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Magnetic properties of dense ferrofluids

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Abstract

Statistical model of the magnetostatic properties of dense ferrofluids has been developed. The model is based on the relation between the magnetization and the pair correlation function of a spatially homogeneous system of dipole particles. This approach allows to calculate the ferrofluid magnetization in a form of expansion over both the particle concentration and the potential of dipole–dipole interaction U_d. The obtained expressions for magnetization and initial magnetic susceptibility with the accuracy $\sim U_d^2$ describe well the experimental data. The model justifies the validity of the "modified mean-field approach", and the effective field is calculated as a function of Langevin magnetization.

Keywords: Dense ferrofluids; Statistical model; Magnetic properties

An evaluation of magnetic characteristics of homogeneous ferrofluids comes up against the well-known problem of taking into account the interparticle dipole–dipole interaction. The latter is most conspicuous in concentrated systems and controls the correlations in mutual position of ferroparticles and in mutual orientation of their magnetic moments. A number of recently developed models describe well the magnetic properties of ferrofluids with low or moderate concentration of magnetic phase $\sim$10–12% under the presence of an arbitrarily valued magnetic field $\boldsymbol{H}$ [1–4]. All these models are valid in the case when the intensity of interparticle dipole–dipole interaction U_d has the order of temperature energy kT or less. For highly concentrated ferrofluids with a magnetic phase concentration over 15–18% this is insufficient. The temperature dependencies of the initial susceptibility of these systems demonstrate the large deviations [5,6] between the theoretical predictions and the experimental data. At low temperatures, the models [1–3] underestimate the values of initial susceptibility by 15–20%. It is clear that this deviation is due to the influence of dipole–dipole interaction.

The ferrofluid magnetization is expressed in terms of the one-particle distribution function $g_1(\boldsymbol{r}_i, \boldsymbol{\Omega}_i)$, representing actually a probability for single particle to be placed at a point $\boldsymbol{r}_i(r_i, \theta_i, \varphi_i)$ and to be oriented in a direction $\boldsymbol{\Omega}_i(\omega_i, \zeta_i)$. For a homogeneous liquid state, the equality $g_1(\boldsymbol{r}_i, \boldsymbol{\Omega}_i) \equiv 1$ holds true [7] in the absence of an external field. Otherwise, this probability depends only on the angle ω_i between an external field direction and the orientation of particle magnetic moment, that is $g_1(\boldsymbol{r}_i, \boldsymbol{\Omega}_i) \equiv g_1(\omega_i)$:

$$M(H) = nm\frac{1}{2}\int_0^\pi \cos\omega_1 g_1(\omega_1)\sin\omega_1\,\mathrm{d}\omega_1, \tag{1}$$

where m and n are the particle magnetic moment and the concentration. The main idea of our approach is that the one-particle distribution function may be connected with the pair correlation function $g_2(\boldsymbol{r}_{12}, \boldsymbol{\Omega}_1, \boldsymbol{\Omega}_2)$ [7,8], which describes the mutual correlations between particles 1 and 2, influenced by the interparticle interaction under the presence of an external field:

$$\frac{\mathrm{d}g_1(\omega_1)}{\mathrm{d}\omega_1} = -\alpha\sin\omega_1 g_1(\omega_1) - \frac{n}{kT}\int \mathrm{d}\boldsymbol{\Omega}_2 \int \mathrm{d}\boldsymbol{r}_2 \frac{\mathrm{d}U_d(12)}{\mathrm{d}\omega_1} g_2(12), \tag{2}$$

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$$\int g_1(\omega_1)\,\mathrm{d}\boldsymbol{\Omega}_1 = 1,\ \mathrm{d}\boldsymbol{\Omega}_i = (4\pi)^{-1}\sin\omega_i\,\mathrm{d}\omega_i\,\mathrm{d}\zeta_i,$$

$$\mathrm{d}\boldsymbol{r}_i = r_i^2\,\mathrm{d}r_i\sin\theta_i\,\mathrm{d}\theta_i\mathrm{d}\varphi_i.$$

