

Linear and nonlinear magnetic properties of ferrofluids

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Within a high-magnetic-field approximation, employing Ruelle's algebraic perturbation theory, a field-dependent free-energy expression is proposed which allows one to determine the magnetic properties of ferrofluids modeled as dipolar hard-sphere systems. We compare the ensuing magnetization curves, following from this free energy, with those obtained by Ivanov and Kuznetsova [*Phys. Rev. E* **64**, 041405 (2001)] as well as with new corresponding Monte Carlo simulation data. Based on the power-series expansion of the magnetization, a closed expression for the magnetization is also proposed, which is a high-density extension of the corresponding equation of Ivanov and Kuznetsova. From both magnetization equations the zero-field susceptibility expression due to Tani *et al.* [*Mol. Phys.* **48**, 863 (1983)] can be obtained, which is in good agreement with our MC simulation results. From the closed expression for the magnetization the second-order nonlinear magnetic susceptibility is also derived, which shows fair agreement with the corresponding MC simulation data.

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I. INTRODUCTION

Dipolar fluids consist of particles which carry a permanent dipole, be it a magnetic one or an electric one. The most prominent examples of the first group are magnetic fluids, while the second group typically corresponds to molecular liquids. Magnetic fluids are colloidal suspensions of single domain magnetic grains dispersed in a solvent [1]. In order to keep such systems stable against aggregation the grains have to be coated with polymers or surfactant layers or they are stabilized by electric double layer formation in the case of water-based ferrofluids. (Of course, there are fluids which consist of molecules carrying a substantial permanent magnetic dipole. One of the most significant representatives of these materials is oxygen, which exhibits strong paramagnetism [2].) In the case of dipolar molecular liquids the electric dipole moments stem from the electronic structure of the molecules. Concerning magnetization versus electric polarization, there is an important difference between these two types of fluids. By applying sufficiently high magnetic fields, for magnetic fluids it is possible experimentally to reach a magnetically saturated state, in which all dipoles are aligned in the direction of the external field \mathbf{H} [3]. Therefore magnetic fluids in applied external magnetic fields allow one to study the strongly nonlinear dependence of the magnetization \mathbf{M} on the field \mathbf{H} . In the case of electrically dipolar liquids saturation cannot be reached with experimentally accessible electric field strengths [4]. (The strong electric fields may destroy the molecules, electric breakdown can occur, and there are technical difficulties to generate very strong electric fields.) Therefore molecular liquids exposed to typical external electric fields exhibit only a weak nonlinear behavior [5]. Accordingly, in the literature the dielectric constant (or permittivity) of dipolar liquids is determined on the basis of linear response theories [6–11]. This means that in practice only the electric field dependence of the polarization for small electric fields matters. In order to understand the linear *and* nonlinear behavior of magnetic fluids, it is necessary to determine the *whole*

magnetization curve $M(H)$, where $H = |\mathbf{H}|$ and $M = |\mathbf{M}|$. Commonly, however, from the magnetization one infers the magnetic susceptibility or, more precisely, the initial magnetic susceptibility or zero-field magnetic susceptibility,

$$\chi_0 = \left(\frac{\partial M}{\partial H} \right)_{H=0}. \quad (1)$$

Here χ_0 is a scalar susceptibility, assuming that the direction of the vector \mathbf{M} is the same as the direction of the vector \mathbf{H} . (For magnetic fluids this assumption is well satisfied.) The difference between electrically and magnetically dipolar fluids is also reflected by the development of their theoretical description. Within the mean spherical approximation (MSA) Wertheim [8] obtained an analytical equation only for the dielectric constant of dipolar fluids. Later, when his theory was transferred to magnetic fluids [12], this linear response theory turned out to be insufficient for the description of magnetic fluids and had to be extended by determining the full magnetization $M(H)$ [13–15]:

$$M = m\rho L \left\{ \beta m H + \frac{3[1 - q(K\eta)]}{m\rho} M \right\} \quad (2)$$

and [see Eq. (1)]

$$\chi_0 = \frac{\chi_L}{q(-K\eta)}. \quad (3)$$

In Eq. (2) $\rho = N/V$ is the number density of the magnetic particles, $\eta = \pi\rho\sigma^3/6$ is the dimensionless packing fraction with the hard-sphere diameter σ , m is the strength of the permanent dipole moment of the particles (see Sec. II below), $\beta = 1/(k_B T)$ is the inverse temperature with the Boltzmann constant k_B , and

$$L(x) = \coth(x) - 1/x \quad (4)$$

is the Langevin function with $L(x \rightarrow 0) = \frac{1}{3}x$. In Eq. (3)

$$\chi_L = \beta\rho m^2/3 \quad (5)$$

is the Langevin susceptibility (see below), $q(x) = (1 + 2x)^2/(1 - x)^4$ is the reduced inverse compressibility function of the hard-sphere fluid, corresponding to the underlying model of dipolar hard spheres with diameter σ . According to MSA theory, $K\eta$ and thus the dimensionless parameter K in Eqs. (2) and (3) is determined by the implicit equation

$$4\pi\chi_L = q(2K\eta) - q(-K\eta), \quad (6)$$

which determines K in terms of χ_L and η (see Ref. [16]). Equation (3) follows from Eqs. (1) and (2). We note that within the framework of MSA the dimensionless parameter K turns out to be given by the expression

$$K = \int_{\sigma}^{\infty} dr_{12} \frac{h_D(r_{12})}{r_{12}}, \quad (7)$$

where $h_D(r_{12})$ is a certain angular projection of the total correlation function of the dipolar hard-sphere systems as function of the interparticle distance.

For dipolar hard-sphere fluids a more reliable, perturbative description was given by Ivanov and Kuznetsova [17] such that their magnetization equation is valid for wider ranges of the number density and the dipole strength:

$$\begin{aligned} M(H) &= M_L(H_e) = m\rho L(\beta m H_e), \\ H_e &= H_e(H) \\ &= H + \frac{4\pi}{3} M_L(H) + \frac{(4\pi)^2}{144} M_L(H) \frac{dM_L(H)}{dH}, \end{aligned} \quad (8)$$

with

$$M_L(H) = m\rho L(\beta m H). \quad (9)$$

In Eq. (8) H_e is the effective magnetic field strength which takes into account that the magnetization modifies the field within the liquid. The Langevin magnetization M_L is defined by Eq. (9) [compare Eq. (2)] and renders the Langevin susceptibility $\chi_L = (\partial M_L / \partial H)|_{H=0}$. We note that the Hamiltonian of dipolar hard-sphere systems in an external field depends parametrically on σ, m, β, V , and H so one might expect that Eqs. (8) and (9) exhibit, *inter alia*, a dependence on σ which, however, is not the case. The reason is that the approximation for the pair-correlation function, the integral of which underlies these equations, contains only contributions linear in the dipole-dipole interaction potential. In order to avoid the occurrence of demagnetization these integrals are calculated for infinitely elongated ellipsoidal samples. In this case only the leading asymptotic behaviors of the hard-sphere potential [$u_{HS}(r \rightarrow \infty) = 0$] and of the corresponding Boltzmann factor [$\exp[-\beta u_{HS}(r \rightarrow \infty)] = 1$], which do not depend on σ , contribute to the corresponding integrals determining Eqs. (8) and (9). Taking into account higher-order contributions from the dipole-dipole interaction render, however, a dependence of Eqs. (8) and (9) on σ . The corresponding zero-field magnetic susceptibility follows from Eq. (1):

$$\chi_0 = \chi_L \left[1 + \frac{4\pi\chi_L}{3} + \frac{(4\pi\chi_L)^2}{144} \right]. \quad (10)$$

With suitable fits for the parameters these results are in good agreement with experimental data. However, simulation data corresponding to higher values of the Langevin susceptibility

and of the density render a magnetic susceptibility which differs significantly from Eq. (10). We note that expanding Wertheim's [8] MSA susceptibility [Eq. (3)] in terms of χ_L up to third order also yields Eq. (10). Considering the dipolar hard-sphere (DHS) fluid, Jepsen [18,19] and Rushbrook [20,21] have augmented the Debye-Weiss equation by a use of a third-order Langevin susceptibility term:

$$\frac{\chi_0}{1 + 4\pi\chi_0/3} = \chi_L - \frac{15\pi^2}{9}\chi_L^3. \quad (11)$$

