for higher concentrations or for ferrofluids containing large particles.

The above theoretical models are in principle based on the assumption of homogeneous distribution of the particle positions. However, when the average size of the particles is large or the temperature is low, the dipole-dipole interaction energy between particles is considerably larger than the thermal energy, i.e., $\lambda \gg 1$. The particles can aggregate to form clusters or chains due to the dipolar interactions. Simulations have shown that the aggregation of the particles can strongly affect the magnetization behavior of the systems [5,6]. This is clearly demonstrated in Fig. 1 which shows the magnetization curves of the systems with fixed Langevin susceptibility $4\pi\chi_L = 1.256$. The dipolar coupling parameter λ is varied from 1 to 5. Correspondingly, the volume fraction of the particles is decreased from $\varphi = 0.157$ to 0.031. For $\lambda = 1$ and 2, the simulation results agree with the theoretical predictions [Eqs. (3) and (5)] very well. But deviation occurs at

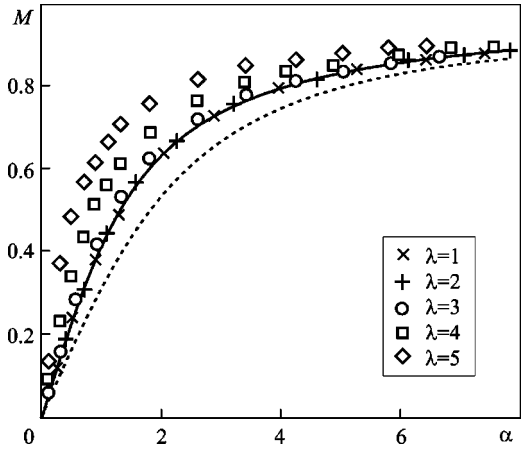

FIG. 1. Simulational results on the equilibrium magnetization as a function of the Langevin parameter α for five dipolar coupling parameters $\lambda=1,\ldots,5$, at the same value of the Langevin parameter $4\pi\chi_L=1.256$. The dashed curve gives the prediction of Eq. (1) and the solid curve gives the prediction of Eq. (3). Note that Eq. (5) would visually give basically the same result as Eq. (3).

$\lambda\geqslant 3$ when the particles begin to aggregate with each other. This effect is more evident at weak fields. It consequently results in higher values of the initial susceptibility χ as shown in Fig. 2. However, the influence of particle aggregations can be well considered in theoretical calculations by employing the chain formation model. In the following sections we will calculate the magnetic properties of different ferrofluid systems within this model and compare them with simulation results.

III. THE CHAIN FORMATION MODEL

The chain formation model was developed in Ref. [7], assuming that the system free energy F is a functional on the concentration g_k of chains containing k particles under the mass balance condition:

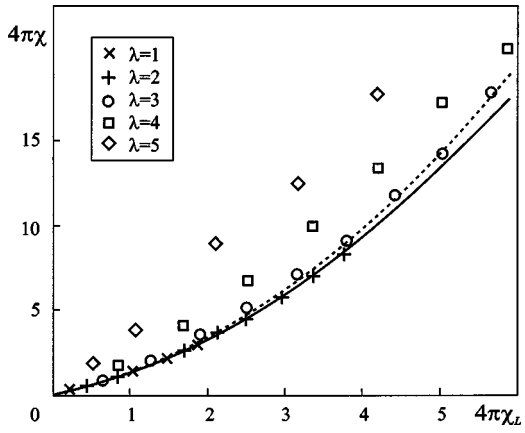

FIG. 2. Simulational results on the initial susceptibility χ as a function of the Langevin susceptibility for five dipolar coupling parameters $\lambda=1,\ldots,5$. The dashed curve gives the prediction of Eq. (4) and the solid curve gives the prediction of Eq. (3).