The solution of Eqs. (1) and (2) gives the expression for magnetization in terms of the pair correlation function:

$$M(H) = nm\Big\{L(\alpha) + \frac{n}{kT}\int \mathrm{d}\boldsymbol{\Omega}_1\,\mathrm{d}\boldsymbol{\Omega}_2 \times [\cos\omega_1 - L(\alpha)]\int \mathrm{d}(\cos\omega_1)\cdot \times \int \mathrm{d}\boldsymbol{r}_{12}\frac{\mathrm{d}U_\mathrm{d}(12)}{\sin\omega_1\,\mathrm{d}\omega_1}g_2(12)\Big\},$$

$$L(\alpha) = \coth\alpha - \frac{1}{\alpha},\quad \alpha = \frac{mH}{kT}. \tag{3}$$

This exact expression includes all corrections to the Langevin magnetization influenced by the multi-particle correlations and is of principal nature. On its basis the cluster expansion methods may be developed to determine the ferrofluid magnetization in an arbitrarily valued external field. An important feature of the method is that the right-hand parts of Eqs. (2) and (3) contain the first orders of particle concentration n and dipole–dipole interaction potential U_d. Thus, the determination of the pair correlation function g_2 up to the order of $\sim n^k$, U_d^k gives the magnetization in terms of the order $\sim n^{k+1}$, U_d^{k+1}.

Allowing for the polydispersity, the governing equation (2) holds true for all fractions of the ferroparticle distribution by size, and the functions g_1 and g_2 are dependent on the particle sizes. For polydisperse system, the mentioned approach was developed in Ref. [8]. The result is that expressions (1) and (3) have to be averaged over all fractions of the particle distribution by size with respect to particles 1 and 2. The approximation of pair correlation function g_2 linear in U_d was considered in Ref. [8], and for a highly elongated cylindrical container with ferrofluid it gives the very complicated expression for magnetization, which contains the first terms in an expansion of the following expression:

$$M(H) = M_\mathrm{L}(H_\mathrm{e}) = n\left\langle mL\left(\frac{mH_\mathrm{e}}{kT}\right)\right\rangle \equiv n\int_0^\infty m(x)f\,(x)L\left[\frac{m(x)H_\mathrm{e}}{kT}\right]\mathrm{d}x, \tag{4}$$

$$H_\mathrm{e} = H + \frac{4\pi}{3}M_\mathrm{L}(H) + \frac{(4\pi)^2}{144}M_\mathrm{L}(H)\frac{\mathrm{d}M_\mathrm{L}(H)}{\mathrm{d}H},$$

$$M(H) = \chi H,\ \chi = \chi_\mathrm{L}\left[1 + \frac{4\pi\chi_\mathrm{L}}{3} + \frac{(4\pi\chi_\mathrm{L})^2}{144}\right],\ H\to 0, \tag{5}$$

$$M(H) = \left(M_\infty - \frac{nkT}{H}\right)\left(1 + \frac{4\pi}{3}\frac{nkT}{H^2}\right),\ H\to\infty, \tag{6}$$

where M_L and M_∞ are the Langevin magnetization and the saturation magnetization, respectively; χ_L is the Langevin susceptibility; $f(x)$ stands for the ferroparticle distribution by magnetic core diameters; and expressions (5) and (6) represent the weak and the strong field asymptotic behaviors. This result is very close to the modified mean-field model [3] in the framework of which the effective field H_e, acting on a single particle, is assumed to be proportional to Langevin magnetization: $H_\mathrm{e} = H + (4\pi/3)M_\mathrm{L}$. As follows from expression (4), for dense ferrofluids one needs to consider the additional term in H_e. It results in cubic parabola behavior (5) of the susceptibility χ as the function of χ_L.