It turns out that in Eq. (11) the expansion of χ_0 in terms of χ_L up to third order reproduces Eq. (10). Although the validity of Eq. (10) has thus been proven in various ways, its range of applicability is not satisfactory. Tani *et al.* [9] carried out perturbation theory in order to calculate the dielectric constant of dipolar hard-sphere fluids. Their results render a density-dependent correction to Eq. (10):

$$\chi_0 = \chi_L \left[1 + \frac{4\pi}{3}\chi_L - \left(\frac{4\pi}{3} \right)^2 \chi_L^2 + I_{dd\Delta}(\rho)\chi_L^2 \right], \quad (12)$$

where

$$I_{dd\Delta}(\rho) = \int d^3r_2 d^3r_3 \frac{3 \cos^2 \gamma_3 - 1}{(r_{13}r_{23})^3} g_{\sigma}^{(3)}(r_{12}, r_{13}, r_{23}). \quad (13)$$

In Eq. (13) $g_{\sigma}^{(3)}$ is the three-point correlation function of the hard-sphere fluid and γ_3 is the interior angle at vertex 3 in the triangle formed by hard spheres 1, 2, and 3. Using the superposition approximation (see below), Tani *et al.* [9] calculated the corresponding integral for various densities and expressed it in terms of a Pade approximant:

$$I_{dd\Delta}(\rho^*) = \frac{17\pi^2}{9} \left[\frac{1 - 0.93952\rho^* + 0.36714(\rho^*)^2}{1 - 0.92398\rho^* + 0.23323(\rho^*)^2} \right], \quad (14)$$

with $\rho^* = \rho\sigma^3$ as the reduced number density in terms of the hard-sphere diameter σ . In the low-density limit one has

$$\lim_{\rho \rightarrow 0} I_{dd\Delta}(\rho^*) = \frac{17\pi^2}{9}, \quad (15)$$

so in this limit Eqs. (12) and (14) reduce to Eq. (10). (Using the weak-field version of an algebraic perturbation theory, Eq. (12) also can be derived rigorously [11].) The main disadvantage of this theory by Tani *et al.* is that it does not provide polarization or magnetization curves $M(H)$.

The main goal of the present analysis is to construct a perturbation theory for dipolar hard-sphere systems which yields magnetization (and polarization) curves which are consistent with Eq. (12). We accomplish this goal of calculating the magnetic properties of magnetic fluids by following a free-energy route, in contrast to Ivanov and Kuznetsova [17], who derived the magnetization curve based on the Bogolyubov-Born-Green-Kirkwood-Ivon formalism, using the angular dependence of the single-particle orientation distribution function. The knowledge of the field-dependent free energy has the advantage that other properties, such as magnetostriction, the compressibility factor, and the field dependence of the phase diagram, can also be studied.

II. MICROSCOPIC MODEL

We consider DHS fluids. Their particles share the same diameter σ and at their center the same point dipole moment of strength m . The fluids are characterized by the pair potential

$$u_{ij}^{\text{DHS}}(\mathbf{r}_i, \mathbf{r}_j, \omega_i, \omega_j) = u^{\text{HS}}(\mathbf{r}_i, \mathbf{r}_j) + u_{ij}^{\text{DD}}(\mathbf{r}_i, \mathbf{r}_j, \omega_i, \omega_j), \quad (16)$$

where u^{HS} and u_{ij}^{DD} are the hard-sphere and the dipole-dipole interaction pair potential, respectively. The hard-sphere pair potential is given by

$$u^{\text{HS}}(\mathbf{r}_i, \mathbf{r}_j) = u^{\text{HS}}(|\mathbf{r}_i - \mathbf{r}_j| = r_{ij}) = \begin{cases} \infty, & r_{ij} < \sigma \\ 0, & r_{ij} \geq \sigma \end{cases}. \quad (17)$$

The dipole-dipole pair potential is

$$\begin{aligned} u_{ij}^{\text{DD}}(\mathbf{r}_i, \mathbf{r}_j, \omega_i, \omega_j) &= u_{ij}^{\text{DD}}(\mathbf{r}_{ij}, \omega_i, \omega_j) \\ &= -\frac{m_i m_j}{r_{ij}^3} D(\omega_i, \omega_i, \omega_j), \end{aligned} \quad (18)$$

with the rotationally invariant function

$$\begin{aligned} D(\omega_i, \omega_i, \omega_j) &= 3[\widehat{\mathbf{m}}_i(\omega_i) \cdot \widehat{\mathbf{r}}_{ij}][\widehat{\mathbf{m}}_j(\omega_j) \cdot \widehat{\mathbf{r}}_{ij}] \\ &\quad - [\widehat{\mathbf{m}}_i(\omega_i) \cdot \widehat{\mathbf{m}}_j(\omega_j)], \end{aligned} \quad (19)$$

where the center of particle i (j) is located at \mathbf{r}_i (\mathbf{r}_j) and carries a dipole moment of strength $m_i = m$ ($m_j = m$) with an orientation given by the unit vector $\widehat{\mathbf{m}}_i(\omega_i)$ [$\widehat{\mathbf{m}}_j(\omega_j)$] with polar angles $\omega_i = (\theta_i, \phi_i)$ [$\omega_j = (\theta_j, \phi_j)$]; $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ with $r_{ij} = |\mathbf{r}_{ij}|$ connects the center of particle i and the center of particle j . For a single magnetic dipole an external magnetic field gives rise to the following additional contribution to the interaction potential:

$$u_i^{\text{DF}}(\omega_i) = u_i^{\text{DF}}(\theta_i) = -\mathbf{m}_i \cdot \mathbf{H} = -mH \cos \theta_i. \quad (20)$$

The angle θ_i measures the orientation of the i th dipole relative to the z axis (see above). This implies that in Eq. (20) the field \mathbf{H} is chosen to point to the z direction, without loss of generality. The potential energy U of the system is the sum of the interparticle interaction energy and the external field contribution U_{DF} :

$$U(\mathbf{r}^N, \omega^N) = U_{\text{DHS}}(\mathbf{r}^N, \omega^N) + U_{\text{DF}}(\omega^N), \quad (21)$$

where

$$U_{\text{DHS}}(\mathbf{r}^N, \omega^N) = \sum_{i < j} [u^{\text{HS}}(\mathbf{r}_i, \mathbf{r}_j) + u_{ij}^{\text{DD}}(\mathbf{r}_i, \mathbf{r}_j, \omega_i, \omega_j)] \quad (22)$$

and

$$U_{\text{DF}}(\omega^N) = -\sum_i \mathbf{m}_i \cdot \mathbf{H} = -mH \sum_i \cos \theta_i. \quad (23)$$

In Eqs. (21)–(23) the notations $\mathbf{r}^N \equiv (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ and $\omega^N \equiv (\omega_1, \omega_2, \dots, \omega_N)$ are used.

III. THEORY

In spatial dimension $d = 3$, for a dense fluid the explicit calculation of the configurational partition function of the interaction energy is not feasible [16]. However, using correlation functions and various expansion methods, for model systems one can obtain valuable approximations thereof. For a

DHS fluid in an external field the configurational contribution to the partition function is

$$\begin{aligned} Q_c &= \frac{1}{N! \Omega^N} \int d^3 r^N d\omega^N \\ &\quad \times \exp[-\beta U_{\text{DHS}}(\mathbf{r}^N, \omega^N) - \beta U_{\text{DF}}(\omega^N)], \end{aligned} \quad (24)$$

where $\Omega = \int d\omega = 4\pi$. Here and in the following the prefactor $1/\Omega^N$ compensates the overcounting of orientational configurations as being distinct such that Q_c reduces to the familiar configurational partition function in the limit where the interaction potentials do not depend on ω . The configurational contribution to the partition function Q_c is not dimensionless because the translational and rotational contributions are not factored in here.

In the following we describe a perturbation theory in which the dipolar hard-sphere system without external field is used as the reference system. The configurational contribution to the partition function of this reference system is

$$Q_0 = \frac{1}{N! \Omega^N} \int d^3 r^N d\omega^N \exp[-\beta U_{\text{DHS}}(\mathbf{r}^N, \omega^N)]. \quad (25)$$

In an external field the partition function for ideal (noninteracting) dipoles can—according to Langevin—be calculated analytically:

$$\begin{aligned} Q_L &= \frac{1}{\Omega^N} \int d\omega^N \exp[-\beta U_{\text{DF}}(\omega^N)] \\ &= \frac{1}{\Omega^N} \int d\omega^N \exp\left[\beta m H \sum_{i=1}^N \cos \theta_i\right] = \left(\frac{\sinh \alpha}{\alpha}\right)^N, \end{aligned} \quad (26)$$

where $\alpha = mH/(k_B T)$ is the Langevin parameter; note that $Q_c[U_{\text{DHS}} \equiv 0] = (V^N/N!) Q_L$, where V is the volume of the sample. Originally, Kalikmanov [10,22] and Szalai *et al.* [11,23,24] proposed application of the algebraic perturbation theory of Ruelle [25] to describe dielectric and magnetic properties of various dipolar systems. Within this approach they considered the interaction between the dipoles and the field as a perturbation, taking into account via the corresponding Mayer function:

$$f(\omega_i) = \exp(\beta m H \cos \theta_i) - 1 = \exp(\alpha \cos \theta_i) - 1. \quad (27)$$