$$F=k_BT\sum_{k=1}^{\infty} g_k\ln\left(\frac{g_kv}{eZ_k}\right),\quad \sum_{k=1}^{\infty} g_kk=\varphi/v, \tag{6}$$

where φ stands as usual for the volume fraction of the ferroparticles, v is the particle volume, and Z_k has the meaning of a k-particle chain partition function. We restrict our model to account only for the magnetic interaction between the nearest neighboring particles in each chain. Accordingly, the partition function can be simply expressed as

$$Z_k=\exp[(k-1)\varepsilon], \tag{7}$$

where ε has the meaning of the dimensionless effective energy of an interparticle bond at zero magnetic field. Its value depends on the definition of a chain. The simplest way is to use Jordan's expression [22]

$$\varepsilon=\ln\left(\frac{\exp(2\lambda)}{3\lambda^3}\right). \tag{8}$$

To find the minimum of the free energy functional under the condition (6) one includes the constraint via a Lagrange multiplier μ and considers the functional Φ:

$$\Phi[g_k]=F[g_k]+\mu\left(\sum_{k=1}^{\infty} g_kk-\frac{\varphi}{v}\right)$$

$$=k_BT\sum_{k=1}^{\infty} g_k\left\{\ln\left(\frac{g_kv}{eZ_k}\right)+\mu k\right\}+\text{const.} \tag{9}$$

The chain distribution g_k is obtained by extremizing $\Phi[g_k]$

$$\partial\Phi[g_k]/\partial g_k=0\Rightarrow g_k=\frac{1}{v}\exp(-\varepsilon)p^k,\quad k=1,2,3\ldots. \tag{10}$$

Here $p=\exp(\varepsilon-\mu)<1$ is the probability of establishing an interparticle bond. The Lagrange multiplier μ (and p as well) is determined in the usual way by substituting g_k into the mass balance condition (6).

When studying the magnetic properties of the aggregated ferrofluid we face the problem of chain orientation in an external magnetic field. Since we do not know any reliable theoretical result that describes the ferrofluid chain formation in the presence of a magnetic field, the following procedures are adopted.

(1) We study an intensively interacting monodisperse ferroparticle system with large coupling $\lambda=3$–5. In this case we can assume that the neighboring particle magnetic moments in each chain are highly correlated (stifflike rotation). This means that the orientation of each k-particle chain to an external field direction is governed by a chain magnetic moment $m_{chain}=km$, where m is the magnetic moment of a single ferroparticle.

(2) We study only the orientation of the chains formed in the absence of an external field; hence we do not take into account any changes in the chain distribution due to an applied field.

(3) To develop an adequate model of the magnetic properties of aggregated ferrofluids, one needs to take into account the dipole-dipole interaction between all pairs of ferroparticles. Here we use the ''modified mean-field model'' (3). Since the magnetic interactions between all nearest neighboring particles in all chains are taken into account exactly (6)–(8), we have to exclude from the effective field H_e the number of these bonds, which is equal to

$$\sum_{k=2}^{\infty}(k-1)g_k=\frac{\varphi}{v}-\sum_{k=1}^{\infty}g_k=\frac{\varphi}{v}\left(1-\frac{1}{\langle k\rangle}\right).$$

In this way a dimensionless effective magnetic field α_e [Eq. (3)] acts on each chain and depends on the Langevin parameter α, the Langevin susceptibility χ_L, and the mean chain length $\langle k\rangle$:

$$\alpha_e=\alpha+4\pi\chi_L L(\alpha)/\langle k\rangle. \tag{11}$$

What is the motivation to introduce into the model an effective field H_e instead of an external one H? In the limiting case of no chains present one can easily get the well known expression for the free energy from the model (6)–(10):

$$F=-\frac{\varphi}{v}k_BT\ln\frac{\sinh\alpha_e}{\alpha_e}, \tag{12}$$

which coincides with the prediction of the ''modified mean-field model.'' We also know that the model (3) describes very accurately the experimental and numerical data for ferrofluids containing weakly and moderately interacting ferroparticles ($\lambda\approx 1-2$). If we used an external field H under such a limitation, we would obtain simply the free energy of an ideal paramagnetic gas, and this approximation is valid only for very dilute and weakly interacting ferrofluids.