Fig. 1 demonstrates the temperature dependencies of the initial magnetic susceptibility for ferrofluids with the magnetic phase concentration over $\simeq 18\%$. These systems represent the dispersions of the so-called "drop-like aggregates", arising during the phase separation of ferrocolloids. The droplets are highly concentrated and are enriched with the large particle fractions. The mean magnetic moment amounts up to $\langle m\rangle \sim 20\times 10^{-19}\,\mathrm{A\,m^2}$. At low temperatures, the susceptibility may be as great as $4\pi\chi \sim 80$. The adequate interpretation of $\chi(T)$ curves needs to take into account the following: the Langevin susceptibility decreases with increasing temperature not only due to the factor $1/T$ but also because of the liquid heat expansion (the number particle density decreases) and of the decreasing magnetization of the particle material. The calculation procedure of such an account is described in Ref. [5]. The fact is that the presented model for the first time shows the good agreement with the experimental data [5,6]. So, the term proportional $\sim\chi_\mathrm{L}^3$ in expression (5) is very important for the dense ferrofluids (Fig. 1).

Model (4) was tested on the experimental magnetization curves [1,6] for ferrofluids with the saturation magnetization $M_\infty = 87.1$ and $88.6\,\mathrm{kA/m}$. The particle

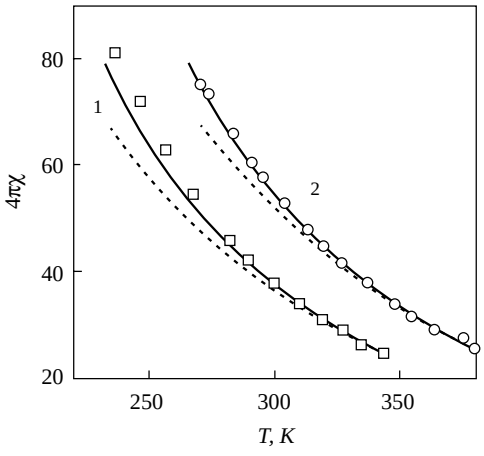

Fig. 1. Temperature dependencies of the initial magnetic susceptibility for dense ferrofluids. Points — the experimental data [5] (◇) and [6] (○). Solid curves 1 and 2 — expression (5); dash curves 1 and 2 — the results of models [1,2].

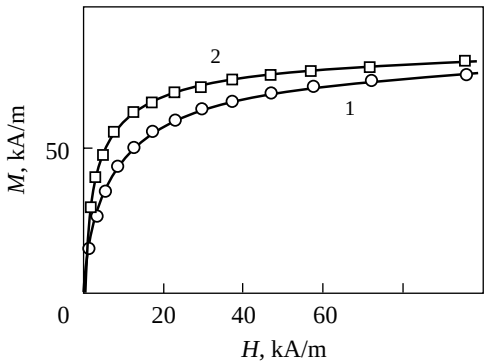

Fig. 2. Magnetization curves for dense ferrofluids. Points — the experimental data [1] (○ and 1) and [5] (◇ and 2); curves — model (4).

polydispersity was described by the gamma distribution. The magnetization curves were calculated in four stages: (a) with the help of strong field asymptotic (6) the fitting of experimental data gives us the particle number density and the mean magnetic moment; (b) the weak field asymptotic (5) allows us to obtain the Langevin susceptibility and, hence, the mean squared magnetic moment; (c) after that we are able to find the parameters of gamma distribution; (d) as a result, we calculate the ferrofluid magnetization (4) in an arbitrarily valued external field. The comparison, presented in Fig. 2, shows a very accurate agreement between the developed model (4)–(6) and the experimental data.

Hence, the presented model describes well the magnetic properties of homogeneous dense ferrofluids. This is due to the fact that our result (4) is expressed in a form of "modified mean-field model". We have shown that this approach represents a special form of perturbation theory, when the ferrofluid magnetization is evaluated as an expansion over the Langevin magnetization. The explicit form of this expansion is controlled by the pair correlations of ferroparticle magnetic moments. The results of our model lead to the correct determination of the ferroparticle size distribution in dense magnetic fluids.

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