Within linear response theory it is sufficient to use a second-order power expansion of the Mayer function in terms of α [$f \simeq \alpha \cos \theta_i + \alpha^2(\cos^2 \theta_i)/2$] in order to obtain the corresponding susceptibility. Since here we aim at calculating the magnetization curves, the power-series expansion of the Mayer function is not successful. In order to improve the convergence of the corresponding perturbation approximation, a special normalization of the Mayer function is introduced. The configurational partition function of the system [see Eq. (24)] can be rewritten as:

$$\begin{aligned} Q_c &= \frac{Q_L}{N! \Omega^N} \int d^3 r^N d\omega^N \\ &\quad \times \exp[-\beta U_{\text{DHS}}(\mathbf{r}^N, \omega^N)] \frac{e^{-\beta U_{\text{DF}}(\omega^N)}}{Q_L}. \end{aligned} \quad (28)$$

In Eq. (28) the field-dependent exponential coefficient can be written as

$$\begin{aligned} \frac{1}{Q_L} \exp[-\beta U_{\text{DF}}(\omega^N)] &= \frac{1}{Q_L} \exp\left(\beta m H \sum_i \cos \theta_i\right) = \left(\frac{\alpha}{\sinh \alpha}\right)^N \prod_{i=1}^N \exp[\alpha \cos \theta_i] \\ &= \prod_{i=1}^N \left(\frac{\alpha \exp[\alpha \cos \theta_i]}{\sinh \alpha}\right) = \prod_{i=1}^N [1 + \tilde{f}(\alpha, \cos \theta_i)] = 1 + \sum_{n=1}^N \left[\sum_{1 \leq i_1, \dots, i_n \leq N} \tilde{f}(\omega_{i_1}) \dots \tilde{f}(\omega_{i_n}) \right], \end{aligned} \quad (29)$$

where

$$\tilde{f}(\omega_i) = \frac{\alpha \exp[\alpha \cos \theta_i]}{\sinh \alpha} - 1 \quad (30)$$

is the so-called special Mayer function. Substituting this expression into Eq. (28) and dividing by $Q_0 Q_L$ [Eqs. (25) and (26)] yields

$$\frac{Q_c}{Q_0 Q_L} = 1 + \sum_{n=1}^N \frac{1}{Z_0} \int d^3 r^N d\omega^N \exp[-\beta U_{\text{DHS}}(\mathbf{r}^N, \omega^N)] \left[\sum_{1 \leq i_1, \dots, i_n \leq N} \tilde{f}(\omega_{i_1}) \dots \tilde{f}(\omega_{i_n}) \right], \quad (31)$$

where Z_0 is the configurational integral of the reference system:

$$Z_0 = \int d^3 r^N d\omega^N \exp[-\beta U_{\text{DHS}}(\mathbf{r}^N, \omega^N)]. \quad (32)$$

For an isotropic reference system Eq. (31) can be rewritten in terms of the n -particle reference correlation functions $g_0^{(n)}(\mathbf{r}^n, \omega^n)$:

$$\frac{Q_c}{Q_0 Q_L} = 1 + \sum_{n=1}^N \frac{1}{n!} \left(\frac{\rho}{\Omega}\right)^n \int d^3 r^n d\omega^n g_0^{(n)}(\mathbf{r}^n, \omega^n) \prod_{i=1}^n \tilde{f}(\omega_i), \quad (33)$$

where ρ is the constant number density of the isotropic fluid and

$$g_0^{(n)}(\mathbf{r}^n, \omega^n) = \frac{\Omega^n}{\rho^n} \frac{N!}{(N-n)!} \frac{1}{Z_0} \int d^3 r^{(N-n)} d\omega^{(N-n)} \exp[-\beta U_{\text{DHS}}(\mathbf{r}^N, \omega^N)]. \quad (34)$$

Following Ruelle's algebraic technique, the right-hand side of Eq. (33) can be written as

$$\frac{Q_c}{Q_0 Q_L} = \exp \left[\sum_{n=0}^N \frac{(\rho/\Omega)^n}{n!} b_n \right] \quad (35)$$

so the configurational free energy $F_c = -k_B T \ln Q_c$ reads (with $F_0 = -k_B T \ln Q_0$ and $F_L = -k_B T \ln Q_L$)

$$\beta F_c = \beta F_0 + \beta F_L - \sum_{n=0}^{\infty} \frac{(\rho/\Omega)^n}{n!} b_n. \quad (36)$$

For $n \leq 2$ the corresponding coefficients b_n are

$$b_0 = 0, \quad (37)$$

$$b_1 = \int d^3 r_1 d\omega_1 \tilde{f}(\omega_1), \quad (38)$$

and

$$b_2 = \int d^3 r_1 d^3 r_2 d\omega_1 d\omega_2 [g_0^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \omega_1, \omega_2) - 1] \tilde{f}(\omega_1) \tilde{f}(\omega_2). \quad (39)$$

In Eq. (36) F_0 is the free energy of the dipolar hard-sphere reference system, without an external field, and F_L is the Langevin free energy of an ideal gas of dipoles in the presence of an external field. Moreover, the dependence on H enters also through the coefficients b_n via \tilde{f} [Eq. (30)]. For determining the coefficients b_n the corresponding correlation functions $g_0^{(n)}$ of the DHS system are required. Since for this system there are no exact expressions for $g_0^{(n)}$, we resort to an approximation introduced by Barker and Henderson [26]. This approximation is an expansion in terms of βm^2 up to second order:

$$g_0^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \omega_1, \omega_2) = g_0^{(2)}(\mathbf{r}_{12}, \omega_1, \omega_2) = g_\sigma^{(2)}(r_{12}) + (\beta m^2) g_1(\mathbf{r}_{12}, \omega_1, \omega_2) + (\beta m^2)^2 g_2(\mathbf{r}_{12}, \omega_1, \omega_2), \quad (40)$$

where [see Eq. (19)]

$$g_1(\mathbf{r}_{12}, \omega_1, \omega_2) = \frac{g_\sigma^{(2)}(r_{12})}{r_{12}^3} D(\omega_{12}, \omega_1, \omega_2) \quad (41)$$

and

$$g_2(\mathbf{r}_{12}, \omega_1, \omega_2) = \frac{g_\sigma^{(2)}(r_{12})}{2r_{12}^6} [D(\omega_{12}, \omega_1, \omega_2)]^2 - \frac{1}{6} \rho D(\omega_{12}, \omega_1, \omega_2) \int d^3 r_3 \frac{1 + 3(\cos \gamma_1)(\cos \gamma_2)(\cos \gamma_3)}{(r_{13} r_{23})^3} g_\sigma^{(3)}(r_{12}, r_{23}, r_{13}) \\ + \frac{1}{3} \rho \Delta(\omega_1, \omega_2) \int d^3 r_3 \frac{3 \cos^2 \gamma_3 - 1}{(r_{13} r_{23})^3} g_\sigma^{(3)}(r_{12}, r_{23}, r_{13}). \quad (42)$$

In Eqs. (40)–(42) $g_\sigma^{(2)}$ and $g_\sigma^{(3)}$ are the two-particle and three-particle correlation functions, respectively, of hard spheres with diameter σ and γ_1 , γ_2 , and γ_3 are the angles of the triangle formed by hard spheres 1, 2, and 3. The definition of $\Delta(\omega_1, \omega_2)$ is

$$\Delta(\omega_1, \omega_2) = \hat{\mathbf{m}}_1(\omega_1) \cdot \hat{\mathbf{m}}_2(\omega_2). \quad (43)$$

In Eq. (42) for $g_\sigma^{(3)}$ Barker and Henderson applied the superposition approximation:

$$g_\sigma^{(3)}(r_{12}, r_{23}, r_{13}) \simeq g_\sigma^{(2)}(r_{12}) g_\sigma^{(2)}(r_{23}) g_\sigma^{(2)}(r_{13}). \quad (44)$$

With this Eq. (42) takes the form (see Ref. [11]):

$$g_2(\mathbf{r}_{12}, \omega_1, \omega_2) = \frac{g_\sigma^{(2)}(r_{12})}{2r_{12}^6} [D(\omega_{12}, \omega_1, \omega_2)]^2 - \frac{1}{6} \rho g_\sigma^{(2)}(r_{12}) a_D(r_{12}) D(\omega_{12}, \omega_1, \omega_2) + \frac{1}{3} \rho g_\sigma^{(2)}(r_{12}) a_\Delta(r_{12}) \Delta(\omega_1, \omega_2) \quad (45)$$

with

$$a_D(r_{12}) = \int d^3 r_3 \frac{1 + 3(\cos \gamma_1)(\cos \gamma_2)(\cos \gamma_3)}{(r_{13} r_{23})^3} g_\sigma^{(2)}(r_{13}) g_\sigma^{(2)}(r_{23}) \quad (46)$$

and

$$a_\Delta(r_{12}) = \int d^3 r_3 \frac{3 \cos^2 \gamma_3 - 1}{(r_{13} r_{23})^3} g_\sigma^{(2)}(r_{13}) g_\sigma^{(2)}(r_{23}). \quad (47)$$