IV. SIMULATION MODEL

The molecular dynamics simulation method is similar to the Langevin dynamics implementation described in previous work [5]. The ferrofluid systems are supposed to be composed of N spherical particles of diameter d distributed in a cubic simulation box of side length L. Each particle has a permanent point dipole moment $\mathbf{m}_i$ at its center. Using periodic boundary conditions in all spatial directions, the dipole-dipole interaction potential between particles i and j is given by

$$U_{ij}^{dip}=\sum_{\mathbf{n}\in\mathbb{Z}^3}\left\{\frac{\mathbf{m}_i\cdot\mathbf{m}_j}{|\mathbf{r}_{ij}+\mathbf{n}L|^3}-\frac{3[\mathbf{m}_i\cdot(\mathbf{r}_{ij}+\mathbf{n}L)][\mathbf{m}_j\cdot(\mathbf{r}_{ij}+\mathbf{n}L)]}{|\mathbf{r}_{ij}+\mathbf{n}L|^5}\right\}, \tag{13}$$

where $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$ is the displacement vector of the two particles. The sum extends over all simple cubic lattice points $\mathbf{n}=(n_x,n_y,n_z)$ with n_x,n_y,n_z integers. In this work, we use the Ewald summation with metallic boundary conditions for dipolar systems to evaluate Eq. (13) effectively. This means that the applied external magnetic field coincides exactly with the internal field. In all the simulations the root mean square (rms) absolute errors in the dipolar forces are fixed to $\Delta F^{dip}\leqslant 10^{-4}m^2/d^4$. The corresponding optimal values of the Ewald parameters are then determined from the theoretical estimates of the cutoff errors in the Ewald summation derived in a previous paper [23].

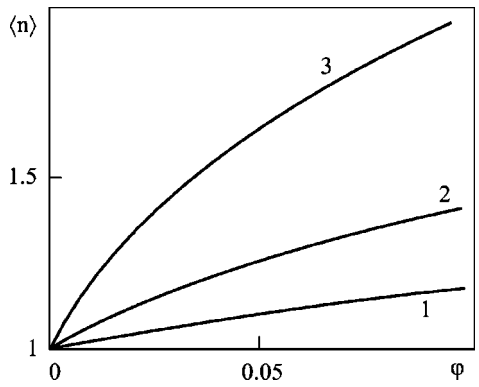

FIG. 3. The average chain length $\langle n\rangle$ as a function of ferrofluid concentration φ as predicted by the chain formation model. The curves 1,2,3 correspond to values of $\lambda=3,4,5$, respectively.

The short-range interactions between the particles are represented by the purely repulsive Lennard-Jones potential

$$U_{ij}^{LJ}=4\varepsilon\left[\left(\frac{d}{r_{ij}}\right)^{12}-\left(\frac{d}{r_{ij}}\right)^{6}-C(R_c)\right], \tag{14}$$

where $C(R_c)=(d/R_c)^{12}-(d/R_c)^6$ with a cutoff radius of $R_c=2^{1/6}d$. In this way the particles have a purely repulsive interaction force which smoothly decays to zero at R_c. The translational and rotational Langevin equations of motion of particle i are given by [5,6]

$$\mathcal{M}_i\dot{\mathbf{v}}_i=\mathbf{F}_i-\Gamma_T\mathbf{v}_i+\boldsymbol{\xi}_i^T, \tag{15}$$

$$\mathbf{I}_i\cdot\dot{\boldsymbol{\omega}}_i=\boldsymbol{\tau}_i-\Gamma_R\boldsymbol{\omega}_i+\boldsymbol{\xi}_i^R, \tag{16}$$

where $\mathcal{M}_i$ and $\mathbf{I}_i$ are the mass and inertia tensors of the particle. Γ_T and Γ_R are the translational and rotational friction constants, respectively. $\boldsymbol{\xi}_i^T$ and $\boldsymbol{\xi}_i^R$ are the Gaussian random force and torque. The variables can be given in dimensionless form as length $r^*=r/d$, dipole moment $m^{*2}=m^2/\epsilon d^3$, moment of inertia $I^*=I/(\mathcal{M}d^2)$, time $t^*=t(\epsilon/\mathcal{M}d^2)^{1/2}$, friction constants $\Gamma_T^*=\Gamma_T(d^2/\mathcal{M}\epsilon)^{1/2}$ and $\Gamma_R^*=\Gamma_R/(\mathcal{M}d^2\epsilon)^{1/2}$, magnetic field $H^*=H(d^3/\epsilon)^{1/2}$ as well as temperature $T^*=k_BT/\epsilon$. The simulations were performed at constant temperature $T^*=1$. A reduced time step $\Delta t^*=0.002$ was employed in all simulations. The runs were started from initial configurations with random particle positions and dipole moment orientations. For each case, the system was at first equilibrated for a dimensionless time of at least $t^*=100$. The magnetization and structural properties were then calculated from the data for another period of at least $t^*=400$, depending on the values of λ. Error bars for the simulation results were determined by dividing the simu-

