



Cluster expansion for ferrofluids and the influence of polydispersity on magnetization

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Abstract

We present the results of a cluster expansion calculation for a ferrofluid modeled as a system of monodisperse or polydisperse dipolar hard spheres. The magnetization is obtained as series expansion in terms of (i) the volume fraction ϕ and (ii) a dimensionless dipolar coupling constant ε . A detailed calculation for the monodisperse case can be found in Phys. Rev. E 62 (2000) 6875.

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1. Introduction

The model of interacting dipolar hard spheres has attracted interest by physicists for a long time, see e.g. [1]. Ferrofluids may be the physical system where the assumptions of this model are fulfilled best since the magnetic component consists of almost spherical particles with a sharply increasing repulsive potential at small distances. The magnetic effects are often strong enough to expect significant deviations from simple Langevin behavior due to dipolar interactions. To describe the equilibrium magnetization quantitatively, it is necessary, however, to include the effect of polydispersity of the particles that strongly influences the strength of dipolar interactions.

2. Model system and expansion technique

In the model system of dipolar hard spheres, the particle–particle–interaction potential consists of two parts: a hard sphere repulsion term V_{ij}^{HC} and a dipolar interaction term

$$V_{ij}^{DD} = -\frac{3(\mathbf{m}_i \cdot \hat{\mathbf{r}}_{ij})(\mathbf{m}_j \cdot \hat{\mathbf{r}}_{ij}) - \mathbf{m}_i \cdot \mathbf{m}_j}{4\pi\mu_0 r_{ij}^3}, \quad (2.1)$$

for two magnetic moments \mathbf{m}_i and \mathbf{m}_j at a distance $\mathbf{r}_{ij} = \hat{\mathbf{r}}_{ij} r_{ij}$.

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Dipolar forces are of long-range nature. This feature results in the well-known geometry dependence of the macroscopic internal magnetic field and thus of the equilibrium magnetization. To take care of this problem we decompose the dipolar interactions into a short-range and a long-range part in the following way. The dipolar fields acting on some particle i are treated explicitly if the generating particles are closer than some distance R_s . The particles outside a sphere of radius R_s around particle i are modeled as a magnetic continuum that contributes a mean field part \mathbf{H}_s to the total magnetic field at the position of i . This mean field is given by $\mathbf{H}_s = \mathbf{H} + \mathbf{M}/3$, where \mathbf{H} and \mathbf{M} are the internal field and the magnetization of the continuum, respectively. $\mathbf{M}/3$ is the demagnetization factor for the spherical cavity considered. Finally, M is identical to the calculated equilibrium magnetization for this model, thus we obtain an implicit equation for M . So far our model resembles the Weiss model [2] where *all* the dipolar fields are modeled in a continuum approximation. The differences between our model and the Weiss model thus stem from the more thorough treatment of the near-particle interactions in our model.

The canonical partition function of our model system is given by

$$Z = \int e^{-(\sum_k V_k + \sum_{i<j} V_{ij})/k_B T} d\Gamma. \quad (2.2)$$

$d\Gamma$ means integration over the configuration space of the positions \mathbf{x}_i and the orientations of the magnetic moments \mathbf{m}_i . V_{ij} contains the hard sphere repulsion term and the dipolar potential (Eq. (2.1)) truncated at a distance R_s reflecting the fact that dipolar interactions beyond this distance contribute to \mathbf{H}_s but not to Eq. (2.2). These interactions enter together with the potential energy in the external field in the potential $V_k = -\mathbf{m}_k \cdot \mathbf{H}_s$ yielding an unambiguous result for Z with no *explicit* geometry dependence. This dependence enters only via \mathbf{H}_s . Kinetic energy terms in the Hamilton function have no influence on the sought equilibrium magnetization and are thus neglected.

The canonical partition function is calculated using the Born–Mayer or cluster expansion method [3]. The key point of this technique is to rewrite the partition function as

$$Z = \int \prod_k e^{-V_k/k_B T} \prod_{i < j} (1 + f_{ij}) d\Gamma, \quad (2.3)$$

where

$$f_{ij} = e^{-V_{ij}/k_B T} - 1, \quad (2.4)$$

and to expand the integrand in powers of the f_{ij} . To allow for an analytical treatment of the integrals, we furthermore expand the f_{ij} itself in powers of the dipolar interaction potential. The resulting expression for Z is a series expansion in the volume fraction ϕ and the dipolar coupling parameter ε defined via

$$\phi = \frac{N \pi D^3}{V 6}, \quad \varepsilon = \frac{m^2}{4\pi\mu_0 k_B T D^3}. \quad (2.5)$$

ε is a typical interaction energy of two dipolar spheres in contact, in terms of $k_B T$.