The angular integrals over ω_1 , ω_2 , and ω_{12} in Eqs. (38) and (39), which enter the expression for the free energy [see Eq. (36)], can be calculated analytically:

$$\int d\omega \tilde{f}(\omega) = 0, \quad (48)$$

$$\int d\omega_1 d\omega_2 \tilde{f}(\omega_1) D(\omega_{12}, \omega_1, \omega_2) \tilde{f}(\omega_2) = 16\pi^2 L^2(\alpha) [3 \cos^2 \theta_{12} - 1], \quad (49)$$

$$\int d\omega_{12} d\omega_1 d\omega_2 \tilde{f}(\omega_1) D^2(\omega_{12}, \omega_1, \omega_2) \tilde{f}(\omega_2) = \frac{128\pi^3}{5} \zeta(\alpha) - \frac{128\pi^3}{3}, \quad (50)$$

$$\int d\omega_1 d\omega_2 \tilde{f}(\omega_1) \Delta(\omega_1, \omega_2) \tilde{f}(\omega_2) = 16\pi^2 L^2(\alpha), \quad (51)$$

where

$$\zeta(\alpha) = 2 - 2 \frac{L(\alpha)}{\alpha} + 3 \left[\frac{L(\alpha)}{\alpha} \right]^2. \quad (52)$$

In view of Eqs. (48) and (38) it is obvious that, within the expansion of the free energy [see Eq. (36)], $b_1 = 0$. The integrands of the spatial integrals containing the function $1/r_{12}^3$ decay so slowly that the numeric values of these integrals depend on the shape of the integration volume. In order to avoid depolarization effects, here we consider infinitely prolate ellipsoidal sample shapes. For calculating the corresponding integrals we follow the method presented in Refs. [27,28]. For such integrals [see the right-hand side of Eq. (49)] one finds

$$\int d^3 r_{12} \frac{(3 \cos^2 \theta_{12} - 1)}{r_{12}^3} = \frac{4\pi}{3}. \quad (53)$$

If the integrand contains in addition the hard-sphere pair-correlation function $g_\sigma^{(2)}(r_{12}, \rho)$, then one finds the same result:

$$\int d^3 r_{12} \frac{(3 \cos^2 \theta_{12} - 1)}{r_{12}^3} g_\sigma^{(2)}(r_{12}, \rho) = \frac{4\pi}{3}. \quad (54)$$

The reason that the factor $g_\sigma^{(2)}(r_{12}, \rho)$ in the integrand does not change the numerical value of this integral is that in this case only the asymptotic value of $g_\sigma^{(2)}$ can contribute to the integral and $g_\sigma^{(2)}(r_{12} \rightarrow \infty) = 1$ (see Refs. [27–29]). Due to $a_D(r_{12} \rightarrow \infty) = 8\pi/(3r_{12}^3)$, a_D also decays slowly so

$$\int d^3r_{12}(3\cos^2\theta_{12} - 1)a_D(r_{12})g_\sigma^{(2)}(r_{12}, \rho) = \frac{8\pi}{3} \int d^3r_{12} \frac{(3\cos^2\theta_{12} - 1)}{r_{12}^3} g_\sigma^{(2)}(r_{12}, \rho) = \frac{8\pi}{3} \frac{4\pi}{3} = \frac{32\pi^2}{9}. \quad (55)$$

The integrands of the remaining integrals decay sufficiently rapidly so it is possible to replace the ellipsoidal shape of the integration volume by that of a sphere. From the point of view of our theory a particularly important integral is $I_{dd\Delta}$ [Eq. (13)], which contains the rapidly decaying function $a_\Delta(r_{12})$ and appears as the contribution $\propto g_2$ [see the last terms in Eqs. (40) and (45)] to b_2 [Eq. (39) and cf. Eq. (61)]:

$$I_{dd\Delta}(\rho) = \int d^3r_{12} a_\Delta(r_{12}) g_\sigma^{(2)}(r_{12}, \rho) = \int d^3r_{12} d^3r_3 \frac{3\cos^2\gamma_3 - 1}{(r_{13}r_{23})^3} g_\sigma^{(2)}(r_{13}, \rho) g_\sigma^{(2)}(r_{23}, \rho) g_\sigma^{(2)}(r_{12}, \rho), \quad (56)$$

where we have used the expression in Eq. (47). This integral can be calculated analytically only at $\rho = 0$, for which $g_\sigma(r_{12}) = 1$ so $I_{dd\Delta}(\rho = 0) = 17\pi^2/9$ [Eq. (15)]. In the Introduction we mentioned that Tani *et al.* [9] have calculated this integral at various densities (using pair-correlation functions obtained from MC simulations) and they transformed their data in terms of a Pade approximation, which is given in Eq. (14). The last remaining integral stems from the first term in Eq. (45) and has a rapidly decaying integrand:

$$I_{dd} = \int d^3r_{12} \frac{g_\sigma^{(2)}(r_{12}, \rho)}{r_{12}^6} = 4\pi \int_\sigma^\infty dr_{12} \frac{g_\sigma^{(2)}(r_{12}, \rho)}{r_{12}^4}. \quad (57)$$

The density dependence of this integral was first determined by Larsen *et al.* [30]:

$$I_{dd}(\rho) = \frac{4\pi}{3} + 2.8287\rho^* + 0.8331(\rho^*)^2 + 0.0317(\rho^*)^3 + 0.0858(\rho^*)^4 - 0.0846(\rho^*)^5, \quad (58)$$

which is also based on MC simulation data for the hard-sphere pair-correlation function $g_\sigma^{(2)}(r_{12}, \rho)$. Collecting the results in Eqs. (37) and (58), Eq. (36) renders the free energy of DHS fluids in an external field:

$$\begin{aligned} \frac{F_c}{Nk_B T} &= \frac{F_0}{Nk_B T} - \ln\left(\frac{\sinh\alpha}{\alpha}\right) - \frac{2\pi}{3}\beta\rho m^2 L^2(\alpha) - \rho\beta^2 m^4 \left[\frac{1}{10}\zeta(\alpha) - \frac{1}{6}\right] I_{dd}(\rho) \\ &\quad + \frac{8\pi^2}{27}\rho^2\beta^2 m^4 L^2(\alpha) - \frac{1}{6}\rho^2\beta^2 m^4 L^2(\alpha) I_{dd\Delta}(\rho). \end{aligned} \quad (59)$$

The magnetization follows from Eq. (59) as

$$M = -\frac{1}{V} \left(\frac{\partial F_c}{\partial H} \right)_{N, V, T}, \quad (60)$$

leading to

$$\begin{aligned} M(H) &= \rho m L(\alpha) + \frac{4\pi}{3}\rho^2\beta m^3 L(\alpha) L'(\alpha) + \frac{1}{10}\rho^2\beta^2 m^5 \zeta'(\alpha) I_{dd}(\rho) - \frac{16\pi^2}{27}\rho^3\beta^2 m^5 L(\alpha) L'(\alpha) \\ &\quad + \frac{1}{3}\rho^3\beta^2 m^5 L(\alpha) L'(\alpha) I_{dd\Delta}(\rho), \quad \alpha = \beta m H, \end{aligned} \quad (61)$$

where $L'(\alpha) = dL(\alpha)/d\alpha$ and $\zeta'(\alpha) = d\zeta(\alpha)/d\alpha$ are the corresponding derivatives. Due to Eqs. (1) and (60) the zero-field magnetic susceptibility can be expressed in terms of the configuration free energy:

$$\chi_0 = -\frac{1}{V} \left(\frac{\partial^2 F_c}{\partial H^2} \right)_{H=0}. \quad (62)$$

According to Eqs. (62) and (59) the zero-field (initial) magnetic susceptibility of the system is

$$\chi_0 = \chi_L \left[1 + \frac{4\pi\chi_L}{3} + \frac{(4\pi\chi_L)^2}{144} f(\rho) \right], \quad (63)$$

where

$$f(\rho) = \frac{9}{\pi^2} I_{dd\Delta}(\rho) - 16. \quad (64)$$

Here we have used $L(0) = 0$, $L'(0) = 1/3$, $L''(0) = 0$, and $\zeta''(0) = 0$. It is reassuring to see that Eq. (63) together with Eq. (64) is identical to Eq. (12). Thus we have succeeded in determining the whole magnetization equation [Eq. (61)] such that it contains Eq. (12) as a limiting case.