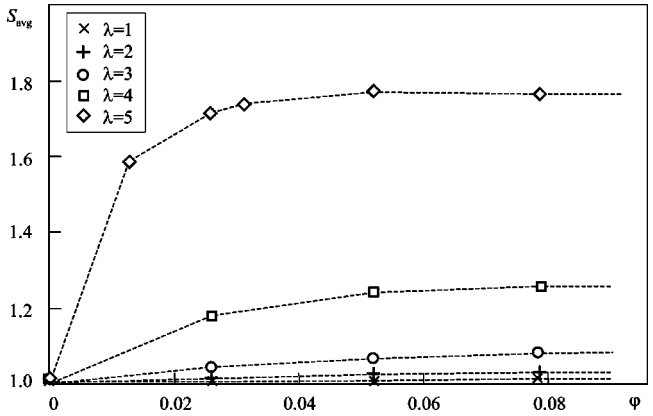

FIG. 4. The average chain length S_{av} as a function of ferrofluid concentration φ as obtained by the simulations for values of the coupling parameter $\lambda = 1-5$.

lation runs into blocks and calculating an estimate for the standard deviation of the mean [24].

The initial susceptibility χ is determined by the linear magnetization response $\mathbf{M}=\chi\mathbf{H}$ at field strength $H\rightarrow 0$. In simulations the values of χ were obtained by calculating the equilibrium magnetization $\mathbf{M}$ for a series of weak fields $\mathbf{H}$ starting from 0 and then performing a linear fitting to the $M(H)$ curves [5,6]. The structures formed in the systems were analyzed by employing an energy criterion. Two particles are considered to be bound if their dipolar potential energy is less than a predetermined value $U_{bond}=-1.5\lambda k_B T$. The average cluster size is defined by

$$S_{av}=\left\langle \sum_s s n_s / \sum_s n_s \right\rangle, \tag{17}$$

where n_s is the number of clusters having size s, and the triangular brackets denote the time average, or, equivalently, the average over the configuration space.

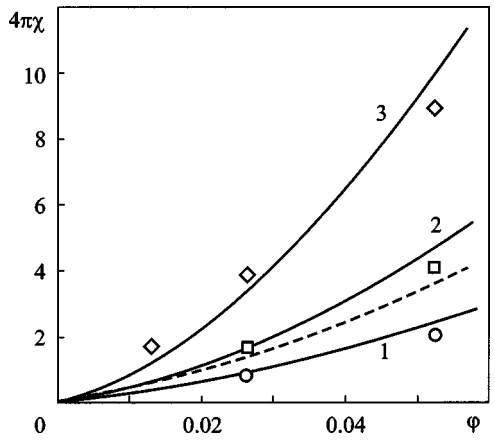

FIG. 5. The initial susceptibility as a function of ferrofluid concentration φ as obtained from the simulations for $\lambda = 3,4,5$. The solid curves 1,2,3 correspond to the predictions of the chain formation model for a value of $\lambda = 3,4,5$, respectively. The dashed curve represents the modified mean-field model prediction for the case $\lambda = 5$.