3. Expressions for the magnetization

We calculated two different expressions for Z : a first-order result in ϕ containing (in principle) arbitrary high orders in ε and a result that is second order in both parameters. The free energy F and the equilibrium magnetization M were then derived from Z in the described order. In the monodisperse case, the combination of these two results can be written as

$$\frac{M(\alpha_s)}{M_{\text{sat}}} = L(\alpha_s) + \phi \sum_{n=2}^{\infty} \varepsilon^n G'_n(\alpha_s) + \frac{1 + 6 \ln 2}{4} \phi^2 \varepsilon^2 G'_2(\alpha_s) - \phi^2 \varepsilon^2 K'(\alpha_s). \quad (3.1)$$

M_{sat} is the saturation magnetization, and $\alpha_s = mH_s/k_B T$. \mathcal{L} is the Langevin function. The first G_n and K are given in Ref. [4] together with details of the calculation. In the polydisperse case α_s , ε , and ϕ are defined for average values \bar{D} , \bar{m} for diameter and magnetic moment, respectively. \mathcal{L} , G_n , and K are

replaced by $k+1$ times averaged values of more complicated expressions that depend on $k+1$ magnetic moment/diameter combinations. Here k is the order of ϕ . For example, the G_n in $O(\phi)$ are then given by an expression of the form

$$G_n(\alpha) = \int \tilde{G}_n(\alpha, \mu_1, \mu_2, \Delta_1, \Delta_2) \times P(\mu_1, \Delta_1) d\mu_1 d\Delta_1 P(\mu_2, \Delta_2) d\mu_2 d\Delta_2. \quad (3.2)$$

Here $\mu_i = m_i/\bar{m}$, $\Delta_i = D_i/\bar{D}$ and $P(\mu, \Delta)$ is their distribution function.

Eq. (3.1) is an implicit equation for M since the equilibrium magnetization appears also in $H_s = H + M/3$. It can be solved self-consistently as in the Weiss model. It should be noted that the $O(\phi^2, \varepsilon^2)$ -approximation does not have self-consistent ferromagnetic solutions $H = 0$, $M \neq 0$ as the Weiss model is correct only in $O(\phi, \varepsilon)$. In fact, the ferromagnetic behavior obtained with the Weiss model for $\phi\varepsilon > 3/8$ could not be observed experimentally.

Since Eq. (3.1) is correct only to a finite order in ε and ϕ , it can also be solved by expanding the right-hand side around $\alpha = mH/k_B T$ using $M_{\text{sat}}m/3k_B T = 8\phi\varepsilon$ and iterating it. Then

$$\frac{M(\alpha)}{M_{\text{sat}}} = \mathcal{L}(\alpha) + 8\phi\varepsilon \mathcal{L}(\alpha) \mathcal{L}'(\alpha) + \phi \sum_{n=2}^{\infty} \varepsilon^n G'_n(\alpha) + \phi^2 \varepsilon^2 \left[64 \mathcal{L}(\alpha) \mathcal{L}'(\alpha)^2 + 32 \mathcal{L}''(\alpha)^2 \mathcal{L}(\alpha) + \frac{1 + 6 \ln 2}{4} G'_2(\alpha) - K'(\alpha) \right]. \quad (3.3)$$

The higher order terms in Eq. (3.1) depend in principle also on the truncation length R_s but are given in the limit $R_s \rightarrow \infty$. This limit is practically reached already at $R_s \approx 10D$ showing that the continuum approximation works well at distances of about $0.1 \mu\text{m}$. H and M can be assumed to be constant on this scale as is necessary for the relation $H_s = H + M/3$ to hold.

The calculation of the higher order terms makes it possible to determine the reliability of the simplest approximation for the magnetization

$$\frac{M}{M_{\text{sat}}} = \mathcal{L}(\alpha) + 8\phi\varepsilon \mathcal{L}(\alpha) \mathcal{L}'(\alpha) + O(\phi^2) + O(\varepsilon^2), \quad (3.4)$$

by investigating the ratios

$$\frac{O(\phi\varepsilon^n) - \text{terms}(n > 1)}{\mathcal{L}(\alpha) + 8\phi\varepsilon \mathcal{L}(\alpha) \mathcal{L}'(\alpha)}$$

and

$$\frac{O(\phi^2) - \text{terms}}{\mathcal{L}(\alpha) + 8\phi\varepsilon \mathcal{L}(\alpha) \mathcal{L}'(\alpha)}. \quad (3.5)$$

For the monodisperse case Eq. (3.4) holds within 1–2 percent for all α if $\varepsilon < 1$ and $\phi\varepsilon < 0.04$ [4]. The first restriction refers to the influence of the $\phi\varepsilon^n$ -terms, the

second to the $\phi^2 \varepsilon^2$ -terms. For ferrofluids with a polydisperse diameter distribution, the reliability limits deduced from Eq. (3.5) are more stringent because of the influence of higher moments of D and m on the correction terms. It is not sufficient to estimate the influence of dipolar interaction regarding, e.g., only the saturation magnetization. Consider a lognormal distribution for D with $\sigma = 0.3$ and $m \sim D^3$. ϕ and ε are defined for $\bar{m} = \langle m \rangle$ and $\bar{D}^3 = \langle D^3 \rangle$, that is, they refer to a monodisperse ferrofluid with the same volume fraction and saturation magnetization. The $\phi \varepsilon^n$ -terms now restrict the region of reliability of Eq. (3.4) to $\varepsilon < 0.25$. The $\phi^2 \varepsilon^2$ -terms are less sensitive to higher orders, they place a second limit of $\phi \varepsilon < 0.03$ only slightly stricter than in the monodisperse case.

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