IV. MONTE CARLO SIMULATIONS

We have carried out Monte Carlo simulations for DHS fluids using NVT ensembles in order to test the reliability of the above perturbation theory. The long-ranged dipolar interactions have been dealt with the reaction-field method with conducting boundary conditions [31]. Boltzmann sampling [31] and periodic boundary conditions with the minimum-image convention [31] have been applied. For the simulation of the magnetization, after 40 000 equilibration cycles, 0.6–0.8 million production cycles were used, involving $N = 512$ particles. In our simulations with an applied field the equilibrium magnetization of the system is obtained from

$$\mathbf{M} = \frac{1}{V} \langle \mathcal{M} \rangle_H, \quad (65)$$

where

$$\mathcal{M} = \sum_{i=1}^N \mathbf{m}_i \quad (66)$$

is the total dipole moment of the system of volume V . From the simulations without external field we have obtained the zero-field magnetic susceptibility from the corresponding fluctuation formula

$$\chi_0 = \frac{\beta}{V} (\langle \mathcal{M}^2 \rangle_0 - \langle \mathcal{M} \rangle_0^2), \quad (67)$$

where $\langle \dots \rangle_0$ denotes the thermal average for $H = 0$. The (second-order) nonlinear magnetic susceptibility (see Ref. [5]) is

$$\chi_2 = \frac{1}{3!} \left(\frac{\partial^3 M}{\partial H^3} \right)_{H=0} = \frac{\beta^3}{90V} (3 \langle \mathcal{M}^4 \rangle_0 - 5 \langle \mathcal{M}^2 \rangle_0^2). \quad (68)$$

The simulations were started from a hexagonal close packing lattice configuration with randomly oriented dipoles. For the simulation of the linear (χ_0) and the nonlinear (χ_2) susceptibility $N = 256$ particles have been used. After 40 000 equilibration cycles 2–4 million production cycles were used. Statistical errors were determined from the standard deviations of subaverages encompassing 0.2 million cycles.

V. NUMERICAL RESULTS AND DISCUSSION

In the following we consider reduced quantities. To this end we define $m^* = m/(\sqrt{k_B T} \sigma^3)$ as the reduced dipole moment, $H^* = H\sqrt{\sigma^3}/(k_B T)$ as the reduced magnetic field strength, $M^* = M\sqrt{\sigma^3}/(k_B T)$ as the reduced magnetization, and $\chi_2^* = \chi_2(k_B T/\sigma^3)$ as the reduced nonlinear magnetic susceptibility and χ_0 is dimensionless and $\rho^* = \rho\sigma^3$ is the reduced density; accordingly, $\alpha = mH/(k_B T) = m^*H^*$. The Langevin susceptibility χ_L is dimensionless and given by $\chi_L = \rho^*(m^*)^2/3$.

Before discussing the magnetization and susceptibility results, we remark on the field dependence of the free energy given by Eq. (59). The field-dependent first three terms of Eq. (59) are the same as the corresponding terms in the high-field approximation theory given in Ref. [24], where the second-order expansion of the dipole-dipole interaction Mayer function is used. If one expands the free energy into a second-order power series in terms of $\alpha = mH/(k_B T) =$

m^*H^* (concerning the magnetization this corresponds to the linear response theory) one obtains a low-field free-energy expression which agrees with that in Ref. [11]. From Eq. (59) one finds the magnetization given by Eq. (61). We note that in terms of the dipole-dipole interaction energy in Ref. [32] Kalikmanov, similarly to Ref. [24], also proposed a second-order high-field approximation. However, there is an error in his calculation of an integral (containing a term linear in u^{DD}) with the consequence that the term $\frac{4\pi}{3}\rho^2\beta m^3 L(\alpha)L'(\alpha)$ [see the second term in Eq. (61)] is missing from his Eq. (4.8). The correct expression for Eq. (4.8) in Ref. [32] is

$$M = \rho m L(\alpha) + \frac{4\pi}{3}\rho^2\beta m^3 L(\alpha)L'(\alpha) + \frac{1}{10}\rho^2\beta^2 m^5 \zeta'(\alpha) I_{dd}(\rho), \quad (69)$$

which agrees with Eq. (61) up to the first three terms.

The thermodynamic properties of DHS fluids in applied magnetic fields were studied recently by Elfimova *et al.* [33–35]. They calculated the corresponding second and third (field-dependent) virial coefficient up to and including the third order of the dipolar coupling constant $\lambda = m^2/(k_B T \sigma^3) = (m^*)^2$. Using the virial expansion of the dipolar free energy the total configurational free energy of the system can be written as

$$\frac{F_c}{Nk_B T} = \frac{F_c^{\text{HS}}}{Nk_B T} - \ln \left(\frac{\sinh \alpha}{\alpha} \right) + \Delta B_2 \rho + \frac{1}{2} \Delta B_3 \rho^2, \quad (70)$$

where $\Delta B_2(\lambda, \alpha, \sigma) = B_2(\lambda, \alpha, \sigma) - B_2^{\text{HS}}(\sigma)$ and $\Delta B_3(\lambda, \alpha, \sigma) = B_3(\lambda, \alpha, \sigma) - B_3^{\text{HS}}(\sigma)$ are the differences between the second and third virial coefficients of the field-dependent DHS system and those of the HS system. F_c^{HS} is the configurational free energy of the HS system. Using the virial coefficients given in Ref. [33] they proposed a logarithmic expression for the Helmholtz free energy:

$$\frac{F_c}{Nk_B T} = \frac{F_c^{\text{HS}}}{Nk_B T} - \ln \left(\frac{\sinh \alpha}{\alpha} \right) - \ln \left[1 - \Delta B_2 \rho + \frac{1}{2} (\Delta B_2^2 - \Delta B_3) \rho^2 \right]. \quad (71)$$

The first two terms of the series expansion of the logarithmic expression in Eq. (71) renders the last two terms in Eq. (70). According to Eq. (59) our free energy is a second-order expression in terms of the dipolar coupling constant $\lambda \sim m^2$, while Eq. (71) is a third-order expression in terms of λ . Because the field-dependent first-order terms in Eqs. (59) and (70) are the same [i.e., $-2\pi\rho^*\lambda L^2(\alpha)/3$] there is agreement between the two equations for small dipolar coupling constants. Concerning a comparison for larger values of λ , due to the present lack of corresponding simulation data for the free energy we do not compare Eq. (59) with Eqs. (70) and (71), but instead we compare the field and density dependencies of the corresponding compressibility factor Z and of the magnetization, because for these quantities MC simulation results are available. (We note that in Ref. [36] for $H = 0$ Elfimova *et al.* have compared their DHS free energy with MC simulation data and reasonable agreement has been obtained.) The compressibility factor follows from the configurational

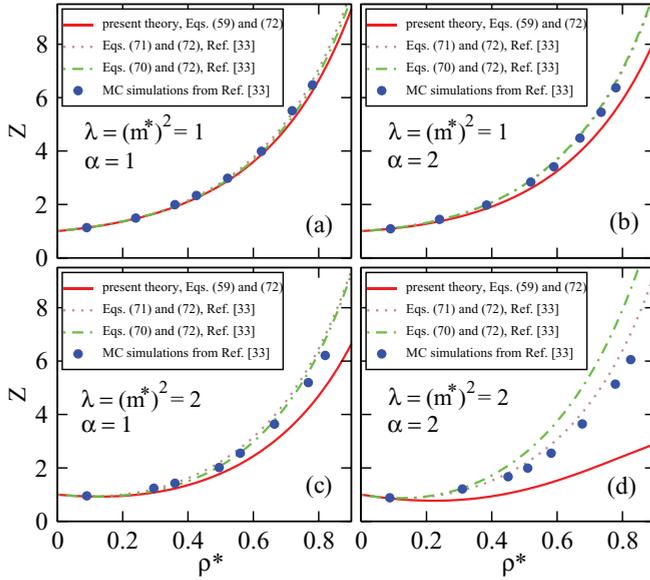


FIG. 1. (Color) Compressibility factor $Z = pV/(Nk_B T)$ [Eq. (72)] of DHS systems as a function of the reduced number density ρ^* for various dipolar coupling constants $\lambda = m^2/(k_B T \sigma^3) = (m^*)^2$ and dimensionless field strengths $\alpha = mH/(k_B T) = m^* H^*$. The red full lines correspond to the results of the present perturbation theory [Eqs. (59) and (72)]. The brown dotted lines [Eqs. (71) and (72)] and the green dash-dotted lines [Eqs. (70) and (72)] represent the theories of Elfimova *et al.* [33]. The symbols are MC simulation data from Ref. [33].