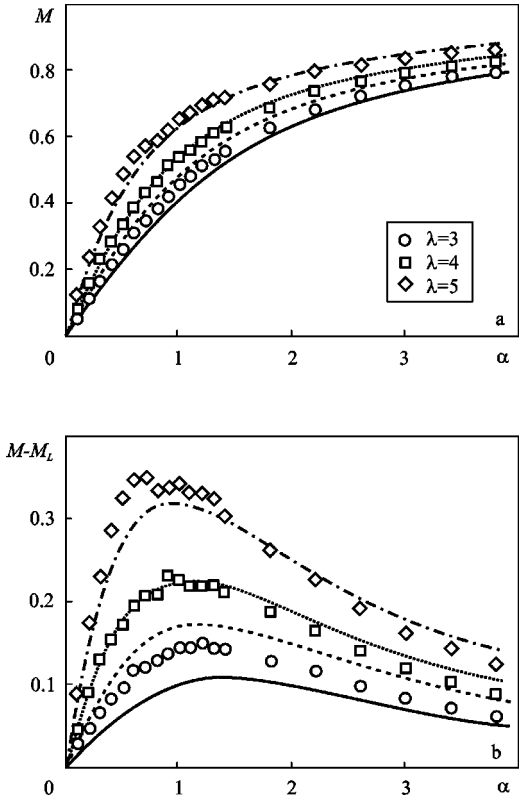

FIG. 6. (a) The relative magnetization M/M_{sat} versus Langevin parameter α as obtained from simulations at the same value of the Langevin susceptibility $4\pi\chi_L = 1.256$ for values of the dipolar coupling $\lambda = 3,4,5$. The solid curve is the universal prediction from Eq. (5), which depends only on the Langevin susceptibility. The other curves are the corresponding predictions from the chain formation model. (b) This curve shows the same data, where for more clarity we plot $(M-M_L)/M_{sat}$.

V. COMPARING THE CHAIN FORMATION MODEL TO SIMULATIONAL DATA

We start out by computing the mean chain length as a function of the ferroparticle concentration at zero external field for the values $\lambda = 3,4,5$ (see Fig. 3). It should be pointed out that the system at these parameters is still weakly aggregated and that the majority of ferroparticles are monomeric at zero field, even for $\lambda = 5$. However, an increase in the magnetic field strength will have the result that the mean chain length increases. The simulational data of the system at the same values of the parameters show qualitatively the same behavior as the chain formation theory (see Fig. 4). It is notable that at larger ferrofluid concentrations the simulations show a saturation in chain length, whereas the chain formation model still predicts an increase in mean chain length. However, at smaller concentrations, even the quantitative agreement is surprisingly good in light of the severe approximations made.

Next we look at the relative magnetization that, according to the definition, one can obtain as a superposition of Langevin functions for different chain structures:

$$M=\frac{1}{\varphi}\sum_{k=1}^{\infty} k g_k L(\alpha_e k). \tag{18}$$

In the limiting case of no chains present this expression takes the form (3) and describes well the magnetization curves for low and moderately concentrated ferrofluids.

Assuming the expansion of the magnetization (18) in a weak field limit with the accuracy of terms linear in α, it is easy to get the expression for initial magnetic susceptibility χ:

$$4\pi\chi = \frac{4\pi\chi_L}{\varphi}\left(1 + \frac{4\pi\chi_L}{3\varphi}\sum_{k=1}^{\infty} g_k\right)\sum_{k=1}^{\infty} k^2 g_k. \qquad (19)$$

Due to the presence of the last summation a small number of chains can greatly influence the value of initial susceptibility.

The concentration dependence of the initial susceptibility (19) is presented in Fig. 5 for various values of coupling parameter λ and compared with the simulation data. For moderate values of $\lambda = 1-2$ Eq. (19) reduces basically to the modified mean-field result shown in Fig. 2. But for sufficiently large coupling parameter $\lambda = 3-5$ the ''modified mean-field model'' greatly underestimates the magnetic susceptibility (Fig. 2). As far as the chain model is concerned, a good quantitative agreement with the simulation data is obtained for a diluted system, and with increasing particle concentration some overestimation occurs. Naturally, this is not surprising since we overestimated the correlations in the magnetic moment orientations by assuming complete alignment. The presence of some uncorrelated magnetic moment orientations to the external field direction will lower the susceptibility.

The same approximations were used for the calculation of the magnetization shown in Fig. 6 and compared to the simulational data. Again we find that the chain formation model describes the numerical data much better than the ''modified mean-field'' model at large values of λ. The very good quantitative agreement can be particularly well seen in the lower part of Fig. 6 where for clarity we plot $(M - M_L)/M_{sat}$.

VI. CONCLUSION

We have presented an extension of the chain formation model as developed in Ref. [7]. We used an approximation of the stiff rodlike orientational chain response to a magnetic field that leads to very simple and physically clear expressions for magnetization and initial magnetic susceptibility. In order to adequately include the dipolar interactions of the chains we applied the ''modified mean-field model'' in a straightforward way. Our model reduces for weak coupling λ to the modified mean-field model [11], including, however, at large coupling the effects of chain formation. When we compare the predictions of the chain formation model to molecular dynamics simulations of the same model, we find that the formation of short chains starts at a dipolar coupling $\lambda \lesssim 3$. The chains appear to be very important for a better understanding of the magnetic properties since our chain model describes the magnetization, as well as the initial susceptibility, in this regime much better than the ''modified mean-field model,'' which is based on a homogeneous distribution of ferroparticles.

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