free energy as

$$Z(\rho, \lambda, \alpha) = \rho \frac{\partial}{\partial \rho} \left(\frac{F_c}{Nk_B T} \right). \quad (72)$$

In Eq. (59) for the DHS free energy F_0 we have used the perturbation theoretical expression of Larsen *et al.* [30]. In all three free-energy expressions [Eqs. (59), (70), and (71)] the free-energy part of the hard-sphere system is described by the corresponding Carnahan-Starling expression [37]. In Fig. 1 we provide a comparison between the compressibility factors, as defined in Eq. (72), calculated from Eqs. (59), (70), and (71). For the dipolar coupling constant $\lambda = 1$ Figs. 1(a) and 1(b) show that the compressibility factor calculated from our theory [Eqs. (59) and (72)] agrees well with the corresponding simulation data and with the theories of Elfimova *et al.* [33]. Upon increasing the dipolar coupling constant to $\lambda = 2$, Figs. 1(c) and 1(d) demonstrate that the agreement with the simulation data and with both theories due to Elfimova *et al.* deteriorates, especially for high dimensionless field strength such as $\alpha = 2$. For these values of λ and α the agreement between the three theories is satisfactory only for low densities.

In the following we compare our theoretical findings concerning the magnetization [Eq. (61)] with our Monte Carlo simulation data. Figures 2(a)–2(d) display the magnetization curves as obtained from three theories for four values of the Langevin susceptibility χ_L . Figure 2(a) shows that at low density and for the Langevin susceptibility of $\chi_L = 1.675$ our theoretical findings are in good agreement with the MC simulation data. The theory given by Ivanov and Kuznetsova [17] [see Eq. (8)] underestimates the simulation

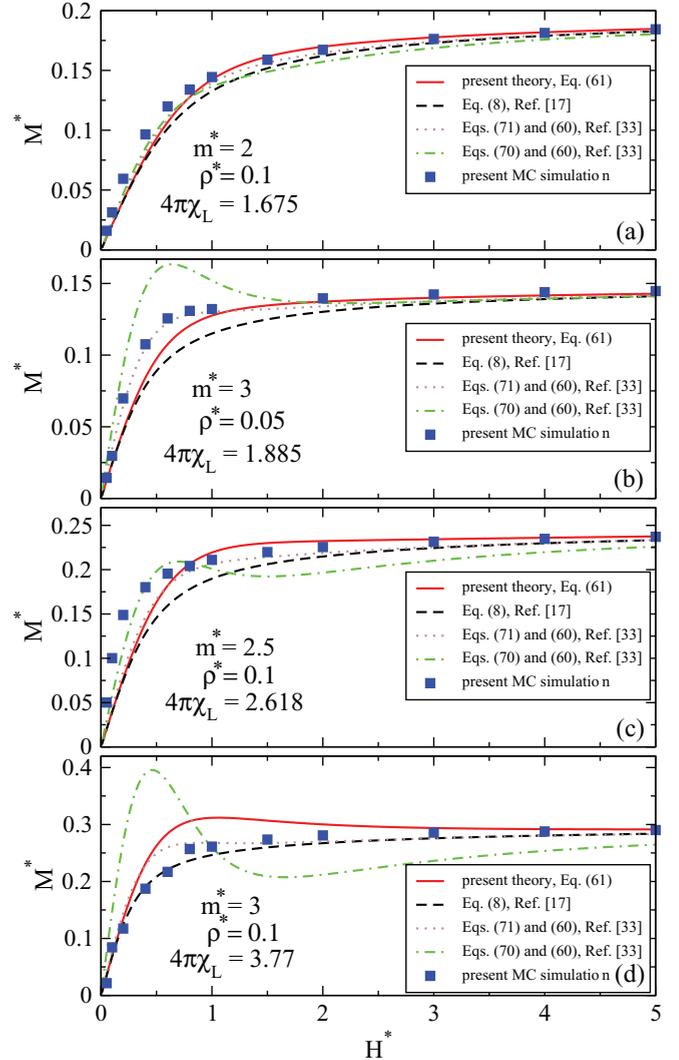


FIG. 2. (Color) Low-density magnetization curves as function of $H^* = H\sqrt{\sigma^3}/(k_B T)$ for DHS fluids for four values of the Langevin susceptibility $\chi_L = \rho^*(m^*)^2/3$. The reduced number densities and dipole moments also vary in accordance with the respective fixed value of the corresponding Langevin susceptibility. The red full lines correspond to the results of the present perturbation theory [see Eq. (61)]. The black dashed lines represent the theory due to Ivanov and Kuznetsova [17] [see Eq. (8)] while the brown dotted lines and the green dash-dotted lines correspond to the two free-energy expressions [Eqs. (71) and (60) and Eqs. (70) and (60)] due to Elfimova *et al.* [33]. The symbols are our MC simulation data. The size of the error bars of the MC data equals the symbol sizes.

data for magnetic field strengths $H^* < 5$. The magnetization calculated from the free-energy expression in Eq. (71) also shows good agreement with our MC simulation data. However, the magnetization data obtained on the basis of the third-order virial expansion directly [Eq. (70)] exhibit less agreement with our MC simulation data. Both theories due to Elfimova *et al.* [33] slightly underestimate the simulation data. The increase of the Langevin susceptibility from $\chi_L = 1.675$ to $\chi_L = 1.885$ changes the agreement between the theories and the simulation data. According to Fig. 2(b) both theories, Eq. (61) and Eq. (8), underestimate the simulation data within the range

$0.2 < H^* < 5$. However, our theory is in better agreement with the simulation data than that of Ivanov and Kuznetsova. Within the range $0 < H^* \leq 1$ the theory due to Elfimova *et al.* [33] [obtained from Eq. (71)] yields the best agreement with the MC simulation data. The direct virial theory by Elfimova *et al.* [35], which produces an unphysical local maximum of the magnetization, again exhibits less agreement with the MC simulation data. This maximum is caused by the truncation of the virial expansion [see Eq. (70)]. The so-called logarithmic free-energy theory contains, instead, contributions of higher-order terms in the virial expansion and therefore renders a better approximation. Figure 2(c) shows the result of a further increase of the Langevin susceptibility to $\chi_L = 2.618$. Close to the elbow of our magnetization curve the level of quantitative agreement is reduced, but on the whole Eq. (61) provides a better description than Eq. (8). For this parameter value and for strong fields both theories due to Elfimova *et al.* (see Eqs. (70) and (71) [33,34]) underestimate the corresponding MC simulation data: The direct virial expansion retains the local maximum. Upon increasing the Langevin susceptibility further to $\chi_L = 3.77$ an unphysical maximum also appears in our magnetization curve [see Fig. 2(d)]. This is caused by the truncation of the series expansion in Eq. (36) leading to the absence of higher-order terms. Our approximation consists of truncating the series expansion of the free energy in terms of the number density ρ after the second-order term [see Eqs. (36)–(39)]. The cluster expansion proposed by Huke and Lücke [38,39] suffers from similar problems due to using only the lower-order terms in that expansion for obtaining the magnetization curves. We note that the original perturbation theory due to Ivanov and Kuznetsova [17] also struggled with these difficulties. However, with a resummation of the

perturbation theory and by introducing a new effective field expression they obtained Eq. (8), which does not exhibit these difficulties. The range and the magnitude of the unphysical behavior of the magnetization curves is widening upon increasing the density or the Langevin susceptibility. For these parameters the theory of Ivanov and Kuznetsova [Eq. (8)] and the logarithmic free-energy theory of Elfimova *et al.* [Eq. (71)] give the best agreement with the MC simulation data. Here, the direct virial free-energy expansion [Eq. (70)] is unsuitable for the description of the magnetization data. Considering Figs. 2(a)–2(d) we conclude that our theory [Eq. (61)] provides reasonable quantitative agreement with the corresponding MC simulation data for $\chi_L \lesssim 3$.

We note that at low concentrations and for high dipolar coupling constants, in ferrofluids there is a strong chain aggregation formation which leads to a significant increase of the magnetic response [40]. Within the MC simulations this phenomenon appears for DHS fluids at low densities, which cannot be described by the aforementioned theories. This behavior is clearly pronounced in Figs. 2(b) and 2(c), for which the dipolar coupling constants are $\lambda_b = (m_b^*)^2 = 9$ and $\lambda_c = (m_c^*)^2 = 6.25$.

In order to extend our theory to larger values of the density and of the Langevin susceptibility, and thereby eliminating unphysical behaviors, we follow the method of Ivanov and Kuznetsova [17] and propose a new version of Eq. (61) which is based on the concept of an effective field strength. As a first step, in Eq. (61) we neglect the third term which is smaller than the other terms and does not contribute to the initial susceptibility. Accordingly, the remaining terms are:

$$M(H) \simeq \rho m L(\alpha) + \frac{4\pi}{3} \rho^2 \beta m^3 L(\alpha) L'(\alpha) - \frac{16\pi^2}{27} \rho^3 \beta^2 m^5 L(\alpha) L'(\alpha) + \frac{1}{3} \rho^3 \beta^2 m^5 L(\alpha) L'(\alpha) I_{dd\Delta}(\rho). \quad (73)$$

Using the expression for the Langevin magnetization [see Eq. (9)] Eq. (73) can be written as

$$\begin{aligned} M(H) &= M_L(H) + \frac{4\pi}{3} M_L(H) \frac{dM_L(H)}{dH} - \frac{16\pi^2}{9} \chi_L M_L(H) \frac{dM_L(H)}{dH} + \chi_L I_{dd\Delta}(\rho) M_L(H) \frac{dM_L(H)}{dH} \\ &= M_L(H) + \frac{dM_L(H)}{dH} \left[\frac{4\pi}{3} M_L(H) - \frac{16\pi^2}{9} \chi_L M_L(H) + I_{dd\Delta}(\rho) \chi_L M_L(H) \right] \\ &= M_L(H) + \frac{dM_L(H)}{dH} \left[\frac{4\pi}{3} M_L(H) + \left(\frac{\pi}{3}\right)^2 f(\rho) \chi_L M_L(H) \right], \end{aligned} \quad (74)$$

where $f(\rho)$ is given by Eq. (64). Using the Taylor expansion $M_L(H + \Delta H) = M_L(H) + [\frac{dM_L(H)}{dH}] \Delta H$, Eq. (74) can be rewritten as

$$\begin{aligned} M(H) &= M_L(H_e), \\ H_e(H) &= H + \frac{4\pi}{3} M_L(H) + \frac{(4\pi)^2}{144} f(\rho) M_L(H) \chi_L, \end{aligned} \quad (75)$$

postulating that Eq. (75) is valid beyond its first-order Taylor expansion. This postulated expression eliminates the unphysical local maximum in the magnetization curves which are caused by the field derivatives of the Langevin function. If we compare the semitheoretical Eq. (75) with the semitheoretical

Eq. (8) from Ivanov and Kuznetsova, then we find two differences in the expression of the effective field strength. First, in Eq. (75) the Langevin susceptibility χ_L appears in the effective field while in Eq. (8) the derivative dM_L/dH turns up. These two quantities are related:

$$\chi_L = \left[\frac{dM_L(H)}{dH} \right]_{H=0}. \quad (76)$$

The ensuing difference results in a better low-field behavior of Eq. (75), but at high field strengths Eq. (8) provides a better description. [In the last term in Eq. (8) the derivative is evaluated at the actual H , whereas the last term in Eq. (75) is taken

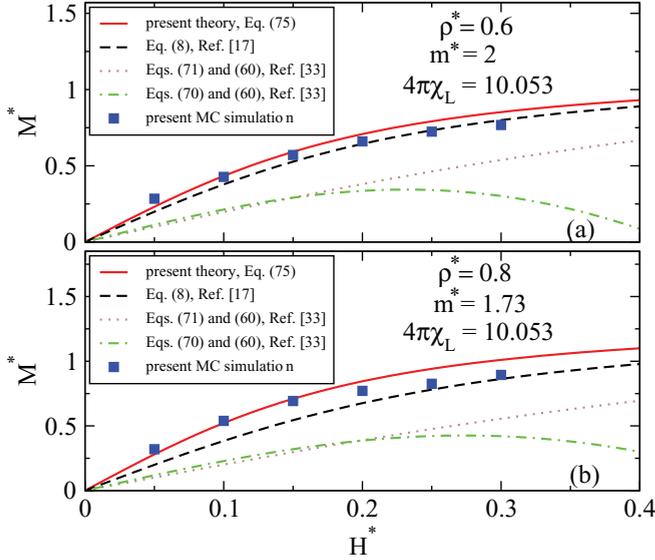


FIG. 3. (Color) Magnetization curves as function of $H^* = H\sqrt{\sigma^3/(k_B T)}$ for DHS fluids at a fixed value of the Langevin susceptibility $\chi_L = \rho^*(m^*)^2/3$ for two high number densities: $\rho^* = 0.6$ (a) and $\rho^* = 0.8$ (b). The red full lines correspond to the results of the present theory [see Eq. (75)]. The black dashed lines represent the theory due to Ivanov and Kuznetsova [17] [see Eq. (8)] while the brown dotted lines and the green dash-dotted lines correspond to the two free-energy expressions [Eqs. (71) and (60) and Eqs. (70) and (60)] due to Elfimova *et al.* [33]. The symbols are our MC simulation data. The size of the error bars of the MC data equals the symbol sizes.

at $H = 0$.] The second difference consists of the appearance of the function $f(\rho)$ in Eq. (75), which also contributes to a better low-field behavior. Figure 3 shows the corresponding low-field magnetization results for the Langevin susceptibility $\chi_L = 10.053$. For the reduced density $\rho^* = 0.6$ and the reduced dipole moment $m^* = 2$ the field dependence of the magnetization given by Eq. (75) and by Eq. (8) in comparison with our MC simulation data are displayed in Fig. 3(a). In order to compare the various theories, the magnetization calculated from the free-energy expressions of Elfimova *et al.* [33] [see Eqs. (70) and (71)] is also displayed in Fig. 3. One infers that, at this density for field strengths $H^* < 0.2$, Eq. (75) exhibits a better agreement with the simulation data than the corresponding equation due to Ivanov and Kuznetsova [17]. However, in the range $0.2 \lesssim H^*$ Eq. (8) provides a better approximation than Eq. (75). A similar behavior can be seen in Fig. 3(b). Both virial-expansion-based theories strongly underestimate the corresponding MC simulation data, which is not surprising because at high densities the contribution of the higher-order terms is very important. These observations lead to the prediction that, at higher densities and compared with the corresponding MC simulation data, the linear and nonlinear susceptibilities obtained from Eq. (75) are more accurate than those obtained from Eq. (8).

It is important and satisfactory to see that both Eq. (61) and the semitheoretical Eq. (75) yield the same expression in Eq. (63) for the zero-field susceptibility. An important property of this expression in Eq. (63) is that in the low-density limit it

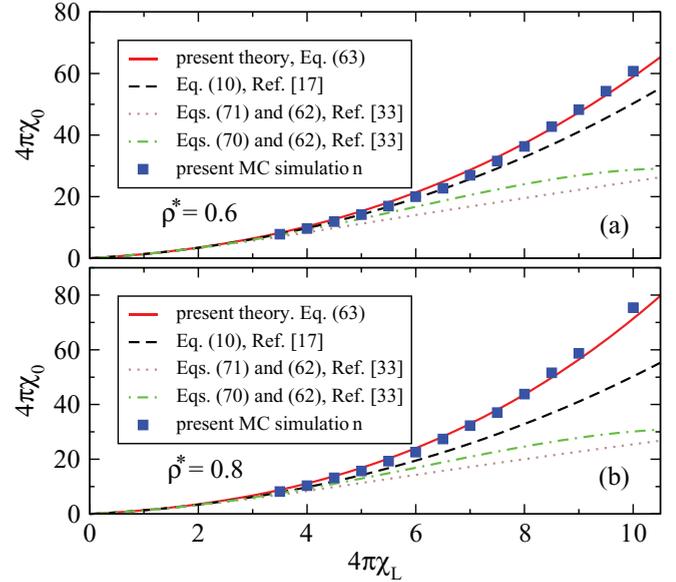


FIG. 4. (Color) Zero-field magnetic susceptibility χ_0 of DHS systems as a function of the Langevin susceptibility $\chi_L = \rho^*(m^*)^2/3$ for two number densities: $\rho^* = 0.6$ (a) and $\rho^* = 0.8$ (b). The red full lines correspond to the results of the present perturbation theory [see Eq. (63)], which is in agreement with the earlier results of Tani *et al.* [9]. The black dashed lines represent the theory due to Ivanov and Kuznetsova [17] [see Eq. (10)] while the brown dotted lines and the green dash-dotted lines correspond to the two free-energy expressions [Eqs. (71) and (62) and Eqs. (70) and (62)] due to Elfimova *et al.* [33]. The symbols are our MC simulation data.

reduces to the expression for the susceptibility due to Ivanov and Kuznetsova [17] [see Eq. (10)], because

$$\lim_{\rho \rightarrow 0} f(\rho) = 1. \quad (77)$$

[For further details see Eqs. (15) and (64).] In the following we compare Eq. (63) due to our theory and Eq. (10) from Ref. [17] with our MC simulation data. Recently, Camp *et al.* [41] studied the effect of polydispersity on the initial susceptibility of ferrofluids by MC simulation and theoretical methods. We note that their susceptibility simulation data for monodisperse systems are very close to our simulation data, although the densities they used were lower by 4.5% than the densities $\rho^* = 0.6$ and $\rho^* = 0.8$ used by us. Figure 4 shows the dependence of the zero-field susceptibility χ_0 on the Langevin susceptibility χ_L for two densities as obtained from Eqs. (63) and (10) and from the Monte Carlo simulations [see Eq. (67)]. For comparison of the various theories, the zero-field susceptibilities calculated from the free-energy expressions due to Elfimova *et al.* [33] [see Eqs. (70) and (71)] are displayed in Fig. 4, too. One can see that the theory of Ivanov and Kuznetsova provides a master curve [Eq. (10)] which is the same for different densities. However, from Figs. 4(a) and 4(b) one infers that at higher densities our perturbation-theoretical equation [see Eq. (63)] shows better agreement with the corresponding MC simulation data than Eq. (10). The master curve due to Ivanov and Kuznetsova is valid only within the range $4\pi\chi_L \lesssim 6$. For higher Langevin susceptibilities the density correction due to the function $f(\rho)$ in Eq. (63) has to

be taken into account. The zero-field susceptibilities calculated from the direct virial and the logarithmic expression for the free energy show good agreement with the MC simulation data only within the range $0 \leq 4\pi\chi_L \lesssim 4$, using the second and third virial coefficients up to their order $\sim\lambda^3$. However, as verified by Elfimova *et al.* [34], using B_2 and B_3 from the direct virial free energy up to their order $\sim\lambda^2$ renders for the zero-field susceptibility the expression due to Ivanov and Kuznetsova [Eq. (10)]. In this case the lower-order ($\sim\lambda^2$) approximation yields a better result than the corresponding higher order ($\sim\lambda^3$) one.

In the following we discuss the second-order nonlinear magnetic susceptibilities as obtained from the aforementioned theories. The nonlinear magnetic susceptibility is defined as

$$\chi_2 = \frac{1}{3!} \left(\frac{\partial^3 M}{\partial H^3} \right)_{H=0} = -\frac{1}{3!V} \left(\frac{\partial^4 F_c}{\partial H^4} \right)_{H=0}. \quad (78)$$

It characterizes the initial curvature of the magnetization curve, which is an important quantity describing the nonlinear behavior of materials [42]. It can be calculated directly from the original equation for the magnetization due to Ivanov and Kuznetsova [Eq. (8)]:

$$\chi_2 = -\frac{1}{45} \beta^3 m^4 \rho \left\{ \left[1 + \frac{4\pi}{3} \chi_L + \frac{(4\pi)^2}{144} \chi_L^2 \right]^3 + \frac{4\pi}{3} \chi_L + \frac{(4\pi)^2}{36} \chi_L^2 \right\}, \quad (79)$$

which at low densities reduces to the Langevin term. Based on Eqs. (75) and (78) the corresponding nonlinear susceptibility from our theory is

$$\chi_2 = -\frac{1}{45} \beta^3 m^4 \rho \left\{ \left[1 + \frac{4\pi}{3} \chi_L + \frac{(4\pi)^2}{144} \chi_L^2 f(\rho) \right]^3 + \frac{4\pi}{3} \chi_L + \frac{(4\pi)^2}{144} \chi_L^2 f(\rho) \right\}. \quad (80)$$

In the low-density limit ($\rho \rightarrow 0$) Eq. (80) does not reproduce Eq. (79) due to the difference between χ_L and dM_L/dH ; the latter depends on the field strength and therefore produces a contribution to the nonlinear term.

Figure 5 provides a comparison between the two theoretical results for the second-order nonlinear susceptibility and the corresponding MC simulation data. In order to compare the various theories the results obtained from the free-energy expressions due to Elfimova *et al.* [33] are displayed, too. As Fig. 5(a) shows, for the dipole moment $(m^*)^2 = 2$ our theory [Eq. (80)] is in good agreement with the simulation data within the studied density range. In contrast, the theory due to Ivanov and Kuznetsova [Eq. (79)] underestimates the absolute values of the corresponding simulation data. Upon increasing the strength of the dipole moment to $(m^*)^2 = 3$ the quantitative agreement deteriorates [see Fig. 5(b)], but our approximation is clearly better than the one due to Ivanov and Kuznetsova. The second-order nonlinear susceptibilities obtained from the theories due to Elfimova *et al.* [33] overestimate the MC simulation data and the aforementioned theoretical results.

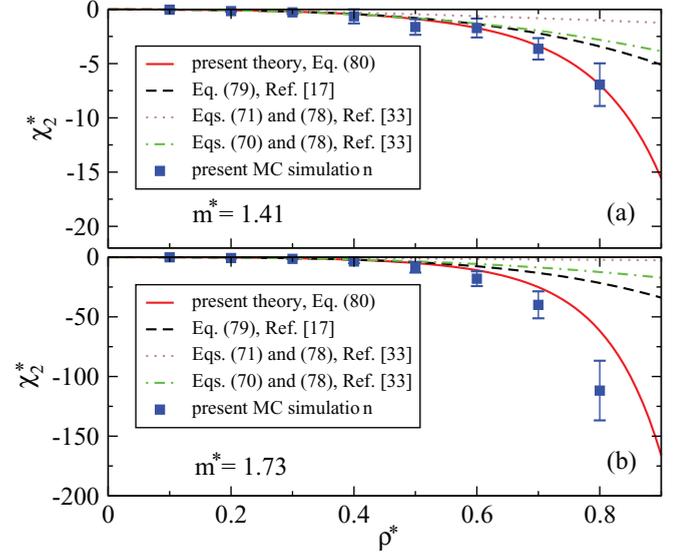


FIG. 5. (Color) Nonlinear magnetic susceptibility χ_2 [Eq. (78)] of DHS systems as a function of the reduced number density ρ^* for two reduced dipole moments: $m^* = \sqrt{2}$ (a) and $m^* = \sqrt{3}$ (b). The red full lines correspond to the results of the present theory [see Eq. (80)]. The black dashed lines are obtained from the magnetization equation due to Ivanov and Kuznetsova [17] [see Eq. (79)] while the brown dotted lines and the green dash-dotted lines correspond to the two free-energy expressions [Eqs. (71) and (78) and Eqs. (70) and (78)] due to Elfimova *et al.* [33]. The symbols are our MC simulation data with the corresponding error bars.

VI. SUMMARY

In the present study of magnetic properties of ferrofluids the following main results have been obtained:

(1) We have applied an extension of the algebraic perturbation theory of Ruelle in order to determine the free energy of dipolar hard-sphere fluids under the influence of magnetic fields.

(2) From the magnetic field dependence of the free energy [Eq. (59)] the magnetization curve [Eq. (61)] and the zero-field susceptibility [Eq. (63)] have been obtained. For Langevin susceptibility values $4\pi\chi_L \lesssim 3$, at low densities these theoretical magnetization data show better agreement with our Monte Carlo simulation data than those obtained from the theory due to Ivanov and Kuznetsova [17] [see Figs. 2(a)–2(d)].

(3) In order to extend our theory to larger values of the density and of the Langevin susceptibility the concept of an effective magnetic field strength has been applied. We have found that the magnetization equation [Eq. (75)] which is derived along this line is in good agreement with our Monte Carlo simulation data only at low field strengths [see Figs. 3(a) and 3(b)].

(4) It has been shown that both magnetization equations [Eqs. (61) and (75)] render the same zero-field magnetic susceptibility expression [Eq. (63)], which is in good agreement with our Monte Carlo simulation data even at high densities [Figs. 4(a) and 4(b)]. This susceptibility expression in Eq. (63) is a natural extension of the corresponding equation [Eq. (10)] due to Ivanov and Kuznetsova [17].

(5) From the magnetic field dependence of the magnetization [Eq. (75)] an analytical equation has been obtained for the nonlinear magnetic susceptibility of dipolar hard-sphere fluids [Eq. (80)]. It has been found that our expression [Eq. (80)] shows better agreement with the simulation data [see Figs. 5(a) and 5(b)] than that obtained from the theory due to Ivanov and Kuznetsova [Eq. (79)].

(6) We have compared our theory with recently published results of Elfimova *et al.* [33–35]. We have found that, concerning the compressibility factor, the latter theory provides a better approximation [see Figs. 1(a) and 1(d)]. However,

concerning magnetic properties—mainly at high densities—our present theory yields a description which is better than the corresponding ones considered by Elfimova and coworkers (see Figs. 2–5).

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